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Wpływ fazy spinelowej i jej prekursorów na właściwości betonów ogniotrwałych korundowo-spinelowych bezzementowych i ultra-niskocementowych.

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2. Streszczenie

2.1. Streszczenie w języku polskim

Materiały ogniotrwałe zgodnie z normą ISO 836:2001 to niemetaliczne materiały lub wyroby (włączając w to materiały zawierające pewną ilość metalu), których fizyczne i chemiczne właściwości umożliwiają ich zastosowanie w środowisku wysokotemperaturowym [1]. Obecnie światowe trendy w dziedzinie materiałów ogniotrwałych wskazują na wzrost zainteresowania materiałami nieformowanymi, poza materiałami formowanymi stosowanymi na szeroką skalę. Nieustannie podkreślany niekorzystny spadek wytrzymałości mechanicznej betonów cementowych w temperaturach 300-1000°C, a także ich niewystarczające właściwości termomechaniczne i odporność korozyjna, uzasadniają potrzebę rozwoju alternatywnych dla cementu glinowo- wapniowego spoiw.

Celem niniejszej rozprawy doktorskiej było określenie mechanizmu formowania się więzby hydraulicznej betonu w wyniku hydratacji składników osnowy w temperaturach poniżej 50°C, a następnie więzby ceramicznej w materiałach ogniotrwałych bezzementowych i ultra-niskocementowych korundowo-spinelowych podczas ich wypalania w temperaturze do 1500°C. W kontekście przyszłej aplikacji materiału, dodatkowym celem pracy było określenie roli ilości, rodzaju oraz składu fazy spinelowej w kształtowaniu właściwości fizycznych, mechanicznych, termomechanicznych i odpornościowych zaprojektowanego betonu. Wyniki badań opublikowano w ramach cyklu pięciu publikacji, a niniejsze prace dotyczyły:

- a) alternatywnego spoiwa bezzementowego: warunków otrzymywania podwójnego warstwowego wodorotlenku magnezowo-glinowego w mieszkankach reakcyjnych $\text{MgO-Al}_2\text{O}_3$ zarówno modelowych, jak i w osnowie betonu w temperaturach poniżej 50°C,
- b) reakcji i przemian zachodzących w trakcie obróbki cieplnej betonu w zakresie temperatur do 1000°C, oraz ich wpływu na właściwości fizyczne oraz mechaniczne materiału,
- c) wpływu ilości, rodzaju, składu fazy spinelowej oraz innych faz modyfikujących na właściwości fizyczne, mechaniczne, termomechaniczne oraz odpornościowe opracowanego materiału.

Otrzymane wyniki badań potwierdziły, że hydratacja osnowy, która zawiera zol glinowy oraz MgO w formie spiekane go proszku, pozwoliła na otrzymanie podwójnego warstwowego wodorotlenku magnezowo- glinowego. Zachodzące w trakcie obróbki

cieplnej i wypalania reakcje rozkładu termicznego, rekombinacji tlenków mieszanych Mg(Al)O , a następnie ich reakcyjne spiekanie prowadzące do powstania fazy spinelowej w temperaturze 700°C zapobiegły obniżeniu wytrzymałości mechanicznej materiału w temperaturach $300\text{-}1000^{\circ}\text{C}$. Otrzymany w wyniku wypalania prefabrykat z bezzementowego betonu korundowo- spinelowego charakteryzował się zwiększonymi właściwościami mechanicznymi oraz termomechanicznymi w porównaniu do otrzymanych jako materiał odniesienia betonów korundowo- spinelowych ultra- niskocementowych.

2.2. Streszczenie w języku angielskim

According to ISO 836:2001 standard, refractory materials are non-metallic materials or products (including those containing some metal) whose physical and chemical properties enable their use in high-temperature environments [1]. Current global trends in the field of refractory materials indicate a growing interest in unshaped materials, in addition to the widely used formed materials. The consistently emphasized unfavorable decrease in the mechanical strength of cement castables at temperatures of 300-1000°C, as well as their insufficient thermomechanical properties and corrosion resistance, justify the need to develop alternative binders to calcium aluminate cement. The aim of this doctoral dissertation was to determine the mechanism of hydraulic bond formation in castables as a result of the hydration of matrix components at temperatures below 50°C, followed by the formation of a ceramic bond in non-cement and ultra-low-cement corundum–spinel refractories during firing at temperatures up to 1500°C. In the context of future material application, an additional objective was to determine the role of the amount, type, and composition of the spinel phase in shaping the physical, mechanical, thermomechanical, and corrosion resistance properties of the designed castable. The research results were published as a series of five articles, and the present work focused on:

- a) alternative non-cement binders: the conditions for obtaining Mg-Al layered double hydroxide in MgO–Al₂O₃ reactive mixtures, both model environment and castable matrix, at temperatures below 50°C,
- b) the reactions and transformations occurring during thermal treatment of castables up to 1000°C, and their impact on the physical and mechanical properties of the material,
- c) the effect of the amount, type, and composition of the spinel phase and other modifying phases on the physical, mechanical and thermomechanical of the castables.

The obtained results confirmed that hydration of the matrix containing alumina sol and deadburned MgO allowed the formation of Mg-Al layered double hydroxide. The thermal decomposition, recombination of mixed oxides Mg(Al)O, and subsequent reactive sintering leading to the formation of the spinel phase at 700°C enabled the reduction of mechanical strength loss in the temperature range of 300–1000°C. The no-cement corundum–spinel castable obtained after firing exhibited improved mechanical and thermomechanical properties compared to the ultra-low-cement corundum–spinel castables used as reference materials.

3. Wprowadzenie

Materiały ogniotrwałe zgodnie z normą ISO 836:2001 to niemetaliczne materiały lub wyroby (włączając w to materiały zawierające pewną ilość metalu), których fizyczne i chemiczne właściwości umożliwiają ich zastosowanie w środowisku wysokotemperaturowym [2]. Stanowią one więc niezwykle ważną grupę materiałów ceramicznych, gdyż umożliwiają produkcję innych materiałów, takich jak stal, szkło czy też cement portlandzki. W zależności od sposobu otrzymywania podzielić je można na materiały ogniotrwałe formowane oraz nieformowane (monolityczne). Przegląd aktualnej literatury naukowej wskazuje na rosnące zainteresowanie oraz dynamiczny rozwój technologii nieformowanych materiałów ogniotrwałych, co związane jest ze zwiększeniem udziału produkcji i stosowania ogniotrwałych tworzyw monolitycznych w stosunku do lat ubiegłych. Już w 2010 roku nieformowane materiały ogniotrwałe stanowiły ponad 50% światowej produkcji [3], a ich udział systematycznie rośnie. Przewaga proponowanego wariantu obejmuje eliminację energochłonnego procesu, który jest związany z wypalaniem tradycyjnych, formowanych materiałów ogniotrwałych. Takie rozwiązanie jest rozwiązaniem korzystnym z ekonomicznego oraz ekologicznego punktu widzenia, gdyż transformacja więzby hydraulicznej w więzbę ceramiczną w wyłożeniach monolitycznych następuje już po instalacji docelowego materiału w urządzeniu cieplnym na skutek dehydratacji i dehydroksylacji faz uwodnionych, a następnie reakcyjnego spiekania produktów rozkładu hydratów. Otrzymywanie wyłożeń z nieformowanych materiałów ogniotrwałych wiąże się więc z ograniczeniem emisji CO₂, redukcją śladu węglowego oraz zmniejszeniem zużycia energii niezbędnej do otrzymania ww. materiałów (w porównaniu do materiałów formowanych), co wpisuje się w aktualną politykę energetyczno-klimatyczną Unii Europejskiej [4].

Materiały ogniotrwałe nieformowane (betony, masy do ubijania, masy do natryskiwania, zaprawy etc.) to grupa materiałów, które otrzymywane są najczęściej jako mieszanki sypkie, z których, po dodaniu wody lub innej cieczy, wykonywane są wyłożenia ogniotrwałe monolityczne albo tzw. prefabrykaty betonowe. Wyłożenia te otrzymuje się zwykle wybraną metodą w technologii wylewania i wibrowania, natrysku lub inną [3, 5]. Materiały monolityczne wykorzystywane są nie tylko do produkcji wyłożeń w nowych urządzeniach, ale także do naprawy i konserwacji już eksploatowanych wyłożeń ogniotrwałych [3]. Szerokie zastosowanie w produkcji części roboczych wyłożeń urządzeń cieplnych przeznaczonych dla przemysłu stalowniczego,

cementowego oraz petrochemicznego znajdują ogniotrwałe betony wysokoglinowe [6, 7].

Betony ogniotrwałe, zgodnie z normą PN EN 1402_1_2005 są mieszaninami kruszyw ogniotrwałych, drobnoziarnistej frakcji wypełniającej, spoiwa lub spoiw oraz dodatków dostarczane głównie w postaci suchej i stosowane po dodaniu oraz homogenizacji z wodą lub inną cieczą. Podzielić je można na betony: zwykłe, z upłynniaczem oraz o wiązaniu chemicznym [8]. Pomimo intensywnych prac badawczo-rozwojowych prowadzonych w ostatnich latach nad alternatywnymi spoiwami beczementowymi, cement glinowo- wapniowy wciąż zachowuje dominującą pozycję wśród spoiw stosowanych w betonach ogniotrwałych. Jednakże, jego zastosowanie związane jest z pewnymi ograniczeniami, które negatywnie wpływają na właściwości gotowego materiału. Analiza literatury naukowej wykazała, że główne problemy związane z monolitycznymi wyłożeniami ogniotrwałymi, w których jako spoiwo stosuje się cement glinowo- wapniowy obejmują: ograniczoną odporność korozyjną, niewystarczające właściwości termomechaniczne oraz wyraźny spadek wytrzymałości mechanicznej w zakresie temperatur 300–1000 °C. Ponadto obserwowana jest tendencja do skracania czasu obróbki cieplnej betonów, związana z wypalaniem w warunkach szybkiego przyrostu temperatury, które ma miejsce po instalacji materiału w urządzeniu cieplnym w trakcie jego pierwszego uruchomienia, co w przypadku zastosowania cementu także jest trudne do osiągnięcia.

W związku powyższym, w ostatnich latach intensywnie rozwijano technologie betonów ogniotrwałych o niskiej (LCC, z ang. low cement castables) i ultraniskiej zawartości cementu (ULCC, z ang. ultra-low cement castables) oraz beczementowych (NCC z ang. no-cement castables). Na chwilę obecną, stosowane w przemyśle i szeroko omówione w literaturze są betony korundowo-spinelowe LCC oraz ULCC, zawierające spinel syntetyczny, tworzący się in situ lub ich kombinację. Wśród spoiw alternatywnych, stosowanych w betonach NCC wyróżnić można reaktywne tlenki: MgO, Al₂O₃ i SiO₂, p-Al₂O₃ (z ang. HA, hydratable alumina) oraz zol krzemionkowy. Aktualna literatura naukowa i praktyka przemysłowa wskazują jednak na problemy związane z utrzymaniem dobrej wytrzymałości mechanicznej ogniotrwałych materiałów beczementowych wiązanych zolem krzemionkowym, bezpośrednio po etapie sezonowania [9]. Zastosowanie HA związane jest z koniecznością dodania większej ilości wody zarobowej w trakcie homogenizacji mieszanki betonowej, co skutkuje większą porowatością oraz obniżoną wytrzymałością mechaniczną materiału. Dostępna literatura naukowa wskazuje

na ograniczoną liczbę badań dotyczących zastosowania kombinacji reaktywnych tlenków $\text{MgO-Al}_2\text{O}_3$ lub $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ jako spoiwa w bezcementowych betonach ogniotrwałych korundowo- spinelowych. Ponadto, wodna zawiesina nanometrycznego proszku Al_2O_3 nie znalazła dotychczas zastosowania w przemyśle materiałów ogniotrwałych jako komponent matrycy betonów NCC.

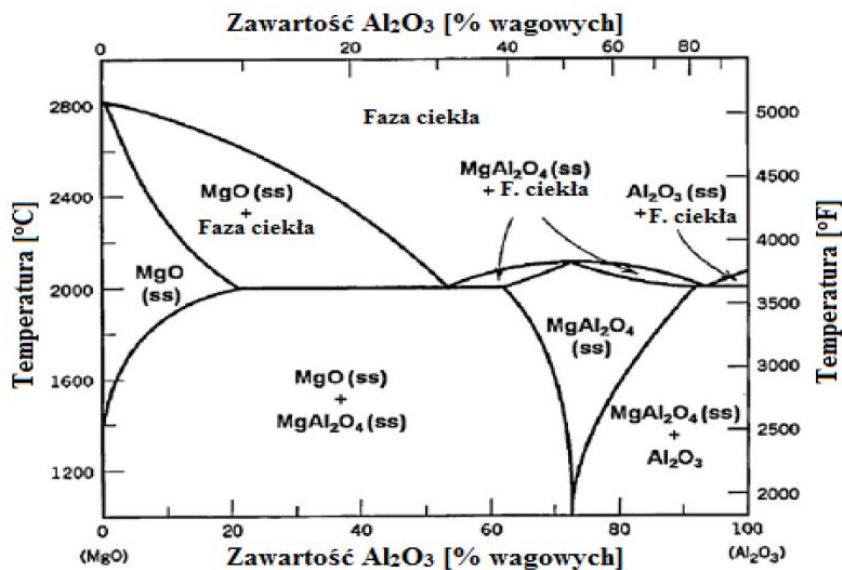
W niniejszej dysertacji podjęta została tematyka dotycząca mechanizmu formowania się więźby hydraulicznej betonu w wyniku hydratacji składników osnowy w temperaturach poniżej 50°C , a następnie więźby ceramicznej w materiałach ogniotrwałych bezcementowych i ultra-niskocementowych korundowo-spinelowych podczas ich obróbki cieplnej i wypalania w temperaturze do 1500°C . Odpowiednio przeprowadzona hydratacja mieszanin reakcyjnych $\text{MgO-Al}_2\text{O}_3$, w których jako źródło Al_2O_3 zastosowano m.in. żol glinowy pozwoliła na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego. Zachodzące w trakcie obróbki cieplnej i wypalania reakcje rozkładu termicznego hydratów tworzących więźbę hydrauliczną, rekombinacji tlenków mieszanych Mg(Al)O , a następnie ich reakcyjne spiekanie prowadzące do powstania fazy spinelowej w temperaturze 700°C umożliwiły stopniowy przyrost wytrzymałości mechanicznej materiału w temperaturach $300\text{-}1000^\circ\text{C}$. Ponadto, otrzymany w wyniku wypalania prefabrykat z bezcementowego betonu korundowo- spinelowego wykazał zwiększone właściwości mechaniczne (wytrzymałość na ściskanie $\sim 220\text{ MPa}$) oraz termomechaniczne (wytrzymałość na zginanie w temperaturze 1450°C $\sim 10\text{ MPa}$, szybkość pełzania $\sim 10^{-5}\%/ \text{min}$) w porównaniu do otrzymanych jako materiał odniesienia betonów korundowo- spinelowych ultra-niskocementowych, (wytrzymałość na ściskanie $\sim 190\text{ MPa}$, wytrzymałość na zginanie w temperaturze 1450°C $\sim 6,5\text{ MPa}$, szybkość pełzania $\sim 10^{-4}\% / \text{min}$). Uzyskane wyniki podkreślają potencjał aplikacyjny opracowanego rozwiązania materiałowego w postaci betonu NCC, stanowiącego odpowiedź na aktualne światowe trendy w projektowaniu urządzeń cieplnych przemysłu stalowniczego.

4. Betony ogniotrwałe korundowo-spinelowe. Aktualny stan wiedzy

Ważną podgrupę nieformowanych materiałów wysokoglinowych stanowią betony korundowo- spinelowe, zawierające spinel syntetyczny lub tworzący się w wyniku reakcji MgO i Al_2O_3 . Pierwsze doniesienia na temat betonów korundowo- spinelowych (ze spinelem syntetycznym) pojawiły się w latach 60-tych XX wieku [10] i po dzień dzisiejszy znajdują się w centrum zainteresowań zarówno naukowców jak i czołowych światowych producentów oraz użytkowników materiałów ogniotrwałych. Materiały te znajdują zastosowanie jako elementy wyłożeń dna (betony zawierające spinel syntetyczny) i ścian bocznych (poniżej strefy żużla, betony zawierające spinel tworzący się w warunkach in-situ) kadzi stalowniczych [11], rur zanurzeniowych RH (z ang. RH snorkels, elementy systemu rafinacji stali metodą RH), dysz napowietrzających (z ang. purging plugs, elementy stosowane do przedmuchiwania gazów przez ciekłą stal w celu jej homogenizacji i usuwania zanieczyszczeń) oraz bloków gniazdowych (z ang. well blocks, elementy wyłożenia kadzi stalowniczej, w których osadzone są dysze lub inne komponenty przepływowe) [12, 13]. Niewątpliwymi zaletami wyłożenia wykonanego z betonu ogniotrwałego korundowo-spinelowego są: dobre właściwości mechaniczne i termomechaniczne, odporność na korozję w kontakcie z zasadowym żużłem stalowniczym oraz odporność na łuszczenie/ termiczne eksplozyjne odpryskiwanie betonu spowodowane gwałtownymi zmianami temperatury (z ang. thermal spalling) [11], co w konsekwencji przekłada się na mniejsze zużycie korozyjne, dłuższą żywotność materiału, lepszą wydajność urządzenia cieplnego, czy nawet lepszą jakość stali [11, 14-20].

Tak jak wspomniano powyżej, w zależności od sposobu wprowadzenia spinelu do materiału wyróżnić można betony ze spinelem tworzącym się w warunkach in situ oraz syntetycznym wprowadzonym jako kruszywo, który może różnić się wielkością ziarna oraz stechiometrią. Zgodnie z dwuskładnikowym układem fazowym $\text{MgO-Al}_2\text{O}_3$ (Rysunek 1) wyróżniamy spinel magnezowo- glinowy: bogaty w Al^{3+} (z ang. Al-rich magnesium- aluminate spinel, $\text{Mg}_{1-x}\text{Al}_{2+x}\text{O}_4$, gdzie $x>0$), stechiometryczny (o stosunku molowym $\text{MgO}:\text{Al}_2\text{O}_3$ wynoszącym 1:1, zawiera odpowiednio 71,67%_{mas} i 28,33%_{mas} Al_2O_3 i MgO) oraz bogaty w Mg^{2+} (z ang. Mg- rich magnesium- aluminate spinel, $\text{Mg}_{1+x}\text{Al}_{2-x}\text{O}_4$, gdzie $x>0$). Spinel stechiometryczny stanowi jedyny termodynamicznie stabilny związek, topiący się kongruentnie w temperaturze 2135°C [21], a dwustopniowe spiekanie mieszanin zawierających np. gibbsyt oraz tlenek magnezu, pozwala na pełną

konwersję substratów do MgAl_2O_4 w temperaturach wynoszących odpowiednio $>1450^\circ\text{C}$ oraz $>1700^\circ\text{C}$ [22, 23].



Rys. 1 Diagram fazowy MgO- Al_2O_3 [21].

Synteza fazy spinelowej ze składników tlenkowych MgO oraz Al_2O_3 jest reakcją w fazie stałej i zachodzi na skutek przeciwnie skierowanej dyfuzji jonów glinu Al^{3+} oraz magnezu Mg^{2+} do stref reakcji: MgAl_2O_4 -MgO oraz MgAl_2O_4 - Al_2O_3 . Uwzględniając równowagę ładunków, reakcja pomiędzy czterema cząsteczkami MgO i dwoma jonami Al^{3+} prowadzi do utworzenia jednej cząsteczki MgAl_2O_4 na granicy MgO- MgAl_2O_4 , podczas gdy reakcja pomiędzy czterema cząsteczkami Al_2O_3 i trzema jonami Mg^{2+} prowadzi do wytworzenia trzech cząsteczek MgAl_2O_4 na granicy Al_2O_3 - MgAl_2O_4 , co w konsekwencji prowadzi do utworzenia warstwy spinelu o teoretycznym stosunku grubości pomiędzy utworzonymi warstwami spinelu przy stronach Al_2O_3 i MgO wynoszącym 3:1 [24]. W przypadku betonów zawierających spinel tworzący się w warunkach in situ, które opracowane zostały na przełomie lat 70-tych i 80-tych XX wieku [21], mieszanka betonowa zawiera MgO jako komponent matrycy, który w wyniku reakcyjnego spiekania z Al_2O_3 tworzy spinel. W zależności od przyjętej koncepcji składu recepturowego materiałów zawierających spinel syntetyczny lub MgO jako składnik osnowy, gotowe materiały różnią się właściwościami, a do chwili obecnej większość wysiłków naukowych koncentrowała się na analizie wpływu zawartości fazy spinelowej oraz wielkości jego ziaren na właściwości betonu ogniotrwałego korundowo- spinelowego [25]. Zgodnie z aktualnym stanem wiedzy optymalna zawartość spinelu magnezowo-glinowego w betonie ogniotrwałym wynosi od 15 do 30 %_{mas}, lecz najbardziej korzystną

jest 20-25 %_{mas} [12, 21]. Rozważane w literaturze warianty technologiczne betonów korundowo- spinelowych, których podsumowanie przedstawiono w Tabeli 1, zawierały w wyjściowej mieszance betonowej maksymalnie 9%_{mas} MgO wprowadzanego jako komponent matrycy. Zastosowanie MgO jako składnika osnowy betonu w ilości od 0,5%_{mas} do 9%_{mas} umożliwia otrzymanie w trakcie wypalania betonu odpowiednio od 1,76%_{mas} do 31,77%_{mas} spinelu.

Tabela 1 Podsumowanie opisywanych w literaturze przykładowych wariantów technologicznych betonów ogniotrwałych korundowo- spinelowych.

Lp.	Zawartość MgO w recepturze betonu [% _{mas}]	Zawartość spinelu syntetycznego [% _{mas}]	Zawartość cementu glinowo-wapniowego [% _{mas}]	Rok publikacji
1	0,0	0,0; 5,0; 10,0; 15,0	4,0	2025 [26]
2	3,0; 6,0; 9,0	0,0	3,0	2025 [27]
3	3,0	3,0	3,0	
4	0,0	10,0; 20,0	4,0	
5	2,8; 5,6	0,0	4,0	2024 [10]
6	0,0	15,0	5,0	2022 [28]
7	0,0	0; 5; 10; 15; 20	5,0	2019 [25]
8	0,5; 1,0; 2,0; 3,0; 4,0; 5,0; 6,0	0,0	0,0	2018 [29]
9	6,0	0,0	6,0	2011 [30] 2008 [31, 32] 2007 [33]
10	0,0	25,0	5,0	2014 [34]
11	6,0	0,0	6,0	2012 [35]
12	0,0	21,0	6,0	
13	6,0	0,0	6,0	
14	0,0	21,0	6,0	2012 [36]
15	5,5	0,0	8,0	2000 [37]
16	0,0	20,0	10,0	
17	5,5	10,0	8,0	

Zgodnie z danymi literaturowymi [10, 25-37] przedstawionymi w Tabeli 1, dobór składu recepturowego materiałów w istotny sposób wpływa na właściwości końcowe betonów korundowo- spinelowych. Zastosowanie spinelu syntetycznego jako składnika osnowy betonu [10, 25, 26, 28, 34-37] prowadziło do poprawy właściwości mechanicznych i termomechanicznych, a także do zwiększenia odporności materiału zarówno na nagłe zmiany temperatury, jak i korozję w porównaniu do materiałów niezawierających spinelu, co było efektem m.in. utworzenia dodatkowych wiązań pomiędzy spinelem a sześcioglinianem wapnia oraz mniejszej ilości powstałej w trakcie wypalania fazy ciekłej. Przykładowo, w pracy [25] wykazano, że najkorzystniejsze właściwości

uzyskano dla betonu zawierającego 10%_{mas} spinelu, w przypadku którego zaobserwowano wzrost wytrzymałości na zginanie w temperaturze otoczenia (CMoR) o 45,8%, a w podwyższonej temperaturze (HMoR) o 110%. Jednocześnie oszacowana na podstawie analizy mikrostrukturalnej SEM ilość fazy ciekłej zmniejszyła się o 1,5 punktu procentowego w stosunku do betonu niezawierającego spinelu syntetycznego. Analogiczne wnioski przedstawili autorzy w pracy [26] zgodnie z którymi dodatek 10%_{mas} syntetycznego spinelu zwiększył CMoR z 30,0 MPa do 33,1 MPa, a HMoR z 14,5 MPa do 32,8 MPa. Zastosowanie spinelu syntetycznego w porównaniu do spinelu tworzącego się in situ skutkowało również mniejszą ekspansją objętościową oraz mniejszą porowatością. Właściwości betonów korundowo-spinelowych, w których zastosowano MgO jako składnik osnowy [10, 27, 29-36] determinowane były zarówno jego ilością, jak i wielkością ziarna. W pracach [31, 32] stwierdzono, że wraz ze wzrostem wielkości ziarna MgO (45-100µm) zaobserwowano: wzrost porowatości i związane z tym zmniejszenie odporności na korozję, zapoczątkowanie tworzenia spinelu w wyższej temperaturze (od 1000-1200°C), niecałkowite przereagowanie MgO w trakcie wypalania, większą ekspansję liniową oraz tworzenie się dodatkowych faz np. forsterytu czy monticellitu, których obecność obniżała właściwości mechaniczne. Zastosowanie MgO o wielkości ziarna <13µm w ilości 3-6%_{mas} wskazywane było w literaturze jako optymalne i umożliwiało otrzymanie materiału charakteryzującego się niską rozszerzalnością liniową (< 2%), dobrą odpornością na nagłe zmiany temperatury i korozję oraz wysokimi właściwościami mechanicznymi (CMoR 20-25MPa, CCS 90-100MPa, [27]). Wykorzystanie zarówno MgO, jak i spinelu syntetycznego jako składników osnowy [27, 37] pozwalało na poprawę odporności na korozję, redukcję porowatości i zwiększenie wytrzymałości mechanicznej. W pracy [27] autorzy wykazali, że betony korundowo- spinelowe, które w recepturze wyjściowej zawierały 3%_{mas} MgO oraz 3%_{mas} spinelu syntetycznego (wielkość ziarna <0,0074 mm) w porównaniu do materiałów zawierających wyłącznie MgO w ilości 3%_{mas}, 6%_{mas} lub 9%_{mas}, charakteryzowały się najlepszymi właściwościami mechanicznymi (CMoR 28,6 MPa, CCS 141,7 MPa), odpornością na nagłe zmiany temperatury oraz korozję. W literaturze odnaleźć można również doniesienia dotyczące wpływu stechiometrii spinelu magnezowo-glinowego na właściwości betonu ogniotrwałego [23, 34, 38], a badania te oparte są na dostępnych komercyjnie kruszywach. Zgodnie z literaturą [39] betony korundowo- spinelowe zawierające cement glinowo- wapniowy, w których w recepturze wyjściowej zastosowano spinel bogaty w jony glinu charakteryzowały się lepszymi

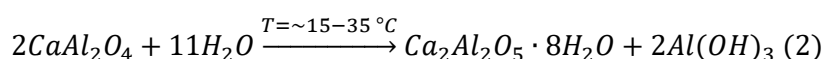
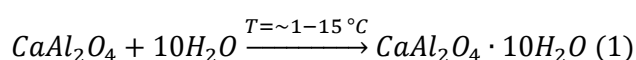
właściwościami mechanicznymi, które wynikały z reakcji CaO ze spoiwa z Al_2O_3 ze spinelu. W efekcie powstawały fazy glinianów wapnia np. sześcioglinian wapniowy, które dodatkowo umacniały wiązania pomiędzy Al_2O_3 , a spinelem.

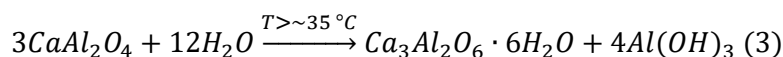
Przedstawiony przegląd literatury jednoznacznie wskazuje, że dobór składu recepturowego, w tym: rodzaju, ilości i wielkości ziarna spinelu syntetycznego oraz MgO w sposób istotny wpływa na właściwości końcowe betonów- korundowo spinelowych. Odpowiedni dobór składu wyjściowego mieszanki betonowej umożliwia uzyskanie pożądanych właściwości mechanicznych, termomechanicznych oraz odpornościowych.

Czołowi światowi producenci materiałów ogniotrwałych (RHI Magnesita, Calderys Zakłady Magnezytowe Ropczyce S.A., ArcelorMittal Refractories) posiadają w swojej ofercie szeroką gamę monolitycznych materiałów ogniotrwałych, co świadczy o wciąż niesłabnącym zainteresowaniu ze strony przemysłu hutniczego, szklarskiego, cementowego etc. Wśród produktów jakie oferują ww. producenci wyróżnić można zarówno betony korundowo-spinelowe jak i materiały betonowe w postaci prefabrykatów (np. prefabrykaty z nisko-cementowych betonów korundowo- spinelowych firmy ArcelorMittal Refractories). Dostępne obecnie rozwiązania technologiczne obejmują betony LCC oraz ULCC, które zawierają spinel syntetyczny, tworzący się w warunkach in situ lub stanowiące ich kombinację. Jednakże wśród oferowanych komercyjnie materiałów brak jest betonów typu NCC, w których składzie wyjściowym zastosowana zostałaby wodna zawiesina nanometrycznego proszku Al_2O_3 jako komponent osnowy.

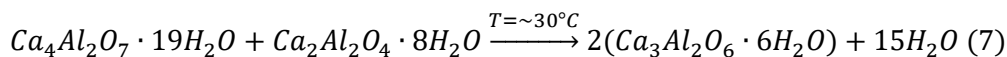
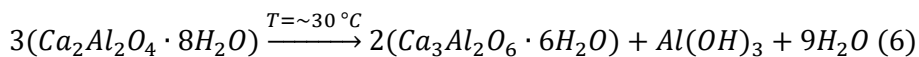
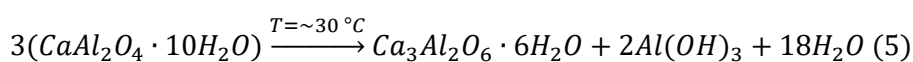
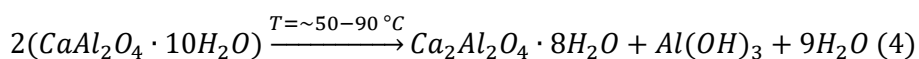
5. Chemia i technologia spoiw cementowych i beczementowych przeznaczonych do zastosowania w betonach ogniotrwałych korundowo - spinelowych

Chociaż w ostatnich dziesięcioleciach włożono wiele wysiłku w rozwój spoiw beczementowych, cement glinowo- wapniowy utrzymuje wciąż swoją dominującą pozycję wśród spoiw stosowanych w betonach ogniotrwałych. W zależności od ilości Al_2O_3 (od 40%_{mas}) w jego składzie, wyróżnia się różne odmiany cementu. Cement glinowo- wapniowy charakteryzuje się między innymi: szybkim wzrostem wytrzymałości, krótkim czasem wiązania oraz atrakcyjną ceną [40-43]. Zgodnie z układem dwuskładnikowym $\text{CaO-Al}_2\text{O}_3$ fazami reaktywnymi w cementach glinowo- wapniowych są: monoglinian wapniowy (CaAl_2O_4 ; CA), dwuglinian wapniowy (CaAl_4O_7 ; CA_2) oraz siedmioglinian dwunastowapniowy ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$; C_{12}A_7). Właściwości wiążące cementów glinowo- wapniowych wynikają z reakcji hydratacji, w wyniku której świeża mieszanka betonowa po homogenizacji z wodą nabiera wytrzymałości mechanicznej. Bezpośrednio po zmieszaniu cementu glinowo- wapniowego z wodą następuje kongruentne rozpuszczanie bezwodnych faz w wyniku czego w roztworze pojawiają się następujące jony: OH^- , Ca^{2+} oraz $[\text{Al}(\text{OH})_4]^-$. W kolejnym etapie obserwuje się zarodkowanie hydratów i ich masowe wytrącanie. Niezwykle istotnym czynnikiem decydującym o przebiegu hydratacji cementu jest temperatura, gdyż determinuje ona rodzaj tworzących się hydratów. Zgodnie z danymi literaturowymi [40-45], w temperaturze do 15 °C główny produkt hydratacji stanowi metastabilna faza CAH_{10} , która w zakresie temperatur 15-35 °C współlistnieje z fazą C_2AH_8 , której ilość jest proporcjonalna do temperatury. Przyjmuje się, że w temperaturze powyżej 25°C faza C_2AH_8 jest głównym produktem hydratacji, który powstaje wraz z uwodnionym tlenkiem glinu, początkowo występującym w formie żelu, z czasem krystalizującym jako gibbsyt AH_3 . W temperaturze powyżej 35 °C w wyniku hydratacji tworzą się C_3AH_6 (sześcioglinian wapniowy, CaAl_2O_4) oraz AH_3 . Podane zakresy temperatur w zależności od wybranych źródeł literaturowych mogą się nieznacznie różnić. Podsumowanie zachodzących reakcji przedstawiono za pomocą równań 1-3:

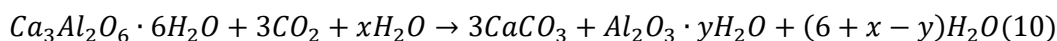
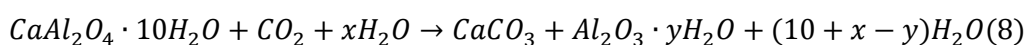




Wraz z upływem czasu następuje konwersja hydratów metastabilnych do regularnego C_3AH_6 , poprzez rozpuszczanie faz heksagonalnych i krystalizację fazy regularnej, a szybkość tej przemiany zależy od temperatury, wilgotności oraz pH układu. Ponadto, zgodnie z [44] konwersja CAH_{10} do C_3AH_6 w temperaturze 50-90 °C zachodzi przez utworzenie produktu przejściowego w postaci C_2AH_8 aż do momentu, w którym C_3AH_6 ulegnie samozarodkowaniu. Przebieg reakcji konwersji przedstawiono za pomocą równań 4-7:



Z uwagi na fakt, iż zastosowanie cementu glinowo- wapniowego jako spoiwa nie odbywa się w układzie zamkniętym, obserwuje się również karbonatyzację utworzonych hydratów, co przedstawiono za pomocą równań 8-10:

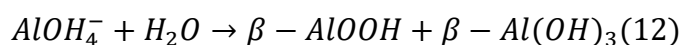
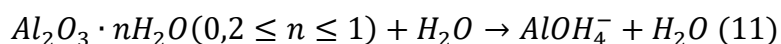


Reakcja konwersji z uwagi na znaczne różnice w gęstości analizowanych faz (CAH_{10} 1,72g/cm³, C_2AH_8 1,95 g/cm³, C_3AH_6 2,52 g/cm³ i AH_3 2,44 g/cm³) oraz wydzielanie się wody związana jest ze wzrostem porowatości i przepuszczalności, a tym samym spadkiem wytrzymałości materiałów na wiązaniu cementowym, co jest zjawiskiem niekorzystnym. Dlatego też w celu jej ograniczenia wprowadzane są do cementów dodatki zawierające reaktywną krzemionkę np.: mielony granulowany żużel wielkopiecowy oraz materiały o właściwościach pucolanowych, jak np. pył krzemionkowy, popioły lotne, naturalne zeolity czy metakaolin [45]. Ponadto w trakcie wypalania materiałów ogniotrwałych na wiązaniu cementowym, przeobrażenie więźby hydraulicznej w więźbę ceramiczną związane jest ze spadkiem wytrzymałości mechanicznych w temperaturach 300-1000°C ze względu na zachodzącą dehydratację i dehydroksylację utworzonych wcześniej hydratów CAH_{10} , C_2AH_8 , C_3AH_6 oraz gibbsytu AH_3 w temperaturach odpowiednio: 120 °C, 170–195 °C, 240–370 °C, oraz 210–300°C. Dochodzi wówczas do zniszczenia sieci hydratów cementu, co w połączeniu ze

wzrostem porowatości na skutek następującego w temperaturach 300-700 °C rozkładu termicznego produktów dehydratacji i dehydroksylacji, prowadzi do spadku wytrzymałości mechanicznej materiału [40-43, 46-49]. Ponadto, zastosowanie cementu glinowo- wapniowego jako spoiwa w kombinacji z nośnikami krzemionki np. nano- lub mikrometryczną krzemionką, zolem krzemionkowym, związane jest z pojawieniem się okresowo faz ciekłych w trakcie wypału/pracy urządzenia cieplnego, których skład chemiczny w temperaturze otoczenia zbliżony jest anortytu ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, temperatura topnienia 1553 °C [50-52]) czy gehlenitu ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, temperatura topnienia 1593 °C [51]). Pojawienie się faz ciekłych prowadzi do pogorszenia właściwości termomechanicznych (ogniotrwałość pod obciążeniem, odporność na pełzanie w podwyższonych temperaturach, wytrzymałość na zginanie w podwyższonych temperaturach) [6]. Dlatego też w ostatnich latach intensywnie rozwijano technologie monolitycznych materiałów ogniotrwałych o niskiej lub ultraniskiej zawartości cementu, a także materiałów bezcementowych [21, 53]. Tendencja ta wymusiła poszukiwanie alternatywnych spoiw, które mogłyby zastąpić cement glinowo- wapniowy lub być z nim stosowane w kombinacji.

Drugim stosowanym spoiwem jest spoiwo bezcementowe stanowiące fazę amorficznego, przejściowego tlenku glinu $\rho\text{-Al}_2\text{O}_3$ (HA, z ang. hydratable alumina), który otrzymywany jest w trakcie błyskawicznej kalcynacji (z ang. flash calcination) gruboziarnistego gibbsytu (10-50 μm). Wykazuje on znaczną rozpuszczalność w wodzie i ulega ponownej hydroksylacji tworząc boehmit ($\beta\text{-AlOOH}$) oraz bajeryt ($\beta\text{-Al}(\text{OH})_3$). Głównymi zaletami betonów wiązanych uwodnionym Al_2O_3 w porównaniu z materiałami opartymi na cemencie glinowo- wapniowym jest lepsza odporność na korozję oraz lepsze właściwości termomechaniczne. Zgodnie z literaturą, nawet śladowe ilości CaO w betonach zawierających krzemionkę negatywnie wpływają na żywotność wyłożenia [54]. Dodatkowo, betony bez CaO , zawierające uwodniony Al_2O_3 jako spoiwo charakteryzują się małą zmianą wymiarów liniowych w trakcie wypalania/pracy z uwagi na brak tworzącego się w warunkach in situ CA_2 oraz CA_6 , których obecność związana jest z dużą ekspansją objętościową [55]. Obecnie $\rho\text{-Al}_2\text{O}_3$ jest szeroko stosowanym spoiwem w prefabrykowanych kształtkach przeznaczonych na wyłożenia kadzi stalowniczych (zwłaszcza ścian bocznych), a ostatnio wykazano, że potencjalnie może zostać zastosowane jako spoiwo w materiałach korundowo- spinelowych bez SiO_2 wykorzystywanych do produkcji dysz napowietrzających [54].

Mechanizm wiązania, tak jak w przypadku spoiwa cementowego, opiera się na reakcji hydratacji. Pierwszy etap związany jest ze zwilżaniem, hydroksylacją i rozpuszczaniem w wyniku czego w układzie pojawiają się jony $[Al(OH)_4]^-$. Wysokie stężenie powstałych jonów $[Al(OH)_4]^-$ nasycza wodę wokół cząstek stałych, co powoduje wytrącanie się pseudo-boehmitu w postaci grubej warstwy amorficznego żelu na ich powierzchniach. W otrzymanym żelu po czasie zwykle krótszym niż 1h (w temperaturach powyżej 20°C) krystalizuje bajeryt [56] oraz, jak podają inne źródła literaturowe [57] w śladowych ilościach boehmit. Zachodzące reakcje podsumowują równania 11 oraz 12:

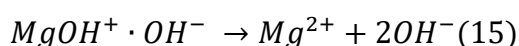
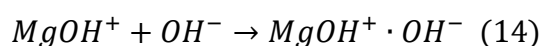
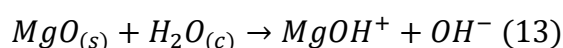


Zgodnie z literaturą hydratacja ρ - Al_2O_3 zależy od temperatury, atmosfery utwardzania oraz obecności innych dodatków, a w przedstawiony powyżej sposób zachodzi w przypadku materiałów, w których zarówno kruszywo jak i matrycę stanowi Al_2O_3 . Jeżeli hydratacja zachodzić będzie w układzie, w którym występuje MgO, wśród produktów hydratacji obecna będzie również faza podobna do hydrotalkitu ($Mg_6Al_2CO_3(OH)_6 \cdot 4H_2O$) [57] co z kolei poprawia wytrzymałość materiału po suszeniu i wypalaniu w temperaturach pośrednich (816 °C) oraz usprawnia odprowadzanie wody z materiału poprzez utworzenie sieci porów [58].

Dehydratacja β - $AlOOH$ i β - $Al(OH)_3$ zgodnie z danymi literaturowymi rozpoczyna się w temperaturze około 270°C i trwa do 350-400°C, w zależności od warunków wygrzewania i prowadzi do spadku wytrzymałości betonów. W wyższych temperaturach (600°C oraz 1000°C) następuje przemiana przejściowego Al_2O_3 (odmiany θ , δ) w α - Al_2O_3 , a zachodzące zmiany strukturalne oraz mikrostrukturalne osnowy przekładają się również na obniżenie właściwości mechanicznych [54].

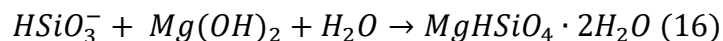
Ze względu na dużą powierzchnię właściwą spoiwo zawierające ρ - Al_2O_3 zwykle wymaga większych ilości wody oraz dłuższych i bardziej intensywnych procesów mieszania niż inne spoiwa hydrauliczne [59]. Dlatego też wiele z ostatnich badań naukowych skupiało się na poprawie jego właściwości reologicznych [54]. Intensywna, relatywnie szybka hydratacja, a także spadek wytrzymałości mechanicznych w temperaturach 300-1000°C oraz odpryskiwanie materiału w trakcie obróbki cieplnej spowodowane małą przepuszczalnością również stanowią kwestie problematyczne, które przyczyniły się do dalszych poszukiwań alternatywnego spoiwa bezcementowego [56].

Alternatywą dla cementu glinowo- wapniowego jest również zastosowanie spoiwa opartego na uwodnionych krzemianach magnezu: fazie M-S-H, zazwyczaj otrzymywanej w wyniku reakcji MgO lub $Mg(OH)_2$ w obecności wody z amorficzną, reaktywną krzemionką [60]. Odpowiednio dobierając substraty do syntezy fazy M-S-H, stosunek molowy Mg/Si , ilość wody, czy też stosując dodatki (np.: heksametafosforan sodu, superplastyfikator na bazie polikarboksylanów, roztwór buforowy $NaHCO_3/Na_2CO_3$) można niejako kształtować właściwości analizowanego spoiwa. Spoiwo to charakteryzuje się wysoką, zwiększającą się wraz ze zmniejszeniem ilości dodanej wody, a proporcjonalną do czasu wytrzymałością na ściskanie, co jest obecnie jednym z ważniejszych aspektów materiałów wiążących [61]. Dodatkowo wykorzystanie MgO z powszechnie dostępnych prekursorów o niskiej zawartości węgla, czy potencjalnie też „niewęglanowych” (np.: zagęszczone solanki, odpady górnicze, żużle stalowe, minerały krzemianowo- magnezowe (oliwin, serpentynit) czyni je przyjaznym dla środowiska poprzez zmniejszenie emisji CO_2 , co dodatkowo przekłada się na jego atrakcyjność [61]. Zgodnie z literaturą synteza fazy M-S-H zachodzi w trzech etapach. Homogenizacja mieszaniny MgO i SiO_2 z wodą prowadzi do rozpuszczania poszczególnych komponentów. Reakcja tworzenia $Mg(OH)_2$ z MgO zachodzi poprzez rozpuszczanie MgO i wytrącanie $Mg(OH)_2$, co podsumowują reakcje 13-15:



MgO jest donorem elektronu dla protonu z wody dzięki czemu ziarna MgO otrzymują dodatni ładunek powierzchniowy zgodnie z równaniem 13, a na skutek elektrostatycznego przyciągania na powierzchni adsorbowane są ujemnie naładowane jony OH^- (równanie 14). Zgodnie z równaniem 15 kompleks zaadsorbowany na powierzchni MgO jest rozpuszczany w środowisku wodnym, powstają jony Mg^{2+} oraz OH^- , a gdy ich stężenie przekroczy rozpuszczalność w roztworze, na powierzchni MgO następuje wytrącanie $Mg(OH)_2$ w postaci warstwy. SiO_2 , w silnie zasadowym środowisku (pH 10–12), które powstaje z uwagi na reakcję MgO oraz wody, częściowo rozpuszcza się i tworzy kwas krzemowy ($HSiO_3^-$) [62]. Następnie $Mg(OH)_2$ reaguje z rozpuszczoną krzemionką, tworząc przejściową fazę M-S-H o niższym stopniu organizacji niż produkt końcowy, która ostatecznie zastępowana jest fazą M-S-H o bardziej uporządkowanej strukturze i potencjalnie innym stosunku Mg/Si (który zależy od stosunku Mg/Si prekursorów). Dostępne źródła literaturowe [60-64] donoszą, że synteza M-S-H odbywa

się przez utworzenie produktu pośredniego jakim jest $Mg(OH)_2$, a przebieg reakcji oprócz reaktywności MgO , wybranego źródła krzemionki, stosunku molowego Mg/Si , ilości wody, determinują również warunki reakcji takie jak temperatura oraz pH. Podsumowanie reakcji otrzymywania fazy M-S-H przedstawiono za pomocą równania 16:

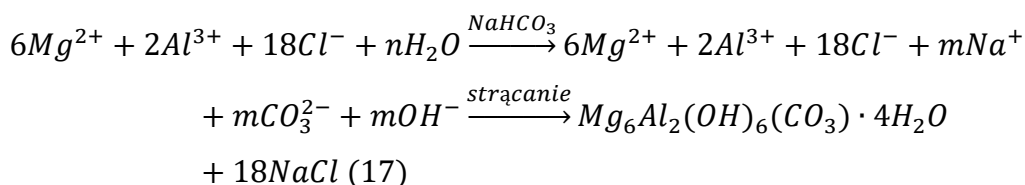


Faza M-S-H charakteryzuje się nieuporządkowaną strukturą warstwową, ze zmiennymi odległościami pomiędzy poszczególnymi warstwami, które determinuje ładunek warstw, a tym samym ilość zaadsorbowanej i wbudowanej wody w przestrzenie międzywarstwowe wody [62]. Rozkład termiczny spoiwa na bazie M-S-H, w zależności od stosunku molowego Mg/Si , prowadzi do syntezy enstatytu ($MgSiO_3$, temperatura topnienia $1557^\circ C$ [63]) i/lub forsterytu (Mg_2SiO_4 , temperatura topnienia $1890^\circ C$ [64]). Synteza forsterytu jest korzystna, gdyż oprócz wysokiej temperatury topnienia charakteryzuje się również niską rozszerzalnością cieplną, dobrą stabilnością chemiczną oraz niskim przewodnictwem cieplnym [7].

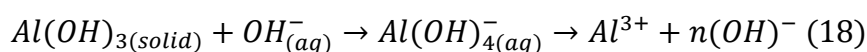
Rozwój nisko- i ultraniskocementowych betonów ogniotrwałych zaowocował badaniami nad zastosowaniem reaktywnych nano- i mikrometrycznych proszków ceramicznych, których wykorzystanie miało na celu zmniejszenie zapotrzebowania na wodę zarobową, poprawę płynności, czy też intensyfikację spiekania [65]. Zgodnie z literaturą przedmiotem badań były między innymi układy zawierające MgO oraz Al_2O_3 , które w wyniku reakcji w obecności wody tworzą fazę M-A-H, strukturalnie zbliżoną do hydrotalkitu magnezowo- glinowego. Hydrotalkit Mg-Al jest podwójnym warstwowym wodorotlenkiem magnezowo-glinowym, którego wzór ogólny opisano w literaturze jako: $[Mg_xAl_y(OH)_{2x+2y}](CO_3)_{y/2} \cdot nH_2O$. Wyróżnia się on budową warstwową (dodatkowo naładowane warstwy brucytopodobne $[Mg_xAl_y(OH)_{2x+2y}]^{x+}$ oraz przeciwnie naładowane warstwy $[(CO_3)_{y/2}^{2-} \cdot nH_2O]^{x-}$), z której wynika stopniowa dehydratacja oraz dehydroksylacja [65]. Badania [57] wykazały, że betony zawierające podwójny warstwowy wodorotlenek magnezowo-glinowy tworzący się w warunkach in situ w matrycy betonu, charakteryzują się wyższą wytrzymałością mechaniczną po etapie pielęgnacji oraz suszenia [56], jego obecność ogranicza ilość $Mg(OH)_2$ w osnowie (podobnie jak faza M-S-H), a dodatkowo wspomaga syntezę spinelu w trakcie wypalania materiału. Ponadto, występowanie fazy strukturalnie zbliżonej do hydrotalkitu jako

komponentu osnowy sprzyja także tworzeniu porów, których sieć usprawnia odprowadzanie wody [64].

Istnieją różne metody syntezy podwójnego warstwowego wodorotlenku magnezowo-glinowego, które różnią się między sobą czasem otrzymywania, ilością zużytej energii, wymaganą czystością substratów i czystością uzyskanego produktu końcowego (np.: synteza mechanochemiczna, hydrotermalna, współstrącanie, zol-żel [66-71]). Najczęściej opisywaną w literaturze metodą otrzymywania fazy M-A-H, jest współstrącanie z wykorzystaniem wodnego roztworu soli magnezu i glinu np. $MgCl_2$ oraz $AlCl_3$ w stosunku molowym 3:1 lub 2:1, a równanie 17 stanowi podsumowanie tej metody.

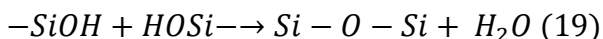


Niewątpliwą zaletą tej metody jest możliwość kontroli nukleacji, a tym samym wielkości cząstek otrzymanego podwójnego warstwowego wodorotlenku magnezowo-glinowego, poprzez zmianę pH roztworu, temperatury, czy też intensywności mieszania. W środowisku obojętnym lub kwaśnym w roztworze współistnieją jony Mg^{2+} , Al^{3+} oraz Cl^{-} , jednakże zwiększenie pH roztworu poprzez dodanie np. $NaHCO_3$ lub NH_4HCO_3 , i tym samym wprowadzenie anionów CO_3^{2-} prowadzi do strącania podwójnego warstwowego wodorotlenku. Istotne jest, iż w tym przypadku w układzie oprócz hydrotalkitu obecne są również inne jony (np. Na^{+}), które muszą zostać usunięte, gdyż ich obecność w postaci zanieczyszczeń skutkować będzie tworzeniem niskotopliwych faz w materiale ogniotrwałym co jest zjawiskiem niepożądanym. Ostatnim etapem otrzymywania M-A-H poprzez współstrącanie jest suszenie lub liofilizacja w celu uzyskania produktu reakcji w postaci proszku, co wymaga dodatkowego nakładu energetycznego [66-71]. Zaproponowany przez R. Salomę [66] mechanizm syntezy M-A-H z wodnych zawiesin MgO i $Al(OH)_3$ opiera się na reakcjach hydratacji-rozpuszczania-współstrącania, które zachodzą jednocześnie. MgO reaguje z wodą zgodnie z reakcjami 13-15 dzięki czemu w roztworze pojawiają się jony Mg^{2+} oraz OH^{-} , a zwiększające się pH roztworu sprzyja hydroksylacji, rozpuszczaniu $Al(OH)_3$ i uwalnianiu jonów Al^{3+} zgodnie z równaniem 18:



Obecność jonów Al^{3+} , Mg^{2+} , OH^- oraz $(CO_3)^{2-}$ w środowisku zasadowym powoduje wytrącanie podwójnego warstwowego wodorotlenku magnezowo-glinowego. W materiałach zarówno magnezjowych, jak i korundowych z dodatkiem MgO wiązanych $\rho-Al_2O_3$ [65] zaobserwowano syntezę fazy strukturalnie zbliżonej do hydrotalkitu [55, 57] jednakże prace dotyczące wykorzystania jako potencjalne spoiwo bezzementowe reaktywnych nano- i mikroproszków MgO oraz Al_2O_3 zostały zapoczątkowane i spopularyzowane dopiero niedawno [65, 72].

W ostatnich latach w technologii materiałów ogniotrwałych popularne stały się również zawiesiny wodne zawierające mikro- lub nanometryczne proszki Al_2O_3 lub SiO_2 , czyli spoiwa koloidalne. Zol krzemionkowy to stabilna (zazwyczaj stabilizowany za pomocą odpychania elektrostatycznego, uzyskiwanego dzięki kontrolowanemu pH roztworu) zawiesina nanocząstek amorficznej krzemionki, który w zależności od sposobu otrzymywania różnić się może zawartością SiO_2 (15-50% wt.), pH, wielkością oraz kształtem cząstek [73]. Zgodnie z literaturą [74], struktura cząstek krzemionki jest tworzona przez sieć siloksanową ($-Si-O-Si-$), podczas gdy warstwę powierzchniową tworzą grupy silanolowe ($-SiOH$) oraz hydroksylowe. Cząsteczki krzemionki koloidalnej mogą łączyć się ze sobą poprzez żelowanie i koagulację, nadając tym samym początkową wytrzymałość. Żelowanie umożliwia łącznie pojedynczych cząstek i utworzenie rozgałęzionego łańcucha w wyniku czego powstaje trójwymiarowa sieć. Oba mechanizmy wiązania są kontrolowane przez: zmianę pH, dodatek elektrolitów i/lub cieczy organicznych oraz zmianę temperatury, a proces rozpoczyna się od destabilizacji zawiesiny [73, 74], która zachodzi na przykład podczas obróbki cieplnej materiału. Podczas ogrzewania następuje odprowadzanie wody, a grupy ($Si-OH$) przekształcają się w wiązania siloksanowe ($Si-O-Si$), zgodnie z reakcją 19 [73]:



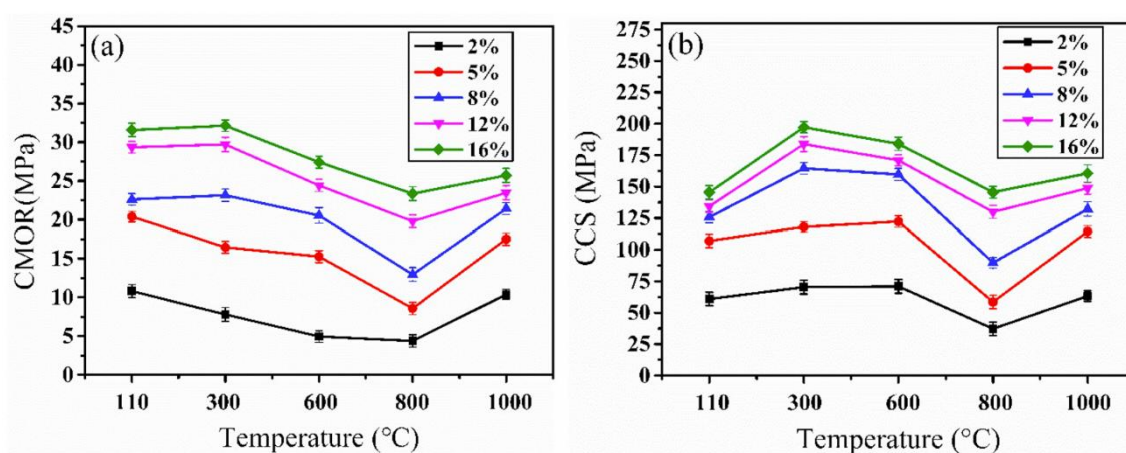
Podczas suszenia cząstki zbliżają się do siebie, tworzy się trójwymiarowa sieć, w której ciecz zatrzymywana jest przez siły kapilarne, następuje wzmocnienie wiązań pomiędzy cząstkami w miejscach ich kontaktu poprzez koalescencję. Na pewnym etapie tworzy się przejrzysty, spójny film żelowy, a dalsze suszenie prowadzi do kurczenia się żelu i jego pęknięcia, czego wynikiem są kruche, włókniste lub przypominające włosy pozostałości żelu krzemionkowego [74].

Zol krzemionkowy cieszy się popularnością jako spoiwo w materiałach wysokoglinowych ze względu na reakcję z Al_2O_3 w wyniku której na wcześniejszym etapie spiekania (temperatura około 1100 °C) powstaje mullit [59, 74, 75], tym samym

w temperaturze niższej niż w materiałach wiązanych cementem glinowo- wapniowym tworzy się wiązanie ceramiczne. Dodatkowo z uwagi na sferyczny kształt nanometrycznych cząstek, jego obecność poprawia właściwości reologiczne co przekłada się na mniejszą ilość dodawanej do betonu wody oraz krótszy niezbędny czas homogenizacji mieszanki betonowej. Umożliwia także szybsze, bezpieczniejsze wygrzewanie materiału, bez konieczności suszenia wstępnego z uwagi na tworzenie bardziej przepuszczalnej i porowatej mikrostruktury [76]. Problemem jest natomiast niska początkowa wytrzymałość, przed wypaleniem, a także aglomeracja i segregacja cząstek w matrycy betonu [8]. Ponadto, jego zastosowanie jest ograniczone ze względu na możliwość obecności wolnego SiO_2 w materiale i tworzenie się fazy ciekłej poniżej 1600°C [77]. Wady zolu krzemionkowego jako spoiwa skierowały uwagę naukowców, w kierunku zolu glinowego, którego zastosowanie zapobiega tworzeniu się fazy ciekłej, zwiększając tym samym spektrum jego zastosowań [7, 77]. Charakteryzuje się on jednak szybszym żelowaniem, co wpływa negatywnie na reologię betonu i powoduje szybsze wiązanie. Dodatkowo, jego zastosowanie wiąże się z otrzymaniem bardziej zwartej mikrostruktury co z kolei przekłada się na zwiększenie wytrzymałości mechanicznej [78] ale także może wiązać się z utrudnionym odprowadzaniem wody i prowadzić do powstawania pęknięć w trakcie obróbki cieplnej materiału. Dlatego też badania nad potencjalnym wykorzystaniem zolu glinowego nadal leżą wśród zainteresowań naukowców.

6. Sposoby kształtowania właściwości betonów ogniotrwałych w temperaturach pośrednich 300-1000°C

Zgodnie z aktualnym stanem wiedzy, zastosowanie cementu glinowo- wapniowego w wysokoglinowych betonach ogniotrwałych związane jest ze spadkiem wytrzymałości mechanicznej materiałów w zakresie temperatur 300-1000 °C [40-43, 46-49]. Jak wspomniano w rozdziale 5, poniżej 400 °C zachodzi odpowiednio dehydratacja i dehydroksylacja utworzonych wcześniej hydratów oraz gibbsytu. Tym samym dochodzi wówczas do zniszczenia sieci hydratów cementu, co w połączeniu ze wzrostem porowatości prowadzi do spadku wytrzymałości mechanicznej materiału [46-49]. Pogorszenie wytrzymałości mechanicznej w temperaturach w zakresie od 700°C do 900°C najprawdopodobniej nie jest związane z zachodzącymi reakcjami rozkładu, a wynika ze znacznej różnicy w morfologii pomiędzy C_3AH_6 oraz gibbsytem, a produktami ich rozkładu [26, 79]. Przykładowy wykres zmian wytrzymałości mechanicznej betonów cementowych przedstawiono na Rysunku 2.



Rysunek 2 Wytrzymałość na ściskanie (a) oraz zginanie (b) prefabrykatów betonowych o różnej zawartości cementu glinowo- wapniowego, poddanych obróbce cieplnej w temperaturze: 300°C, 600°C, 800°C lub 1000°C [79].

Z technologicznego punktu widzenia omawiane tutaj pogorszenie wytrzymałości mechanicznych materiału jest niekorzystne, gdyż z uwagi na występujący gradient temperatury w trakcie pracy urządzenia, w którym został zastosowany beton na wiązaniu cementowym, może dochodzić do odpryskiwania i pęknięcia wyłożenia, co znacząco skraca jego żywotność. Dlatego też niezwykle istotne jest poszukiwanie nowych rozwiązań pozwalających na całkowite wyeliminowanie lub ograniczenie spadku wytrzymałości mechanicznej w temperaturach 300-1000°C.

Aktualna literatura naukowa donosi, iż podjęte zostały próby mające na celu ograniczenie ww. spadku wytrzymałości poprzez zastosowanie dodatków inicjujących

wcześniejsze spiekanie oraz wspomagających zagęszczenie mikrostruktury [80]. Takie rozwiązanie często skorelowane jest ze zmniejszeniem ilości lub całkowitym zastąpieniem cementu glinowo- wapniowego innym spoiwem bezcementowym. Wykorzystanie nanododatków lub związków takich jak: zawiesiny koloidalne, materiały na bazie krzemionki lub boru [74, 80-82] może przyspieszyć przemiany fazowe zachodzące w matrycy betonu, a tym samym skutkować wcześniejszym tworzeniem się wiązania ceramicznego z uwagi na tworzenie się fazy ciekłej w temperaturze 600-1000°C. Jednakże, obecność fazy ciekłej wpływa negatywnie na właściwości termomechaniczne materiału, dlatego też w ostatnich latach projektowano materiały, w których faza ciekła tworzyła się tylko podczas pierwszej obróbki cieplnej, w wyniku której powstawały nowe, wysokoogniotrwale fazy np. $\text{Al}_{18}\text{B}_4\text{O}_{33}$ lub $\text{Al}_6\text{Si}_2\text{O}_{13}$ [80-82]. W literaturze [83] opisywano również pozytywny wpływ CaCO_3 w materiałach wysokoglinowych, którego dodatek przełożył się na poprawę właściwości mechanicznych w temperaturach 300-1000°C (w porównaniu do materiałów wiązanych cementem glinowo- wapniowym) poprzez zjawisko spiekania-wzrostu ziaren i koalescencji (z ang. SCC sintering-coagulation-coalescence). Zastosowanie CaCO_3 prowadziło jednak do otrzymania materiałów, które charakteryzowały się niską wytrzymałością na etapie pielęgnacji oraz suszenia [80]. Ponadto, w przypadku materiałów magnezjowych, w których zastosowano $\rho\text{-Al}_2\text{O}_3$ jako spoiwo hydrauliczne, zaobserwowano poprawę właściwości mechanicznych w temperaturach pośrednich, co przypisywane jest pojawieniu się fazy strukturalnie zbliżonej do hydrotalkitu w osnowie w trakcie jego sezonowania.

7. Właściwości technologiczne betonów ogniotrwałych korundowo- spinelowych.

Zgodnie z podziałem zaproponowanym przez F. Nadachowskiego [84], właściwości materiałów ogniotrwałych można podzielić na fizyczne (własności: związane ze zwartością, mechaniczne, cieplne oraz przewodność elektryczna) i technologiczne (własności ogniowe oraz odpornościowe). Jedną z istotniejszych właściwości użytkowych materiałów ogniotrwałych jest wytrzymałość mechaniczna, gdyż wpływa bezpośrednio na inne właściwości na przykład odporność na nagłe zmiany temperatury. Najogólniej, pojęcie to określa zdolność do przenoszenia obciążeń i zależy od budowy materiału na poziomie atomowym, mikrostruktury i warunków obciążania [85]. Wytrzymałość na ściskanie (z ang. cold crushing strength, CCS) oraz wytrzymałość na zginanie w temperaturze otoczenia (z ang. cold modulus of rupture, CMoR) stanowią dwie najczęściej wyznaczane wytrzymałości mechaniczne materiałów ogniotrwałych. Wytrzymałości te zależą od mikrostruktury im bardziej zwarta i jednorodna mikrostruktura oraz im mniej jest w niej pęknięć oraz porów, tym wyższa jest wytrzymałość. Modelowanie mikrostruktury poprzez odpowiedni dobór składu ziarnowego oraz właściwie przeprowadzone etapy pielęgnacji, suszenia oraz wypalania mają realny wpływ na właściwości końcowe materiału. Jednakże, biorąc pod uwagę temperaturę pracy wyłożeń wykonanych z materiałów ogniotrwałych, istotna jest również wytrzymałość mechaniczna materiału, który poddany został jednocześnie działaniu wysokiej temperatury i obciążenia. Jednym z badań pozwalających na jakościową ocenę wytrzymałości w podwyższonej temperaturze jest badanie wytrzymałości na zginanie (HMoR), które opisuje norma PN-EN ISO1927-6:2013-06 [86]. Wynik badania wytrzymałości na zginanie w podwyższonej temperaturze zależy od parametrów mikrostruktury, a także od ilości fazy ciekłej, a więc od składu chemicznego i fazowego materiału ogniotrwałego.

Ogniotrwałość zwykła to parametr określający temperaturę, w której dany materiał ogniotrwały zaczyna mięknąć i deformować się pod własnym ciężarem i stanowi podstawową własnością materiałów ogniotrwałych, ponieważ determinuje możliwość jego zastosowania. Niemniej jednak, w bardzo rzadkich przypadkach zniszczenie wyłożenia następuje wyłącznie na skutek działania wysokiej temperatury. W każdym urządzeniu cieplnym wiele czynników oddziałuje jednocześnie na materiał powodując jego zużycie w temperaturze niższej aniżeli wynikałoby to z ogniotrwałości zwykłej, która zależy głównie od składu chemicznego, fazowego oraz mikrostruktury [84].

Bardziej istotnym parametrem jest ogniotrwałość pod obciążeniem (z ang. refractoriness under load, RUL), która według normy PN-EN ISO 1893 :2008 [87] stanowi miarę zachowania się materiału ogniotrwałego, który poddany został kompleksowemu oddziaływaniu obciążenia, rosnącej temperatury oraz czasu. Podczas pomiaru rejestrowane jest odkształcenie próbki, na którą działa stałe obciążenie wynoszące 0,2 MPa, temperatura natomiast jest parametrem zmiennym. Początek deformacji próbki połączony jest z powstawaniem fazy ciekłej w materiale. Zgodnie z normą, miarą ogniotrwałości pod obciążeniem są temperatury charakterystyczne odpowiadające określonym odkształceniom, a literatura wskazuje temperaturę $T_{0,5}$ jako maksymalną zalecaną temperaturę pracy betonu ogniotrwałego [87, 88]. Ogniotrwałość pod obciążeniem determinowana jest przez skład ziarnowy, chemiczny i fazowy, jak również przez mikrostrukturę i właściwości fazy ciekłej. Wypalanie materiałów ogniotrwałych także odgrywa kluczową rolę w kształtowaniu analizowanej właściwości, gdyż decyduje nie tylko o składzie fazowym, ale także o zrastaniu się faz stałych, rekrytalizacji i porowatości (parametrach mikrostruktury).

Kolejną istotną właściwość technologiczną stanowi pełzanie. Pełzanie pozwala określić przebieg deformacji próbki w trakcie długoczasowych pomiarów przy niezmiennych wartościach temperatury oraz obciążenia. Wynik analizy pełzania materiałów ogniotrwałych dostarcza dodatkowych informacji dotyczących zachowania się tych materiałów w podwyższonej temperaturze, które nie wynikają z badania ogniotrwałości pod obciążeniem. Pomimo, że w obu przypadkach bada się odkształcenie materiału, to w przypadku oznaczania odporności na pełzanie pomiar jest dłuższy. Oprócz badania pełzania przy ściskaniu (z ang. creep in compression, CIC) popularne jest również pomiar pełzania przy skręcaniu [84]. Zgodnie z normą PN-EN 993-9:1999 [89] pełzanie przy ściskaniu określa się jako izotermiczne odkształcenie materiału poddanego naprężeniu ściskającemu w funkcji czasu. W trakcie pomiaru na próbkę działa stałe obciążenie wynoszące 0,2 MPa, szybkość przyrostu temperatury wynosi od 4,5 do 5,5°C/min, a standardowy czas badania wynosi 25 godzin. Ocena odporności materiału na pełzanie odbywa się w oparciu o model projekcji parametru θ (z ang. θ -projection model), zgodnie z którym porównuje się szybkość pełzania ($\theta_3 \cdot \theta_4$ %/min) w fazie drugiej (faza stacjonarna ze stałą szybkością pełzania) [90]. Podobnie jak w przypadku ogniotrwałości pod obciążeniem, skład ziarnowy, chemiczny, fazowy oraz charakter fazy ciekłej i mikrostruktura determinować będą odporność materiału na pełzanie.

Wykładziny urządzeń cieplnych narażone są na gwałtowne zmiany temperatury, co stanowi jedną z przyczyn ich zniszczenia poprzez powstawanie pęknięć oraz odpryskiwanie materiału. Powstawanie pęknięć spowodowane jest występowaniem naprężeń, które są wynikiem pojawienia się gradientu temperatur (naprężenia cieplne drugiego rodzaju). Różnica temperatur pomiędzy warstwami materiału powoduje, iż jedna warstwa rozszerza się lub kurczy szybciej lub wolniej od drugiej, a wzajemne blokowanie swobodnego rozszerzania się i kurczenia obszarów o różnej temperaturze prowadzi do pojawienia się naprężeń cieplnych drugiego rodzaju. Jeżeli powstałe naprężenie przekroczy wartość krytyczną dla danego materiału, to spowoduje inicjację, a następnie propagację pęknięć, co w rezultacie doprowadzi do zniszczenia materiału. W latach 50-tych XX wieku Kingery [91] wskazał, iż na odporność na nagłe zmiany temperatury (OWT) materiału ogniotrwałego wpływ mają: przewodnictwo cieplne, rozszerzalność cieplna, wytrzymałość, kształt i wymiary próbki oraz własności sprężyste. Dodatkowo, w latach 60-tych XX w. Hasselmann [92] w oparciu o bilans energetyczny zdefiniował warunki, jakie muszą zostać spełnione, aby doszło do propagacji już istniejących pęknięć w materiale. Niestety opracowane teorie odporności na wstrząsy cieplne lepiej sprawdzają się przy wyjaśnianiu mechanizmów degradacji materiałów, aniżeli przy obliczaniu rzeczywistych wartości naprężeń. Niemniej jednak, można stwierdzić, iż na odporność materiału na nagłe zmiany temperatury wpływ mają: struktura, mikrostruktura, skład fazowy oraz chemiczny, a kształtowanie ww. własności odbywać się może poprzez odpowiedni dobór składu oraz właściwie przeprowadzony proces otrzymywania i obróbkę termiczną. W literaturze opisane są zróżnicowane metody badań odporności na nagłe zmiany temperatury [93-95], a zastosowana metoda pomiarowa jest tym lepsza, im warunki badania bardziej odwzorowują autentyczne warunki pracy badanego materiału. Określenie odporności w sposób empiryczny sprowadza się do umownej oceny skutków wywołanych przez bezpośrednie poddawanie materiałów cyklicznym zmianom temperatury.

Kompleksowa analiza wymienionych w niniejszym rozdziale właściwości jest niezwykle istotna pod kątem prawidłowej oceny potencjalnego zastosowania materiału ogniotrwałego. W przypadku właściwości termomechanicznych betonów ogniotrwałych w literaturze wyróżnia się dwa podejścia do badań: wykorzystanie próbek wypalonych w docelowej temperaturze lub próbek poddanych wstępnej obróbce cieplnej (np. w temperaturze 600°C). W zależności od zastosowanego podejścia, uzyskane wyniki badań różnią się, w związku z czym nie należy ich ze sobą bezpośrednio porównywać

[29, 88, 96]. W trakcie realizacji rozprawy doktorskiej do badań wykorzystano próbki betonów wypalonych w temperaturze 1500°C.

8. Podsumowanie części literaturowej

Rosnące zainteresowanie betonami typu LCC, ULCC i NCC oraz nieustanny rozwój przemysłu m.in. cementowego, hutniczego i szklarskiego, związane są z koniecznością poszukiwania nowych, lepszych rozwiązań materiałowych. Mimo postępujących badań i rozwoju technologii spoiw bezcementowych, cement glinowo-wapniowy wciąż odgrywa kluczową rolę jako podstawowy składnik wiążący w betonach ogniotrwałych. Przedstawiona w niniejszej dysertacji analiza literatury naukowej wykazała, że główne problemy związane z monolitycznymi wyłożeniami ogniotrwałymi, w których jako spoiwo stosuje się cement glinowo-wapniowy dotyczą ograniczonej odporności korozyjnej, niewystarczających właściwości termomechanicznych oraz wyraźnego spadku wytrzymałości mechanicznej w zakresie temperatur 300–1000°C. Ponadto, ze względów zarówno ekologicznych jak i ekonomicznych skracanie czasu obróbki cieplnej i wypalania betonów stało się jednym z kluczowych kierunków rozwoju. Podjęte próby zastąpienia spoiwa cementowego spoiwem alternatywnym w postaci p - Al_2O_3 lub zolu krzemionkowego okazały się niewystarczające ze względu na odpowiednio: zwiększoną porowatość prowadzącą do obniżenia wytrzymałości mechanicznej oraz niską wytrzymałość na etapie sezonowania oraz suszenia. Jednocześnie, dostępne dane literaturowe dotyczące zastosowania reaktywnych tlenków $MgO-Al_2O_3$ lub $MgO-Al_2O_3-SiO_2$ jako spoiwa w bezcementowych betonach ogniotrwałych korundowo-spinelowych są ograniczone. Również słabo udokumentowane jest zastosowanie wodnej zawiesiny nanometrycznego proszku Al_2O_3 (zolu glinowego) jako składnika osnowy betonu, co znajduje odzwierciedlenie w braku wdrożeń przemysłowych tego typu rozwiązań. Wskazane braki w literaturze naukowej, ograniczenia związane z zastosowaniem spoiwa cementowego oraz praktyka przemysłowa stanowią uzasadnienie podjętej tematyki badawczej.

W niniejszej dysertacji wyjaśniono mechanizm formowania więźby hydraulicznej betonu w wyniku hydratacji reaktywnych tlenków $MgO-Al_2O_3$ jako składników osnowy, wśród których wyróżnić można m.in. zol glinowy. Odpowiednio przeprowadzona hydratacja umożliwiła otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w matrycy betonu w temperaturach poniżej 50°C. Ponadto, zachodzące w trakcie obróbki cieplnej i wypalania reakcje rozkładu termicznego, rekombinacji tlenków mieszanych $Mg(Al)O$, a następnie ich reakcyjne spiekanie prowadzące do powstania fazy spinelowej w temperaturze 700°C umożliwiły stopniowy przyrost wytrzymałości mechanicznej materiału w temperaturach 300-

1000°C. Otrzymany prefabrykat betonowy korundowo- spinelowy wykazywał podwyższone właściwości mechaniczne, termomechaniczne i odpornościowe względem rozwiązań opisywanych w literaturze, co podkreśla jego potencjał aplikacyjny.

9. Hipoteza i cel badań

Celem niniejszej rozprawy doktorskiej było określenie mechanizmu formowania się więzby hydraulicznej betonu w wyniku hydratacji składników osnowy w temperaturach poniżej 50°C, a następnie więzby ceramicznej w materiałach ogniotrwałych bezcementowych i ultra-niskocementowych korundowo-spinelowych podczas ich obróbki cieplnej i wypalania w temperaturze do 1500°C poprzez:

- zdefiniowanie warunków otrzymywania podwójnego warstwowego wodorotlenku magnezowo-glinowego w mieszkankach reakcyjnych $\text{MgO-Al}_2\text{O}_3$ zarówno modelowych, jak i wewnątrz ogniotrwałego bezcementowego betonu korundowo-spinelowego na etapie formowania,
- rozpoznanie reakcji zachodzących w toku rozkładu termicznego składników osnowy betonu, w tym głównie podwójnego warstwowego wodorotlenku magnezowo-glinowego, rekombinacji struktur przejściowych tj. tlenków mieszanych typu Mg(Al)O , a następnie ich reakcyjnego spiekania prowadzącego do powstania fazy spinelowej w temperaturze niższej niż wynika to z tradycyjnej technologii.

W kontekście przyszłej aplikacji materiału, dodatkowym celem pracy było określenie roli ilości, rodzaju oraz składu fazy spinelowej w kształtowaniu właściwości fizycznych, mechanicznych, termomechanicznych i odpornościowych opracowanego betonu.

Na podstawie wskazanego celu badawczego sformułowano następujące hipotezy badawcze:

- właściwości betonu w stanie surowym można kształtować poprzez dobór składników spoiwa oraz warunków sezonowania, które determinują przebieg reakcji powstawania więzby hydraulicznej,
- o właściwościach betonu w zakresie temperatur do 1000°C decyduje charakter przemian składników osnowy zachodzący z utworzeniem reaktywnych faz przejściowych,
- ilość, rodzaj, skład fazy spinelowej oraz innych faz modyfikujących decydują o ukształtowaniu mikrostruktury, a tym samym warunkują właściwości fizyczne, mechaniczne, termomechaniczne i odpornościowe betonu korundowo-spinelowego.

10. Przewodnik po publikacjach cyklu przedstawionego jako rozprawa doktorska

10.1. *Effect of the particle size on the reactivity of MgO-Al₂O₃ hydrating mixtures: A long-term kinetic investigation of hydrotalcite synthesis, Karina Warmuz, Dominika Madej, Applied Clay Science, 211, 2021, s. 1-14.*

Pierwsze prace badawcze koncentrowały się na otrzymaniu mieszanin zawierających różne rodzaje proszków MgO (M) i Al₂O₃ (A), pretendujących do roli spoiw w bezcementowych betonach ogniotrwałych. Do badań wytypowano komercyjnie dostępne odczynniki chemiczne (Acros Organics, Aldrich) oraz dedykowane surowce przemysłowe o wysokiej czystości chemicznej (Almatis) w formie proszków nanometrycznych (nM, nA) i mikrometrycznych (μM, μA). Na podstawie studium literaturowego zaprojektowano serię mieszanin o różnych kompozycjach składu (nM_nA, nM_μA i μM_nA), dla których zachowano proporcję molową M:A wynoszącą 1:1. Kolejnym etapem badań, było przeprowadzenie analizy postępu hydratacji tych mieszanin w kierunku otrzymania podwójnego warstwowego wodorotlenku magnezowo-glinowego, który najlepiej można przybliżyć wzorem Mg₆Al₂CO₃(OH)₁₆·4H₂O.

Zastosowanie różnych prekursorów w postaci odczynników chemicznych oraz surowców przemysłowych wymagało przeprowadzenia badań umożliwiających porównanie ich reaktywności. Zmierzono potencjał zeta oraz powierzchnię właściwą, a także wykonano analizy XRD, FTIR, SEM-EDS oraz TG-EGA (MS), zarówno przed, jak i w trakcie procesu hydratacji proszków wyjściowych nM, nA, μM, μA. Wyniki potwierdziły, że Al₂O₃ w postaci nanometrycznego proszku wykazywał wyższą reaktywność niż jego mikrometryczny odpowiednik, co potwierdzono obecnością Al(OH)₃ jako produktu reakcji hydratacji. Większa reaktywność nA w porównaniu do μA wynikała z większego rozwinięcia powierzchni właściwej, odmiany polimorficznej oraz wyższej mobilności jonów w środowisku zasadowym. Natomiast, różnice w szybkości reakcji hydratacji MgO, pomiędzy nM, a μM były mniej wyraźne i wynikały głównie z rozwinięcia powierzchni właściwej, wielkości kryształitów oraz skłonności do aglomeracji. Podsumowanie wspomnianych właściwości przedstawiono w Tabeli 2.

Tabela 2 Podsumowanie różnic w reaktywności zastosowanych proszków wyjściowych.

Proszek wyjściowy	nM	μM	μA	nA
Odmiana polimorficzna	-	-	α	δ, γ
Wielkość kryształitów [nm]	11.75	45.05	65.23	6.66
Mobilność jonów (pH= ~10,5) [umcm/VS]	1,46	1,34	0,75	1.55
Powierzchnia właściwa BET [m ² /g]	28.20	10.90	6.6 0	56.60
Stopień aglomeracji	5.07	3.42	3.48	4.41

Analizę postępu hydratacji zaprojektowanych mieszanin dwuskładnikowych M–A prowadzono dla próbek pobranych po 12 godzinach oraz 3, 7, 14, 56 i 98 dniach od jej rozpoczęcia. Przebieg reakcji monitorowano na podstawie obecności podwójnego warstwowego wodorotlenku magnezowo-glinowego identyfikowanego według modelowego dyfraktogramu rentgenowskiego odpowiadającego strukturze $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$, oraz zmian w intensywności głównych linii dyfrakcyjnych MgO i $\text{Mg}(\text{OH})_2$. Analogiczne obserwacje prowadzono również w oparciu o potwierdzenie obecności lub braku charakterystycznych pasm w widmach FTIR. Analizy XRD oraz FTIR wykazały, że w próbkach nM_nA oraz μM_nA otrzymano podwójny warstwowy wodorotlenek magnezowo-glinowy, co potwierdziła obecność charakterystycznej dla $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ linii dyfrakcyjnej w pozycji $2\theta=11,62^\circ$ [98] oraz szerokiego pasma w położeniu $3000\text{--}3700\text{cm}^{-1}$ [98–100] już po 12h od rozpoczęcia hydratacji. Po 12h od rozpoczęcia hydratacji potwierdzono również występowanie $\text{Mg}(\text{OH})_2$ w każdej z trzech mieszanin reakcyjnych. Produktami końcowymi hydratacji mieszanin nM_nA oraz μM_nA były: podwójny warstwowy wodorotlenek magnezowo-glinowy, Al_2O_3 oraz faza amorficzna, podczas gdy w próbce nM_μA po 98 dniach od rozpoczęcia hydratacji obecny był $\text{Mg}(\text{OH})_2$ oraz nieprzereagowany proszek wyjściowy μA. Mieszanina reakcyjna nM_nA w porównaniu do μM_nA zawierała większą ilość podwójnego warstwowego wodorotlenku magnezowo-glinowego i mniejszą ilość fazy amorficznej, a więc charakteryzowała się większym stopniem przereagowania. Przeprowadzone badania potwierdziły, że reaktywność układów hydratacyjnych była ściśle zależna od właściwości zastosowanych substratów, w szczególności rodzaju Al_2O_3 o czym świadczył brak podwójnego warstwowego wodorotlenku magnezowo- glinowego w mieszaninie reakcyjnej nM_μA.

Przeprowadzone obliczenia termodynamiczne wskazały, że otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w wyniku hydratacji mieszanin reakcyjnych M-A poprzez etap pośredni, jakim jest utworzenie $\text{Mg}(\text{OH})_2$, jest procesem termodynamicznie uprzywilejowanym ($\Delta_r G < 0 \text{ kJ/mol}$), w porównaniu do bezpośredniej reakcji jonów w roztworze ($\Delta_r G > 0 \text{ kJ/mol}$).

Podsumowując uzyskane wyniki można stwierdzić, że hydratacja mieszanin reakcyjnych M-A prowadziła do otrzymania podwójnego warstwowego wodorotlenku magnezowo-glinowego, a przebieg reakcji (czas, stopień przereagowania) warunkowały wykorzystane surowce. Biorąc pod uwagę szybkość zachodzącej reakcji hydratacji, kluczowym aspektem determinującym ją jest zastosowanie nanometrycznego proszku Al_2O_3 . Mieszanina reakcyjna nM_nA ze względu na najszybszy przebieg reakcji oraz najwyższy stopień przemiany została wytypowana do dalszych badań, których celem było rozpoznanie reakcji zachodzących w toku rozkładu termicznego składników osnowy betonu, w tym głównie podwójnego warstwowego wodorotlenku magnezowo-glinowego, rekombinacji i reakcyjnego spiekania struktur przejściowych, które prowadziły do otrzymania fazy spinelowej w temperaturze niższej niż wynika to z tradycyjnej technologii. Wyniki wspomnianych badań przedstawiono w publikacji 10.3.

10.2. Comparison of the CAC-containing and CAC-free hydraulic binders in term of the hydrated matrix formation within refractory castables designed for the fast drying procedure, Karina Warmuz, Dominika Madej, Journal of Thermal Analysis and Calorimetry, 147, 18, 2022, s. 9975-9986.

Następne prace badawcze koncentrowały się na określeniu przebiegu reakcji hydratacji w temperaturze 20°C oraz 50°C modelowych mieszanin reakcyjnych zawierających surowce przemysłowe oraz nanometryczny proszek Al_2O_3 . Drugi etap badań ukierunkowany był na porównanie spoiw cementowych oraz bezcementowych pod kątem ich zastosowania jako komponentów matrycy betonów ogniotrwałych przeznaczonych do wygrzewania w warunkach szybkiego przyrostu temperatury. Mechanizm wiązania spoiw bezcementowych opierał się na procesie hydratacji mieszanin dwuskładnikowych zawierających tlenki MgO (M) i Al_2O_3 (A). Natomiast mechanizm wiązania spoiw cementowych były wynikiem reakcji hydratacji cementu glinowo-wapniowego (CAC) w obecności MgO , Al_2O_3 oraz składnika inertnego w postaci syntetycznego spinelu magnezowo-glinowego. Do badań wytypowano zarówno komercyjnie dostępny odczynnik chemiczny (nanometryczny proszek Al_2O_3 : nA, Aldrich) jak i dedykowane surowce przemysłowe o wysokiej czystości chemicznej (Almatis, Górka Cement). Przyjęto następujące oznaczenia surowców przemysłowych: spiekane MgO –SpM, topione MgO –TopM, reaktywny Al_2O_3 CTC 40 – μA , cement glinowo-wapniowy –CAC, oraz syntetyczny spinel magnezowo-glinowy: bogaty w jony glinu Al-rich spinel –AR78 lub bogaty w jony magnezu Mg-rich –MR66. Na podstawie studium literaturowego oraz wyników przedstawionych w publikacji 10.1 zaprojektowano serię mieszanin o zróżnicowanym składzie: SpM_nA, TopM_nA, MR66_CAC_ μA (próbka MR66_5M) oraz AR78_CAC_ μA _SpM (próbka AR78_5M). W przypadku próbek bezcementowych, analogicznie jak we wcześniejszych etapach badań, zachowano stosunek molowy M:A równy 1:1. Ponadto, dla wszystkich modelowych mieszanin reakcyjnych przyjęto stałą zawartość MgO .

Wpływ składu próbki oraz temperatury na przebieg hydratacji spoiw oceniano za pomocą analiz strukturalnych XRD oraz FTIR produktów reakcji, a także kalorymetrii izotermicznej, prowadzonej w dwóch temperaturach: 20°C oraz 50°C. Wyniki analiz XRD i FTIR wykazały, że proces hydratacji mieszanin dwuskładnikowych SpM_nA oraz TopM_nA, prowadzony odpowiednio w temperaturze 50°C i 20°C, prowadził do

otrzymania podwójnego warstwowego wodorotlenku magnezowo-glinowego po 12 oraz 72 godzinach od rozpoczęcia reakcji. Ponadto, brak charakterystycznej dla $\text{Mg}(\text{OH})_2$ linii dyfrakcyjnej w pozycji $2\theta = 37,966^\circ$ [72, 98] oraz ostrego pasma na widmie FTIR w położeniu 3699 cm^{-1} [98-100] wskazuje na jego natychmiastowe zużycie w przebiegu reakcji, co potwierdza wcześniej zaobserwowany przebieg reakcji otrzymywania podwójnego warstwowego wodorotlenku magnezowo-glinowego z udziałem $\text{Mg}(\text{OH})_2$ jako produktu pośredniego.

W przypadku próbek cementowych, również nie zaobserwowano obecności $\text{Mg}(\text{OH})_2$ na żadnym etapie hydratacji. Brak $\text{Mg}(\text{OH})_2$ w próbce MR66_5M wynikał prawdopodobnie z występowania MgO wewnątrz inertnych ziaren spinelu syntetycznego, natomiast w próbce AR78_5M jego brak sugeruje, że cement glinowo-wapniowy ograniczał hydratację MgO . Dodatkowo, wyższa intensywność refleksów uwodnionych faz glinokrzemianowych w próbce MR66_5M wskazała na jej większą reaktywność.

Kalorymetria izotermiczna została zastosowana do oceny kinetyki hydratacji zarówno spoiw cementowych, jak i bezcementowych, poprzez pomiar ilości oraz szybkości wydzielania ciepła. Analiza krzywych mikrokalorymetrycznych próbek bezcementowych zarówno w temperaturze 20°C jak i 50°C potwierdziła, że procesy związane ze zwilżaniem, rozpuszczaniem i wytrącaniem krystalicznych produktów hydratacji widoczne są jako jeden efekt egzotermiczny. Taki przebieg krzywych prezentowały próbki cementowe tylko w temperaturze 50°C , podczas gdy na krzywej mikrokalorymetrycznej próbek cementowych w temperaturze 20°C obecne były dwa efekty egzotermiczne rozdzielone wyraźnym okresem indukcji. Ponadto, na podstawie uzyskanych wyników można zauważyć, że hydratacja spoiw bezcementowych w porównaniu do spoiw cementowych w obu temperaturach szybciej kontrolowana była przez dyfuzję, na co wskazywało wypłaszczenie krzywej mikrokalorymetrycznej po osiągnięciu maksimum wydzielania ciepła.

Wyniki przedstawione w publikacji potwierdziły, że hydratacja mieszanin dwuskładnikowych M-A, zawierających MgO w postaci surowca przemysłowego oraz nA, prowadzi do powstania podwójnego warstwowego wodorotlenku magnezowo-glinowego zarówno w temperaturze 20°C , jak i 50°C . Zgodnie z otrzymanymi wynikami, temperatura stanowiła kolejny czynnik warunkujący przebieg (szybkość) reakcji hydratacji. Ponadto, porównanie hydratacji w matrycach tradycyjnych betonów cementowych i bezcementowych, prowadzonej w temperaturze 50°C , wskazuje na

zbliżony przebieg reakcji, co podkreśla ich potencjał aplikacyjny. Mając na uwadze, że stosowanie nanometrycznego proszku Al_2O_3 w warunkach przemysłowych wiąże się z licznymi trudnościami takimi jak: duża objętość, intensywne pylenie oraz utrudniona homogenizacja, w kolejnej publikacji oceniono możliwość zastosowania wodnej zawiesiny nanometrycznego proszku Al_2O_3 w modelowych mieszaninach reakcyjnych oraz jako komponent matrycy betonu.

10.3. *Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures, Karina Warmuz, Dominika Madej, Journal of the European Ceramics Society, 42, 5, 2022, s. 2545-2555.*

Trzecia publikacja zatytułowana "Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures" łączy badania dotyczące modelowych mieszanin reakcyjnych $\text{MgO-Al}_2\text{O}_3$ z analizą zwartości oraz wytrzymałości na zginanie i ściskanie opracowanego betonu ogniotrwałego na etapie jego obróbki cieplnej w temperaturach do 1000°C . Wyniki przedstawione w pracy dotyczyły możliwości zastosowania mieszanin reakcyjnych zawierających surowce przemysłowe jako składniki osnowy betonu, których hydratacja w temperaturach poniżej 50°C ukierunkowana była na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego. W trakcie realizacji tej części badań zastosowano komercyjnie dostępne odczynniki chemiczne (Evonik, Aldrich): nanometryczne proszki MgO (M) i Al_2O_3 (A), a także dedykowane surowce przemysłowe: spiekane (d-M) lub topione (f-M) MgO . Należy podkreślić, że Al_2O_3 zastosowano również w postaci wodnej zawiesiny nanometrycznego proszku (As). Kolejnym etapem była analiza zmian strukturalnych i mikrostrukturalnych osnowy zachodzących w trakcie obróbki cieplnej betonu w zakresie temperatur od 20°C do 1000°C , i ich powiązanie z wytrzymałością na zginanie oraz ściskanie betonu. Kierunek zachodzących zmian oceniano na podstawie badań strukturalnych XRD i FTIR produktów kalcynacji modelowej mieszaniny reakcyjnej M-A, otrzymanej w wyniku 110 dniowej hydratacji. Głównym produktem hydratacji próbki M-A był podwójny warstwowy wodorotlenek magnezowo-glinowy, który najlepiej można przybliżyć wzorem $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$.

Modelowe mieszaniny reakcyjne obejmowały następujące kombinacje: d-MA, f-MA oraz d_MAs, dla których zachowano proporcję molową M:A równą 1:1. Czas hydratacji próbek wynosił odpowiednio: 12 oraz 24 godziny, a także 3 i 7 dni. Przebieg reakcji monitorowano na podstawie obecności i intensywności głównych linii dyfrakcyjnych MgO i $\text{Mg}(\text{OH})_2$, a także podwójnego warstwowego wodorotlenku magnezowo-glinowego (w porównaniu do dyfraktogramu rentgenowskiego modelowej mieszaniny M-A). Analiza XRD potwierdziła obecność podwójnego warstwowego

wodorotlenku magnezowo-glinowego we wszystkich otrzymanych mieszaninach reakcyjnych, jednakże po różnym czasie od rozpoczęcia hydratacji, podczas gdy $\text{Mg}(\text{OH})_2$ w żadnej z ww. mieszanin nie został zidentyfikowany. Charakterystyczna dla $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ linia dyfrakcyjna, wskazująca na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego została rozpoznana na dyfraktogramie próbek d-MA i f-MA oraz d-MAs po odpowiednio 12 godzinach i 3 dniach. Wolniej przebiegająca reakcja wynikała z obecności kwasu cytrynowego jako stabilizatora wodnej zawiesiny, który w rezultacie ograniczał hydratację MgO . Reasumując, każda z otrzymanych mieszanin reakcyjnych może zostać zastosowana jako spoiwo w betonach bezcementowych. Jednakże ze względu na niedogodności związane z zastosowaniem nanometrycznych proszków w warunkach przemysłowych (duża objętość, utrudniona homogenizacja, zapylenie) w zaprojektowanym betonie wykorzystano wodną zawiesinę nanometrycznego proszku Al_2O_3 .

Kalcynację próbki M-A otrzymanej w wyniku 110 dniowej hydratacji, przeprowadzono w celu wyznaczenia temperatury oraz mechanizmu reakcji syntezy spinelu magnezowo-glinowego z prekursora w postaci podwójnego warstwowego wodorotlenku magnezowo-glinowego. Temperatury kalcynacji określone zostały na podstawie analizy termicznej, która wykazała, że w przeciwieństwie do $\text{Mg}(\text{OH})_2$, podwójny warstwowy wodorotlenek magnezowo-glinowy ulega dehydratacji i dehydroksylacji w sposób stopniowy w szerokim zakresie temperatur wynoszącym od 250-424°C. Produkty otrzymane w wyniku kalcynacji próbki M-A w temperaturach 250°C, 340°C, 390°C, 425°C, 500°C, 600°C, 700°C 800°C, 900°C oraz 1000°C poddano analizie XRD oraz FTIR. Uzyskane wyniki potwierdziły syntezę spinelu magnezowo-glinowego w temperaturze 700°C, na co wskazała obecność charakterystycznej linii dyfrakcyjnej w pozycji $2\theta=36,91^\circ$ oraz dwóch pasm na widmie FTIR w położeniu 513 oraz 694 cm^{-1} .

Na podstawie dotychczas otrzymanych wyników badań zaprojektowano mieszankę betonową, zawierającą d-M oraz As jako komponenty matrycy. Próbki po zaformowaniu sezonowane były w temperaturach 50°C, 70°C i 90°C przez łączny czas 5 dni. Kolejnym etapem była obróbka cieplna w temperaturach odpowiadających przeprowadzonej wcześniej kalcynacji. Wyniki analiz XRD, FTIR matrycy betonu oraz badania SEM-EDS próbek po wygrzewaniu potwierdziły syntezę spinelu magnezowo-glinowego w temperaturze 900°C. Dodatkowo, analiza FTIR próbek poddanych obróbce cieplnej w temperaturach 500°C i 700°C wykazała obecność pasma w zakresie 3000–

3700 cm^{-1} , odpowiadającego drganiom grup hydroksylowych, co wskazuje na rehydratację składników osnowy. Na podstawie pomiarów prędkości propagacji fali ultradźwiękowej po każdym etapie obróbki cieplnej wykazano, że istnieje bezpośrednia korelacja pomiędzy zmianami strukturalnymi i mikrostrukturalnymi zachodzącymi w osnowie (tj. rozkładem termicznym podwójnego warstwowego wodorotlenku magnezowo-glinowego, rehydratacją pośrednich produktów rozkładu, niskotemperaturową syntezą spinelu, spiekaniem), a właściwościami betonów ogniotrwałych korundowo-spinelowych. Przeprowadzone badanie wytrzymałości na ściskanie oraz zginanie potwierdziło, że betony na bazie reaktywnych tlenków charakteryzowały się stopniowym przyrostem wytrzymałości mechanicznej w zakresie temperatur pośrednich (300–1000°C), co wynikało z stopniowej dehydratacji składników osnowy i ich rehydratacji, utworzenia uwodnionych faz przejściowych, a następnie tlenków mieszanych, syntezy fazy spinelowej zapoczątkowanej w temperaturze 700°C oraz spiekania. Otrzymane wyniki stanowiły więc punkt wyjścia do dalszych badań, których rezultaty przedstawiono w publikacji 10.4 oraz 10.5. Wspomniane prace dotyczyły charakterystyki gotowego materiału wypalonego w temperaturze 1500°C, w którym jako składniki osnowy wykorzystano spiekane MgO oraz wodną zawiesinę nanometrycznego proszku Al_2O_3 .

10.4. Thermomechanical evaluation and thermodynamic simulation via FactSage of NCCs and ULCCs with different MgO content, Karina Warmuz, Krzysztof Ziewiec, Dominika Madej, Journal of the European Ceramics Society, 44 [2] 2024, 1239-1255

Kolejne prace badawcze koncentrowały się na analizie wpływu zawartości, rodzaju oraz składu fazy spinelowej magnezowo-glinowej na wybrane właściwości mechaniczne, termomechaniczne i odpornościowe prefabrykatu betonowego korundowo- spinelowego wypalonego w temperaturze 1500°C. Przygotowano dwa rodzaje betonów: pierwszy beczementowy, zawierający wyłącznie spinel tworzący się wewnątrz materiału w trakcie wypalania, drugi ultra-niskocementowy, stanowiący materiał odniesienia, zawierający kombinację spinelu tworzącego się w warunkach in situ oraz spinel syntetyczny. Do badań wykorzystano jako składniki osnowy dedykowane surowce przemysłowe o wysokiej czystości chemicznej: spiekane MgO, reaktywny Al₂O₃ (Almatis, CTC 40), mikrokrzemionkę (Elkem, 971), syntetyczny spinel przemysłowy (Almatis, AR 90) oraz wodną zawiesinę nanometrycznego proszku Al₂O₃ (Evonik, Aerodisp W 450 ZX). Celowe zastosowanie dwóch koncepcji składu ukierunkowane było na ukształtowanie mikrostruktury materiału pod względem składu oraz rozmieszczenia fazy spinelowej w osnowie. Dodatkowo, w celu uzupełnienia analizy eksperymentalnej, przeprowadzono symulacje termodynamiczne z wykorzystaniem programu FactSage 8.2 pod kątem składu i ilości fazy ciekłej oraz składu fazy spinelowej w zakresie temperatur odpowiednio 1500-2000°C oraz 1000-2000°C.

Zaprojektowane i otrzymane betony beczementowe zawierały w recepturze wyjściowej jako spoiwo spiekane MgO w ilości 3%_{mas} (NCC_3M), 5%_{mas} (NCC_5M) lub 7%_{mas} (NCC_7M) oraz 2%_{mas} wodnej zawiesiny nanometrycznego proszku Al₂O₃ oraz pozostałe drobnoziarniste składniki osnowy. Betony ultra-niskocementowe (ULCC) charakteryzowały się zbliżonym składem ziarnowym do betonu NCC_3M i zawierały łącznie 3%_{mas} MgO wprowadzonego zarówno w postaci surowca spiekane (Mw) oraz syntetycznego spinelu magnezowo-glinowego: ULCC_3M_2Mw (2%_{mas} spiekane MgO), ULCC_3M_1Mw (1%_{mas} spiekane MgO). W betonach ULCC nie stosowano wodnej zawiesiny nanometrycznego proszku Al₂O₃, natomiast utrzymano taką samą ilość wody zarobowej jak w betonach NCC. Sezonowanie mieszanek betonowych odbyło się z zachowaniem warunków (temperatura, czas, wilgotność), które jak wykazano poprzednio, umożliwiły otrzymanie podwójnego warstwowego wodorotlenku

magnezowo-glinowego w wyniku hydratacji wewnątrz osnowy betonu. Otrzymane w toku wypalania w temperaturze 1500°C betony korundowo- spinelowe poddano badaniom istotnym w kontekście aplikacyjnym: wytrzymałości mechanicznej (wytrzymałość na zginanie oraz ściskanie), ogniotrwałości pod obciążeniem, odporności na pełzanie, wytrzymałości na zginanie w temperaturze 1450°C oraz odporności na nagłe zmiany temperatury. Podsumowanie uzyskanych wyników badań mechanicznych, termomechanicznych i odpornościowych przedstawiono w Tabeli 3. Zgodnie z przedstawionym studium literaturowym, ogniotrwałość pod obciążeniem oraz odporność na pełzanie otrzymanych betonów oceniano na podstawie odpowiednio temperatury charakterystycznej $T_{0,5}$ oraz szybkości pełzania $\theta_3 \cdot \theta_4$. Natomiast, odporność na nagłe zmiany temperatury porównywano w oparciu o zarówno procentowy spadek prędkości przechodzącej fali ultradźwiękowej jak i zmianę wytrzymałości na ściskanie i zginanie po 1., 3., oraz 5. cyklu grzania i chłodzenia. W Tabeli 3 przedstawiono procentowy spadek wytrzymałości na zginanie i ściskanie betonów na po piątym cyklu. W przypadku betonów, których $T_{0,5}$ wynosiła powyżej 1500°C w Tabeli 3 uwzględniono wartość teoretyczną.

Tabela 3 Podsumowanie właściwości mechanicznych, termomechanicznych i odpornościowych otrzymanych betonów NCC oraz ULCC

Beton	CMoR [MPa]	CCS [MPa]	HMoR [MPa]	RUL $T_{0,5}$ [°C]	CIC $\theta_3 \cdot \theta_4$ [%/min]	OWT CMoR [MPa]	OWT CCS [MPa]
NCC_3M	34,30	211,60	14,30	1658	$-5,37 \cdot 10^{-5}$	91,75	20,52
NCC_5M	34,80	253,80	10,95	1604	$-4,20 \cdot 10^{-5}$	93,33	35,58
NCC_7M	34,50	226,80	7,52	1596	$-7,01 \cdot 10^{-5}$	95,26	51,31
ULCC_3 M_2Mw	47,91	185,73	6,26	1427	$-2,98 \cdot 10^{-4}$	95,26	28,59
ULCC_3 M_1Mw	47,99	198,83	6,79	1549	$-4,02 \cdot 10^{-4}$	94,35	25,56

Otrzymane w wyniku wypalania beczementowe prefabrykaty betonowe wykazały zwiększone właściwości mechaniczne (wytrzymałość na ściskanie >210 MPa) oraz termomechaniczne w porównaniu do betonów ultra-niskocementowych. Szybkość pełzania betonów NCC była o rząd wielkości niższa niż betonów ULCC, a sugerowana temperatura pracy betonu NCC_3M wyższa o 231°C od tej wyznaczonej dla betonu ULCC_3M_2Mw. Analiza wytrzymałości na zginanie w podwyższonej temperaturze również wykazała, że efektywniejszym rozwiązaniem pod względem siły wiązania

gruboziarnistego szkieletu betonu w temperaturze 1450°C była więźba ceramiczna nie zawierająca po wypaleniu sześcioglinianu wapnia. Wzrost udziału procentowego MgO w recepturze betonów bezcementowych prowadził do rozluźnienia tekstury w trakcie wypalania, co miało swoje skutki w pogorszeniu właściwości termomechanicznych. Wyniki analizy XRD wykazały zbliżone położenie charakterystycznej dla spinelu linii dyfrakcyjnej w zakresie 2θ równym 36,928-36,999° oraz 37,052-37,083°, co może sugerować, że po wypaleniu wszystkie materiały charakteryzowały się zbliżonym składem fazy spinelowej: obecny był zarówno spinel stechiometryczny $MgAl_2O_4$ jak i roztwór stały Al_2O_3 w $MgAl_2O_4$. Tak niewielkie różnice w składzie fazy spinelowej prawdopodobnie nie wpływały znacząco na właściwości mechaniczne i termomechaniczne otrzymanych betonów korundowo- spinelowych.

Przeprowadzone symulacje termodynamiczne w programie FactSage 8.2 wskazały, że zmniejszenie zawartości MgO do 3%_{mas} oraz wyeliminowanie spoiwa cementowego przyczyniło się do poprawy właściwości termomechanicznych, gdyż wiązało się z mniejszą ilością fazy ciekłej w temperaturach przekraczających 1500°C. Ponadto, przewidywany skład chemiczny fazy ciekłej zależał od obecności cementu glinowo- wapniowego oraz temperatury: wraz z jej wzrostem następowało dosycanie fazy ciekłej w jony glinu.

Niniejsza publikacja miała na celu analizę właściwości mechanicznych, termomechanicznych i odpornościowych prefabrykatów betonowych, które stanowią kluczowy element oceny ich możliwości aplikacyjnych. Podsumowując otrzymane wyniki można stwierdzić, że bezpośredni wpływ na końcowe właściwości mechaniczne, termomechaniczne i odpornościowe materiału miały: ilość, skład i rozkład faz ciekłych; ilość, wielkość cząstek i rozkład fazy spinelowej oraz porowatość. Prefabrykat betonowy niezawierający CA_6 w matrycy wykazywał wyższą wytrzymałość na ściskanie oraz lepsze właściwości termomechaniczne niż betony zawierające cement glinowo- wapniowy jako spoiwo. Wraz ze wzrostem zawartości fazy spinelowej następowało pogorszenie właściwości termomechanicznych otrzymanych prefabrykatów betonowych.

Zgodnie z przeprowadzonym studium literaturowym, jednym z kluczowych aspektów dotyczących betonów ogniotrwałych zawierających cement glinowo- wapniowy jest poprawa ich właściwości termomechanicznych. Dlatego też ze względu na wyraźnie lepsze właściwości termomechaniczne betonów bezcementowych w porównaniu z otrzymanymi betonami ultra-niskocementowymi, kolejna publikacja koncentrowała się wyłącznie na analizie betonów zawierających jako spoiwo reaktywne

tlenki MgO i Al₂O₃. Przedstawiono w niej wyniki badań odporności na nagłe zmiany temperatury, uzupełnione o rozważania teoretyczne oraz symulacje termodynamiczne FactSage 8.2.

10.5. *Comprehensive experimental verification and theoretical modeling of cement-free alumina-based castables forming in-situ spinel ($MgAl_2O_4$) with enhanced thermal shock resistance, Ryszard Prorok, Karina Warmuz, Dominika Madej, Ceramics International, dostępny online od 23.07.2025.*

Z punktu widzenia potencjalnej aplikacji, odporność na nagłe zmiany temperatury stanowi kluczowy parametr determinujący wybór materiału przeznaczonego do pracy w warunkach gradientu temperatury. Dlatego, w niniejszej publikacji podjęta została tematyka odporności na nagłe zmiany temperatury prefabrykatów betonowych korundowo- spinelowych zróżnicowanych pod kątem składników osnowy w recepturze wyjściowej. Zaprojektowano i otrzymano materiały, które zawierały w różnej kombinacji spiekane MgO, mikrometryczny proszek SiO_2 oraz wodną zawiesinę nanometrycznego proszku Al_2O_3 . Głównym celem pracy było określenie wpływu ww. składników osnowy i elementów mikrostruktury na właściwości odpornościowe otrzymanych bezcementowych betonów korundowo- spinelowych. Eksperymentalna analiza odporności na nagłe zmiany temperatury odbyła się w oparciu o własną procedurę laboratoryjną, a dodatkowo została uzupełniona o symulacje przeprowadzone w programie FactSage 8.2 oraz teoretyczną oceną ww. odporności. Podstawą rozważań teoretycznych były teorie wprowadzone przez Kingery'ego i Hasselmana [91, 92], zgodnie z którymi obliczono parametry R (R , R'' , R''' , R_{st}) opisujące odporność materiału na inicjację i propagację pęknięcia. Niezbędne do obliczeń współczynniki przewodności cieplnej i rozszerzalności liniowej, moduł Younga, liczba Poissona, wytrzymałość na zginanie i ściskanie oraz zwartość, wyznaczono w sposób eksperymentalny dla każdego z badanych materiałów, co dodatkowo umożliwiło pełną charakterystykę właściwości fizycznych otrzymanych betonów.

Zaprojektowane betony korundowo-spinelowe jako spoiwo zawierały dedykowane surowce przemysłowe o wysokiej czystości chemicznej: wodną zawiesinę nanometrycznego proszku Al_2O_3 (S) (Evonik), spiekane MgO (M) oraz mikrometryczny proszek SiO_2 (S) (Elkem) w różnej kombinacji. Zaprojektowano i otrzymano betony o następujących kompozycjach składu osnowy: 1%_{mas} μSiO_2 , 2%_{mas} zolu oraz 3%_{mas}, 5%_{mas} lub 7%_{mas} MgO (beton odpowiednio: 3M_SA, 5M_SA oraz 7M_SA); 5%_{mas} MgO i 1%_{mas} SiO_2 (5M_S) oraz tylko 5%_{mas} MgO. Przygotowane mieszanki betonowe sezonowano łącznie przez 4 dni w temperaturze od 22°C (temperatura pokojowa) do

90°C, a następnie wypalano w temperaturze maksymalnej wynoszącej 1500°C. Analiza jakościowa XRD potwierdziła obecność fazy spinelowej o zróżnicowanym składzie: zbliżonym do stechiometrycznego oraz zawierającym nadmiar Al_2O_3 . Zgodnie z analizą ilościową XRD, wyższą zawartością fazy spinelowej zawierającej nadmiar Al_2O_3 charakteryzowały się betony, w których recepturze wyjściowej znajdowała się wodna zawiesina nanometrycznego proszku Al_2O_3 , co wynikało z większej mobilności jonów Al^{3+} . Wspomniane betony wyróżniały się również wyraźnie bardziej zwartą mikrostrukturą, co potwierdziła przeprowadzona analiza SEM EDS. W przypadku betonu 3M_SA obserwacje mikroskopowe ujawniły obecność charakterystycznej sieci mikropęknięć oraz fazy amorficznej, której obecność wynikała z dodatku μSiO_2 do receptury wyjściowej betonu. Faza amorficzna, której skład zbliżony był do mullitu, występowała również w pozostałych materiałach, które zawierały początkowo μSiO_2 .

Obliczenia termodynamiczne przeprowadzone w programie FactSage 8.2 dotyczyły ilości, składu oraz lepkości powstającej w materiale fazy ciekłej w trakcie wypalania. Analiza uzyskanych wyników wykazała, że obecność SiO_2 w recepturze wyjściowej betonu skutkowała pojawieniem się fazy ciekłej w temperaturach powyżej 1471°C, której ilość rosła wraz ze wzrostem temperatury. Skład chemiczny omawianej fazy ciekłej nie zależał od zawartości MgO w początkowej recepturze betonu, jednakże zmieniał się wraz z temperaturą. W obliczeniach zmian lepkości wykorzystano fazę ciekłą o składzie: Al_2O_3 39,95%_{mas}, MgO 16,43%_{mas} i SiO_2 43,62%_{mas} wyznaczonym w temperaturze 1500°C, odpowiadającej maksymalnej temperaturze wypalania. Uzyskane wyniki wykazały, że znaczące zmiany w lepkości fazy ciekłej następują w trakcie obróbki cieplnej materiału w temperaturach do 850°C, co sugeruje, że obecność oraz ilość fazy ciekłej będzie mieć znaczący wpływ na odporność betonu na nagłe zmiany temperatury.

Analiza eksperymentalna odporności na nagłe zmiany temperatury potwierdziła, że najlepszymi właściwościami odpornościowymi charakteryzował się prefabrykat betonowy 3M_SA, o czym świadczy najmniejszy całkowity procentowy spadek prędkości przechodzącej fali ultradźwiękowej. Obserwacje mikrostrukturalne SEM wspomnianego prefabrykatu wykazały obecność charakterystycznej sieci mikropęknięć, która w rezultacie wpływała na zwiększenie odporności na nagłe zmiany temperatury poprzez zwiększenie energii pęknięcia (wydłużenie drogi pęknięcia). Analiza obliczonych parametrów R potwierdziła, że zwiększenie ilości spinelu tworzącego się w warunkach in situ, a więc ilości MgO w kompozycji wyjściowej betonu, zwiększa odporność na

inicjację pęknięcia jednocześnie pogarszając odporność na jego propagację. Świadczą o tym wyniki obliczeń parametru R (maksymalna różnica temperatur przy której dochodzi do pęknięcia) oraz R''' (krytyczna długość pęknięcia), których wartości odpowiednio rosły oraz malały wraz ze wzrostem zawartości MgO. Ponadto, występująca w materiale faza amorficzna, wynikająca z obecności μSiO_2 w recepturze wyjściowej betonu, przyczyniła się do zwiększenia odporności na nagłe zmiany temperatury poprzez zwiększenie odporności na inicjację pęknięcia, podczas gdy dodatek wodnej zawiesiny nanometrycznego proszku Al_2O_3 związany był ze wzrostem wytrzymałości mechanicznej, otrzymaniem bardziej zwartej mikrostruktury betonów oraz obniżeniem ww. odporności.

Podsumowując otrzymane wyniki, w kontekście właściwości odpornościowych bezcementowych betonów ogniotrwałych rekomenduje się zastosowanie μSiO_2 w recepturze wyjściowej betonu oraz ograniczenie zawartości MgO. Jest to związane, jak pokazały wyniki badań, z występowaniem sieci mikropęknięć oraz fazy amorficznej po wypalaniu, gdyż odpowiednio zwiększają odporność na propagację i inicjację pęknięcia. Dlatego też, najbardziej korzystnym wariantem technologicznym był beton 3M_SA.

11. Dyskusja wyników

Dyskusja wyników przedstawionych w niniejszej rozprawie koncentruje się na analizie mechanizmu formowania się więźby hydraulicznej betonu w wyniku hydratacji składników osnowy w temperaturach poniżej 50°C, a następnie więźby ceramicznej w materiałach ogniotrwałych beczementowych i ultra-niskocementowych korundowo-spinelowych podczas ich obróbki cieplnej i wypalania w temperaturze do 1500°C, a także określeniu roli ilości, rodzaju oraz składu fazy spinelowej magnezowo-glinowej i innych faz modyfikujących w kształtowaniu właściwości fizycznych, mechanicznych, termomechanicznych i odpornościowych zaprojektowanego betonu. W oparciu o cel pracy sformułowane następujące hipotezy badawcze:

- właściwości betonu w stanie surowym można kształtować poprzez dobór składników spoiwa oraz warunków sezonowania, które determinują przebieg reakcji powstawania więźby hydraulicznej,
- o właściwościach betonu w zakresie temperatur do 1000°C decyduje charakter przemian składników osnowy zachodzący z utworzeniem reaktywnych faz przejściowych,
- ilość, rodzaj, skład fazy spinelowej oraz innych faz modyfikujących decydują o ukształtowaniu mikrostruktury, a tym samym warunkują właściwości fizyczne, mechaniczne, termomechaniczne i odpornościowe betonu korundowo–spinelowego.

Dyskusja wyników stanowi synergiczne połączenie wyników badań przedstawionych w cyklu pięciu publikacji będącym niniejszą dysertacją. Została ona podzielona na zagadnienia dotyczące: przebiegu oraz warunków reakcji hydratacji w modelowych mieszaninach reakcyjnych $MgO-Al_2O_3$ oraz matrycy betonu (publikacje zatytułowane: *“Effect of the particle size on the reactivity of $MgO-Al_2O_3$ hydrating mixtures: A long-term kinetic investigation of hydrotalcite synthesis”*[10.1], *“Comparison of the CAC-containing and CAC-free hydraulic binders in term of the hydrated matrix formation within refractory castables designed for the fast drying procedure”*[10.2] oraz *“Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures”*[10.3]), reakcji oraz zmian mikrostrukturalnych i strukturalnych zachodzących w trakcie obróbki cieplnej betonu w kontekście właściwości betonu w temperaturach 300-1000°C (publikacja zatytułowana *“Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures,”*[10.3]) oraz wpływu fazy spinelowej (ilość, rodzaj, skład) i ukształtowanej z jej udziałem mikrostruktury na

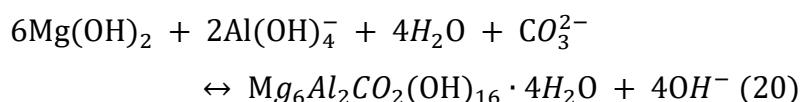
właściwości mechaniczne, termomechaniczne i odpornościowe gotowego materiału (publikacje zatytułowane “*Thermomechanical evaluation and thermodynamic simulation via FactSage of NCCs and ULCCs with different MgO content*” [10.4] oraz “*Comprehensive experimental verification and theoretical modeling of cement-free alumina-based castables forming in-situ spinel ($MgAl_2O_4$) with enhanced thermal shock resistance*”[10.5]).

W oparciu o przeprowadzone studium literaturowe przygotowano serię modelowych mieszanin reakcyjnych MgO (M) i Al_2O_3 (A), o stosunku molowym M:A wynoszącym 1:1, których zamierzeniem było przybliżenie mechanizmu formowania się więźby hydraulicznej w betonie bezcementowym w wyniku reakcji hydratacji. W celach porównawczych przebiegu hydratacji przygotowano mieszaniny reakcyjne zawierające w różnej kombinacji: cement glinowo-wapniowy, syntetyczny spinel, spiekane MgO oraz reaktywny Al_2O_3 . Ze względu na możliwość poprawy reologii, zmniejszenia ilości wody zarobowej oraz poprawę właściwości mechanicznych betonów, mikrometryczny proszek SiO_2 (S) stanowi jeden z częściej stosowanych składników osnowy betonów ogniotrwałych. Dlatego, zweryfikowano także zdolność do tworzenia podwójnego warstwowego wodorotlenku magnezowo-glinowego w wyniku hydratacji mieszaniny M-A w obecności SiO_2 . Do badań wykorzystano zarówno komercyjnie dostępne odczynniki chemiczne (Acros Organics, Aldrich) jak i dedykowane surowce przemysłowe o wysokiej czystości chemicznej (Almatis, Elkem). Przygotowano 6 mieszanin reakcyjnych dwuskładnikowych M-A, 1 mieszaninę reakcyjną M-A-S oraz 2 mieszaniny reakcyjne cementowe, których podsumowanie przedstawiono w Tabeli 4. Obliczenia mas poszczególnych składników mieszanin reakcyjnych uwzględniały czystość reagentów oraz straty prażenia. Po przeprowadzeniu wstępnej homogenizacji, mieszaniny reakcyjne mieszano z wodą, której ilość dobierana była w sposób eksperymentalny, tak aby możliwe było otrzymanie próbek o konsystencji pasty, które przechowywano w laboratoryjnej szafie klimatycznej w temperaturze 20°C oraz 50°C. Po odpowiednim czasie od rozpoczęcia hydratacji pobierano próbki, które przemywano acetonem w celu zatrzymania reakcji oraz usunięcia wody związanej fizycznie. Tak przygotowane próbki poddano analizie: XRD, FTIR DSC-TG-MS oraz SEM EDS.

Tabela 4 Podsumowanie otrzymanych modelowych mieszanin reakcyjnych wraz z ich nazewnictwem.

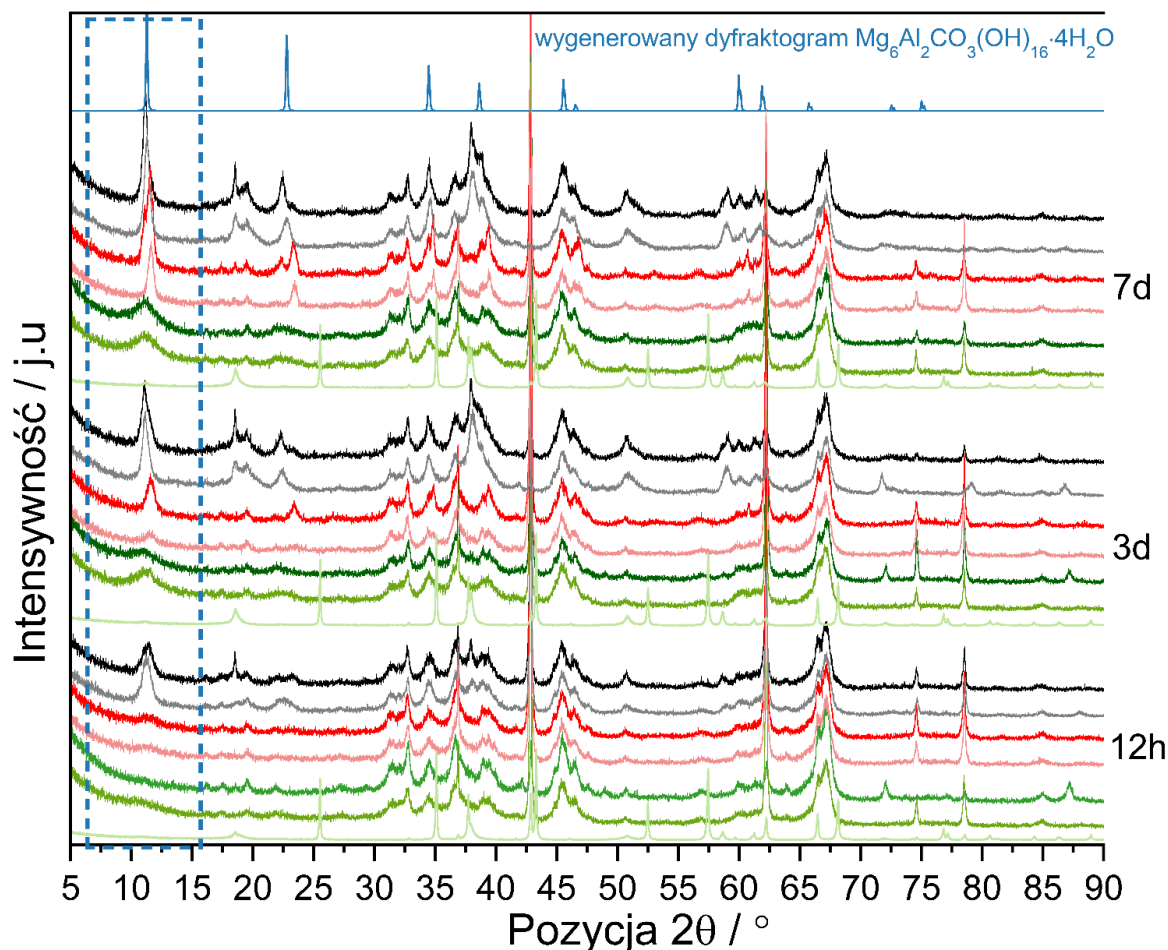
Nanometryczny proszek MgO (nM)+ nanometryczny proszek Al ₂ O ₃ (nA) [10.1, 10.3]	nM_nA
Mikrometryczny proszek MgO (μM)+ nanometryczny proszek Al ₂ O ₃ (nA) [10.1]	μM_nA
Nanometryczny proszek MgO (nM)+ mikrometryczny proszek Al ₂ O ₃ (μA) [10.1]	nM_μA
Spiekane MgO (SpM)+ nanometryczny proszek Al ₂ O ₃ (nA) [10.2, 10.3]	SpM_nA
Topione MgO (TopM)+ nanometryczny proszek Al ₂ O ₃ (nA) [10.2, 10.3]	TopM_nA
Spiekane MgO (SpM)+ nanometryczny proszek Al ₂ O ₃ w postaci wodnej zawiesiny (zol) (nAs) [10.3]	SpM_nAs
Spiekane MgO (SpM)+ nanometryczny proszek Al ₂ O ₃ w postaci wodnej zawiesiny (zol) (nAs)+ mikrometryczny proszek SiO ₂ (S)	SpM_nA_s
Syntetyczny spinel Mg-rich MR66+ reaktywny Al ₂ O ₃ + cement glinowo-wapniowy [10.2]	MR66_5M
Syntetyczny spinel Al-rich AR78+reaktywny Al ₂ O ₃ +spiekane MgO (SpM)+ cement glinowo-wapniowy [10.2]	AR78_5M

Hydratacja mieszanin M-A ukierunkowana była na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego, który najlepiej można przybliżyć wzorem Mg₆Al₂CO₃(OH)₁₆·4H₂O. W związku z tym przeprowadzono uproszczone obliczenia termodynamiczne, mające na celu ocenę przebiegu reakcji w układzie MgO-Al₂O₃-CO₂-H₂O, przyjmując, że produktem końcowym był hydrotalkit [10.1]. Wyniki obliczeń wskazały, że otrzymywanie podwójnego warstwowego wodorotlenku magnezowo- glinowego jest termodynamicznie uprzywilejowane ($\Delta_r G = -214,84$ kJ/mol), jeżeli odbywa się poprzez utworzenie najpierw Mg(OH)₂, a nie jest wynikiem bezpośredniej reakcji jonów Al³⁺, Mg²⁺ CO₃²⁻ oraz wody ($\Delta_r G > 724,48$ kJ/mol). Równanie sumaryczne reakcji otrzymywania hydrotalkitu w wyniku hydratacji mieszanin reakcyjnych M-A zostało sformułowane jako:



Pomiary dyfrakcji rentgenowskiej i spektroskopii w podczerwieni mieszanin reakcyjnych po wybranym czasie hydratacji dostarczyły wglądu w mechanizm powstawania podwójnego warstwowego wodorotlenku magnezowo- glinowego. Przebieg reakcji monitorowano na podstawie obecności podwójnego warstwowego wodorotlenku magnezowo-glinowego według wygenerowanego dyfraktogramu rentgenowskiego, który otrzymano w oparciu o dane strukturalne zawarte w karcie

JCPDS nr 00-022-0700 (hydrotalkit magnezowo-glinowy) oraz zużycia zarówno MgO , jak i $\text{Mg}(\text{OH})_2$ poprzez analizę zmian intensywności głównych linii dyfrakcyjnych. Wynik analizy XRD dla wszystkich modelowych mieszanin reakcyjnych M-A [10.1, 10.2, 10.3] poddanych hydratacji w temperaturze 50°C przedstawiono na Rysunku 3.

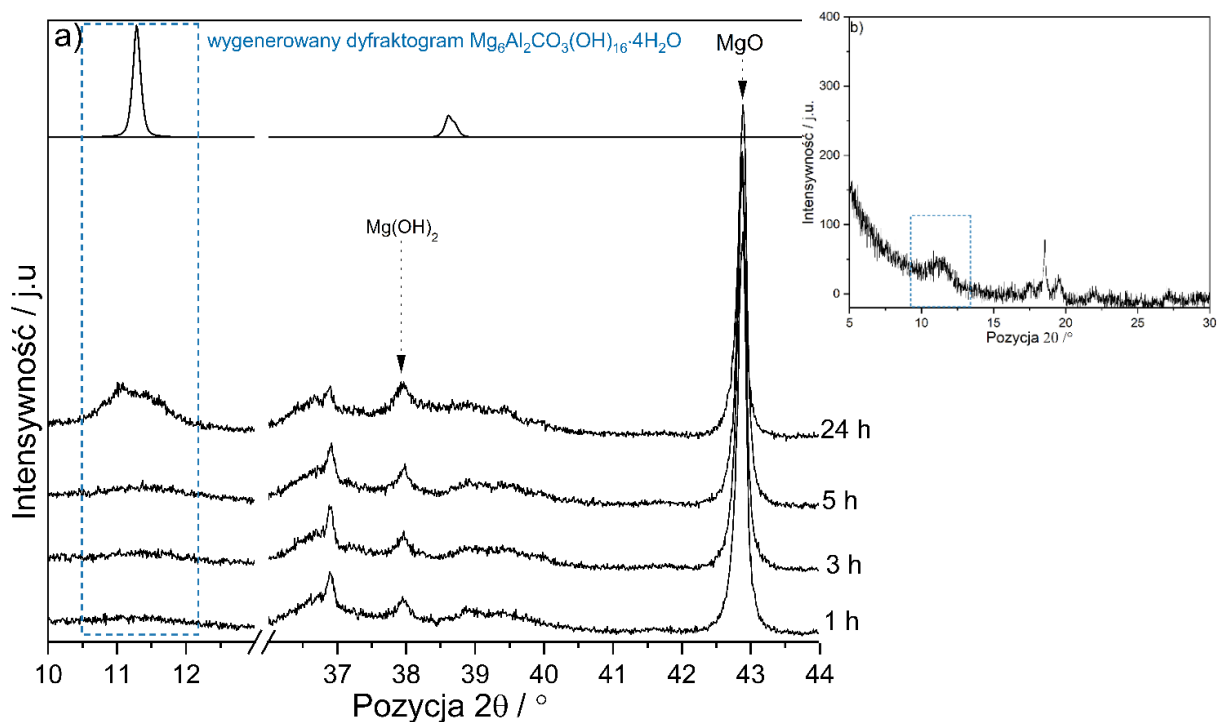


Rys. 3. Wynik analizy XRD próbek po określonym czasie hydratacji (50°C) oraz symulowany dyfraktogram $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00-022-0700) w zakresie od $5-90^\circ$: (od góry) nM_nA, μM_nA , SpM_nA, TopM_nA, SpM_nAs, SpM_nAs_S oraz nM_μA [10.1; 10.2; 10.3].

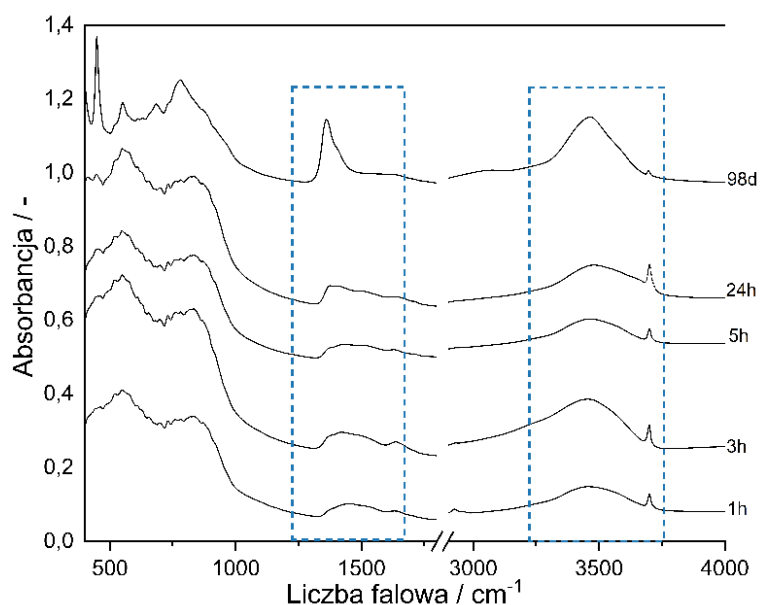
Porównując otrzymane wyniki z wygenerowanym dyfraktogramem $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (Rysunek 3) można zauważyć, że uwodnienie próbek, które w swoim składzie zawierały nA prowadziło do powstania podwójnego warstwowego wodorotlenku magnezowo- glinowego w przeciwieństwie do kompozycji z μA [10.1, 10.2, 10.3]. Sugeruje to, że zastosowanie nA stanowi pierwszy warunek determinujący otrzymywanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w wyniku hydratacji mieszanin dwuskładnikowych. Analiza XRD wykazała obecność podwójnego warstwowego wodorotlenku magnezowo-glinowego już po 12 h od rozpoczęcia hydratacji w próbkach nM_nA, μM_nA , TopM_nA oraz SpM_nA, natomiast w SpM_nAs i M_nAs_S po 72 h. Po upływie wspomnianych 12 h od

rozpoczęcia hydratacji tylko w próbkach nM_nA, μ M_nA oraz nM_ μ A zidentyfikowany został również $\text{Mg}(\text{OH})_2$. W miarę postępu reakcji obserwowano zanik MgO, na rzecz tworzącego się $\text{Mg}(\text{OH})_2$, który całkowicie przekształcał się w podwójny warstwowy wodorotlenek magnezowo- glinowy [10.1]. Produktem końcowym hydratacji (po 98 dniach) był podwójny warstwowy wodorotlenek magnezowo glinowy, faza amorficzna oraz nA [10.1]. Otrzymane wyniki sugerują, że wybór MgO wpływał na otrzymywanie podwójnego warstwowego wodorotlenku magnezowo-glinowego, gdyż w zależności od zastosowanego proszku wyjściowego (nM, μ M, SpM lub TopM) zaobserwowano różną szybkość tworzenia $\text{Mg}(\text{OH})_2$, który stanowił produkt pośredni. Ograniczona hydratacja MgO wynikająca z obecności kwasu cytrynowego jako stabilizatora w wodnej zawiesinie nanometrycznego proszku Al_2O_3 (próbka SpM_nAs) zadecydowała o zdecydowanie wolniejszym przebiegu reakcji [10.3]. Analogiczny wpływ na otrzymywanie podwójnego warstwowego wodorotlenku magnezowo-glinowego miała niższa temperatura. Przeprowadzenie hydratacji w temperaturze 50°C zwiększało szybkość reakcji, co potwierdziła analiza XRD próbek SpM_nA oraz TopM_nA [10.2, 10.3].

Aby lepiej uchwycić kwestię tworzenia $\text{Mg}(\text{OH})_2$ jako pierwszego produktu hydratacji mieszaniny M-A, a następnie jego konwersję w podwójny warstwowy wodorotlenek magnezowo-glinowy przeprowadzono badania XRD oraz FTIR na początkowym etapie hydratacji próbki nM_nA, których wynik przedstawiono na Rysunku 4a,b oraz Rysunku 5. Analiza otrzymanych wyników wskazuje na tworzenie się krystalicznego $\text{Mg}(\text{OH})_2$ natychmiast po homogenizacji mieszaniny proszków z wodą o czym świadczy obecność charakterystycznej dla $\text{Mg}(\text{OH})_2$ linii dyfrakcyjnej w pozycji $2\theta = 37,966^\circ$ oraz ostrego pasma na widmie FTIR w położeniu 3699cm^{-1} [98-100]. Występowanie szerokiego pasma w zakresie $3200\text{-}3700\text{ cm}^{-1}$ oraz 1360 cm^{-1} (Rys.5) już po upływie 1h od rozpoczęcia hydratacji świadczy o syntezie podwójnego warstwowego wodorotlenku magnezowo- glinowego [98-100], co jest zgodne z wynikiem analizy XRD wspomnianej próbki, gdzie obecne jest lekkie podniesienie widma w pozycji 2θ około $11,100^\circ$. Otrzymane wyniki sugerują, że tworzący się podwójny warstwowy wodorotlenek magnezowo-glinowy początkowo występował w formie amorficznej.



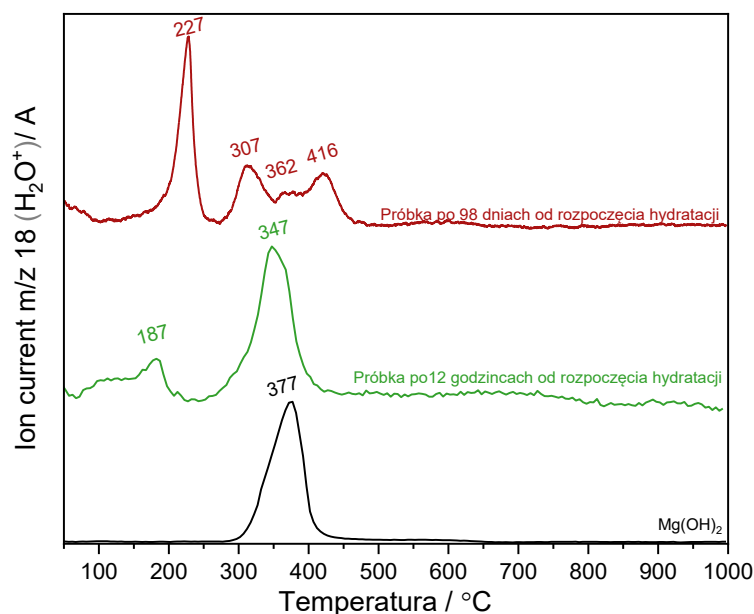
Rys. 4. Wynik analizy XRD próbki nM_nA po określonym czasie od rozpoczęcia hydratacji (po 1h, 3h, 5h oraz 24h) w zakresie 10-44°(a) oraz 5-30° (b).



Rys. 5. Wynik analizy FTIR próbki nM_nA po określonym czasie od rozpoczęcia hydratacji (po 1h, 3h, 5h, 24h oraz 98dn.).

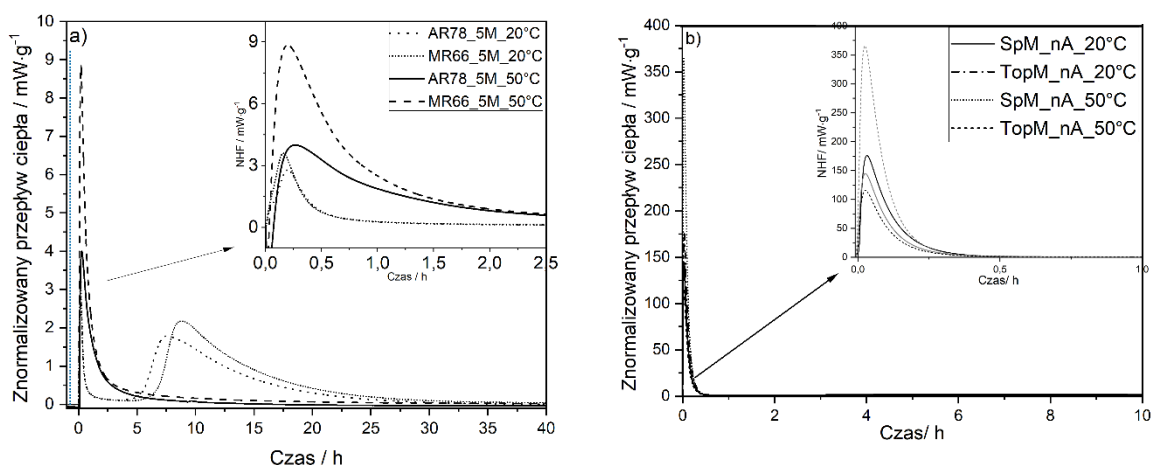
Wszystkie mieszaniny reakcyjne M-A, na każdym etapie hydratacji poddane zostały również analizie termicznej DTA-TG_MS. W przypadku próbek, które zawierały podwójny warstwowy wodorotlenek magnezowo-glinowy [10.1] w temperaturach od około 200 do 450°C zaobserwowano cztery efekty, które związane były z: eliminacją

wody międzywarstwowej, dehydroksylacją warstw hydrotalkitowych $\text{OH}-(\text{Mg}_3)$, dehydroksylacją pozostałości $\text{Mg}(\text{OH})_2$ /dehydroksylacją warstw brucytopodobnych i dehydroksylacją warstw hydrotalkitowych $\text{OH}-(\text{Mg}_2\text{Al})$ [98-100]. Dehydroksylacja $\text{Mg}(\text{OH})_2$ następuje gwałtownie w wąskim zakresie temperatur (obecny jest 1 efekt na krzywej MS, Rysunek 6) [72], a związane z tym nagłe usuwanie wody z materiału w trakcie jego wygrzewania nierzadko prowadzi do jego pęknięcia i łuszczenia [101]. Uzyskane wyniki wskazują na możliwość stopniowego usuwania wody z osnowy, w której obecny jest podwójny warstwowy wodorotlenek magnezowo- glinowy w trakcie obróbki cieplnej, co w przypadku betonów zawierających MgO w recepturze wyjściowej jest pożądane. Sugeruje to, że korzystnym jest, aby sezonowanie materiałów, w których jako spoiwo zastosowano mieszaniny reakcyjne M-A odbyło się w warunkach umożliwiających otrzymanie ww.



Rys. 6. Krzywe MS próbki nM_nA po 12 godzinach i 98 dniach od rozpoczęcia hydratacji oraz $\text{Mg}(\text{OH})_2$ [10.1].

Możliwość zastosowania mieszanek reakcyjnych M-A jako spoiwo w betonach ogniotrwałych beczementowych oceniono również poprzez porównanie krzywych mikrokalorymetrycznych próbek TopM_nA i Sp_nA z mieszanekami cementowymi MR66_5M oraz AR78_5M w temperaturze 20°C oraz 50°C (Rysunek 7) [10.2]. Zaprojektowane mieszaniny reakcyjne cementowe zawierały surowce dostępne komercyjnie i stosowane w przemyśle materiałów ogniotrwałych w produkcji betonów cementowych [34].



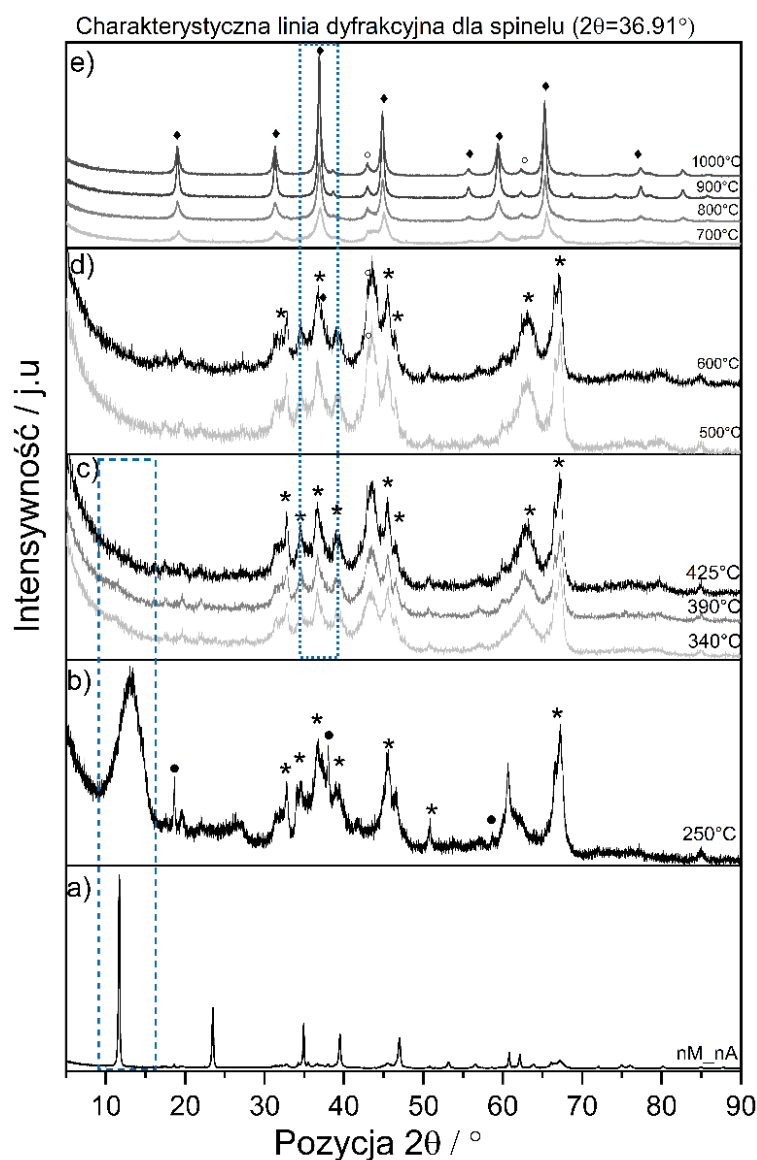
Rys. 7. Krzywe mikrokalorymetryczne próbek SpM_nA, TopM_nA, MR66_5M oraz AR78_5M uzyskane w temperaturze 20°C oraz 50°C [10.2].

Porównywane mieszaniny charakteryzowały się jednakową zawartością MgO, a w obliczeniach mas składników poszczególnych próbek uwzględniono MgO dodane zarówno jako surowiec, jak i składnik spinelu magnezowo-glinowego. Wyniki badań wskazują na wyraźny wpływ temperatury na kinetykę reakcji mieszanin cementowych. Krzywe mikrokalorymetryczne MR66_5M oraz AR78_5M w temperaturze 20°C wykazały typowy dla spoiw cementowych przebieg hydratacji: zarejestrowano dwa efekty egzotermiczne rozdzielone okresem indukcji, a maksimum okresu przyspieszenia reakcji występowało odpowiednio po 9 oraz 7,5 godzinach od rozpoczęcia reakcji [102]. Natomiast w temperaturze 50°C nastąpiła intensyfikacja procesu hydratacji, okres indukcji nie wystąpił, co prawdopodobnie przyczyniło się do szybszego rozwoju wytrzymałości wczesnej. Wyniki uzyskane dla próbek TopM_nA oraz SpM_nA były zbliżone do tych otrzymanych dla próbek cementowych w 50°C. Na krzywej mikrokalorymetrycznej zaobserwowano tylko jeden efekt egzotermiczny, na który składały się procesy związane ze zwilżaniem, rozpuszczaniem i wytrącaniem krystalicznych produktów hydratacji [10.2]. Maksimum okresu przyspieszenia reakcji spoiw beczementowych zarówno w temperaturze 20°C jak i 50°C zarejestrowano na mniej niż 30 minut od rozpoczęcia hydratacji, co powinno gwarantować odpowiedni przyrost wytrzymałości wczesnych umożliwiając skrócenie czasu sezonowania prefabrykatów betonowych.

Reasumując przedstawione do tej pory wyniki, proces formowania się więzby hydraulicznej w ogniotrwałym betonie beczementowym, w którym jako komponenty osnowy wykorzystano MgO oraz Al₂O₃ można regulować poprzez dobór składników matrycy oraz temperatury sezonowania materiału, a także zastosowanie dodatków ograniczających hydratację MgO [10.1, 10.2, 10.3]. Z uwagi na szybkość zachodzącej

reakcji hydratacji ukierunkowanej na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w matrycy betonu, kluczowym aspektem jest zastosowanie nanometrycznego proszku Al_2O_3 oraz przeprowadzenie reakcji w podwyższonej temperaturze. Dobór MgO i/lub dodatków ograniczających jego hydratację determinuje natomiast występowanie $\text{Mg}(\text{OH})_2$ w matrycy betonu. Tworzenie się w osnowie $\text{Mg}(\text{OH})_2$, jak pokazały wyniki badań oraz przeprowadzone obliczenia termodynamiczne, jest etapem koniecznym w otrzymywaniu podwójnego warstwowego wodorotlenku magnezowo- glinowego, jednakże poprzez zastosowanie odpowiednich surowców np. spiekanego lub topionego MgO , można ograniczyć jego zawartość do takiej, która jest na bieżąco zużywana w reakcji tworzenia produktu końcowego.

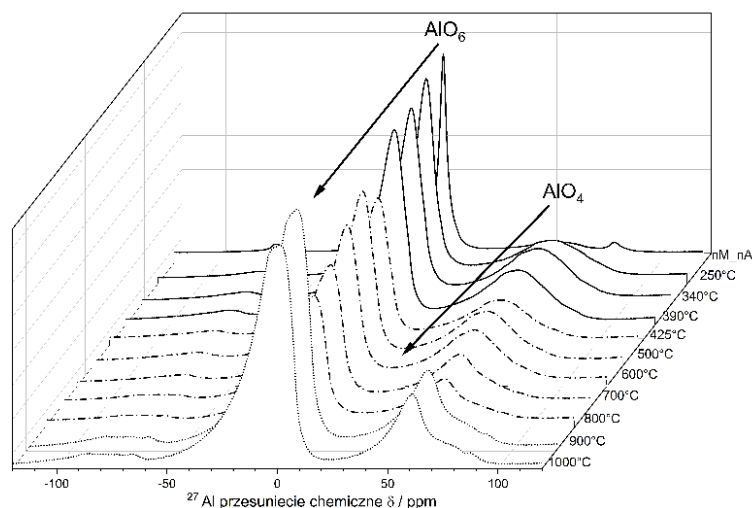
Analiza ilościowa mieszanin reakcyjnych po 98 dniach od rozpoczęcia hydratacji wykazała, że największym stopniem przereagowania oraz najmniejszą zawartością fazy amorficznej charakteryzowała się próbka nM_nA, co zadecydowało o jej wykorzystaniu do dalszych badań [10.3]. Przeprowadzono kalcynację próbki nM_nA otrzymanej po 110 dniach od rozpoczęcia hydratacji, w temperaturach 250°C, 340°C, 390°C, 425°C, 500°C, 600°C, 700°C 800°C, 900°C oraz 1000°C, a otrzymane produkty poddano analizie XRD, FTIR oraz ^{27}Al MAS NMR. Analiza XRD (Rysunek 8) wykazała, że w temperaturze, w której zachodzi usuwanie wody międzywarstwowej (tj. 250°C) następuje amorfizacja układu, co obserwowane było jako poszerzenie charakterystycznej linii dyfrakcyjnej [103]. W temperaturze 700°C potwierdzono obecność charakterystycznej dla spinelu magnezowo-glinowego linii dyfrakcyjnej, co wskazało na jego syntezę. Produkty kalcynacji w temperaturach do 700°C charakteryzowały się niskim stopniem krystaliczności i stanowiły mieszaninę reaktywnych faz przejściowych, którymi były tlenki mieszane $\text{Mg}(\text{Al})\text{O}$, struktury przejściowe Al_2O_3 oraz niekrystaliczne zarodki fazy spinelowej [104-106]. Kalcynacja w temperaturze 1000°C próbki nM_nA, prowadziła do otrzymania spinelu magnezowo-glinowego oraz MgO .



Rys. 8. Wynik analizy XRD produktów otrzymanych w wyniku kalcynacji próbki nM_nA w wybranych temperaturach [10.3].

Spektroskopia ^{27}Al MAS NMR (Rysunek 9) została wykorzystana w celu określenia otoczenia chemicznego atomów glinu w spinelu magnezowo- glinowym oraz jego prekursorze. Analizie ^{27}Al MAS NMR poddana została próbka nM_nA po 110 dniach od rozpoczęcia hydratacji, produkty jej kalcynacji oraz spinel referencyjny otrzymany w wyniku trzystopniowego spiekania równomolowej mieszaniny mikrometrycznych proszków MgO i Al_2O_3 w 1700°C . Widmo próbki przed kalcynacją wykazało stosunkowo wąski pik rezonansowy przy przesunięciu chemicznym $\delta \sim 4,0$ ppm, co świadczy o koordynacji oktaedrycznej glinu (AlO_6) w strukturze podwójnego warstwowego wodorotlenku magnezowo-glinowego [107]. Wzrost temperatury kalcynacji powodował zauważalne poszerzenie oraz przesunięcie

(w kierunku bardziej ujemnych przesunięć chemicznych) linii widmowej AlO_6 co sugeruje zmianę w lokalnych środowiskach atomowych jonów Al^{3+} . Dodatkowo w przypadku próbek kalcynowanych zaobserwowano drugi pik rezonansowy, świadczący o tetraedrycznej koordynacji glinu (AlO_4), który wraz ze wzrostem temperatury malał. Prawdopodobnie był to wynik trzech nakładających się procesów: konwersji odmian przejściowych Al_2O_3 do odmiany najbardziej stabilnej tzn. $\alpha\text{-Al}_2\text{O}_3$, migracji jonów Al^{3+} w strukturze tlenków mieszanych oraz powstawania spinelu [10.3].

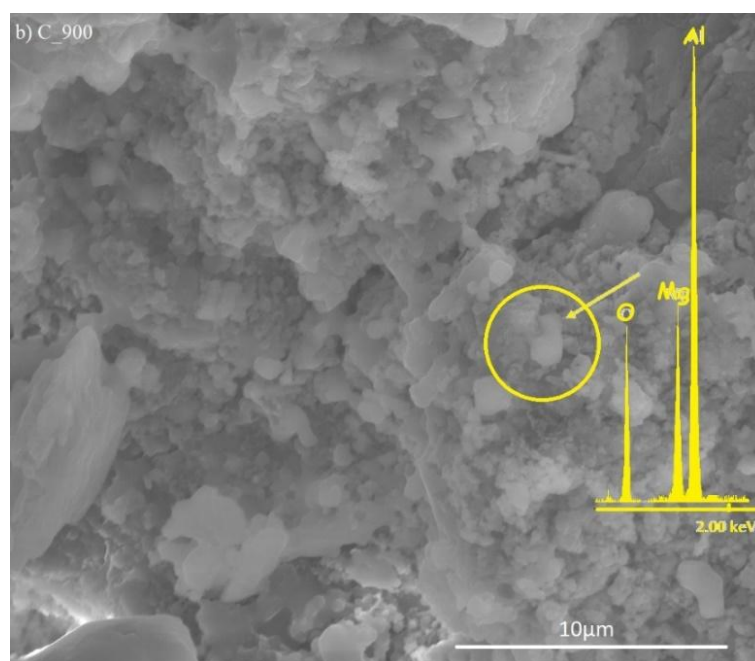


Rys. 9. Wynik analizy ^{27}Al MAS NMR produktów otrzymanych w wyniku kalcynacji próbki nM_nA w wybranych temperaturach [10.3].

Uzyskane wyniki potwierdziły, że zachodzące w toku rozkładu termicznego podwójnego warstwowego wodorotlenku magnezowo-glinowego reakcje dehydratacji i dehydroksylacji prowadziły do powstania reaktywnych struktur przejściowych tj. tlenków mieszanych typu $\text{Mg}(\text{Al})\text{O}$ oraz odmian przejściowych Al_2O_3 , których rekombinacje, a następnie reaktywne spiekanie umożliwiły syntezę spinelu w temperaturze 700°C . W porównaniu do tradycyjnych technologii otrzymywania spinelu magnezowo-glinowego, gdzie stosowane jest spiekanie dwustopniowe, najpierw w temperaturze minimum 1450°C , a następnie 1700°C [22, 23], otrzymane rezultaty wskazują na możliwość znacznego obniżenia temperatury procesu.

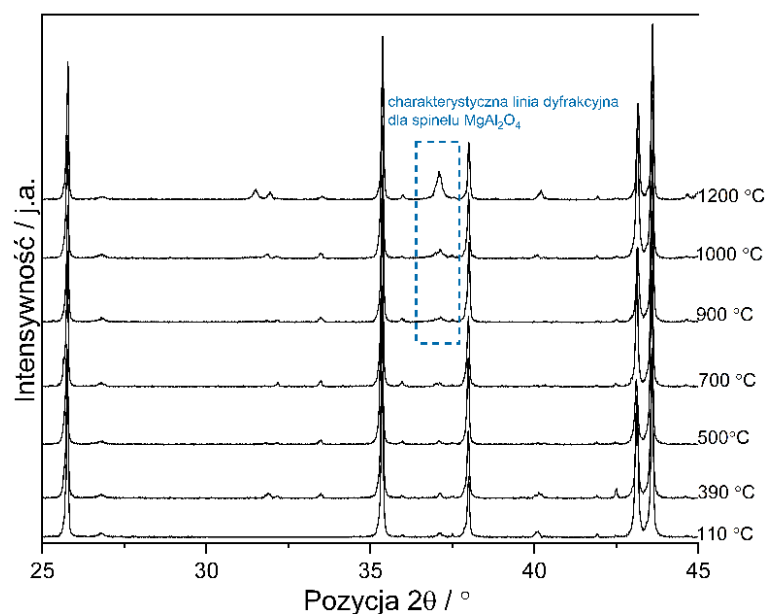
W oparciu o uzyskane wyniki przygotowano świeżą mieszankę betonową zawierającą kruszywo korundowe, reaktywne Al_2O_3 spiekane MgO , wodną zawiesinę nanometrycznego proszku Al_2O_3 oraz dodatki upłynniające, która po zaformowaniu sezonowana była w warunkach opracowanych na podstawie badań opublikowanych w [10.1, 10.2, 10.3]. Taki zabieg technologiczny miał na celu otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w wyniku hydratacji bezpośrednio

w matrycy betonu. Na podstawie obserwacji mikroskopowych SEM w połączeniu z analizą punktową EDS (Rysunek 10) prefabrykatu betonowego potwierdzono obecność pierwiastków Mg, Al oraz O w mikroobszarach, co wskazuje na syntezę spinelu w temperaturze 900°C. Potwierdzeniem otrzymania spinelu magnezowo-glinowego w temperaturze 900°C była również obecność charakterystycznej linii dyfrakcyjnej w pozycji $2\theta=37,14^\circ$ (Rysunek 11) oraz pasm na widmie FTIR (Rysunek 12) w położeniu 553cm^{-1} i 692cm^{-1} [23, 25]. Synteza spinelu w temperaturze 900°C prawdopodobnie przyczyniła się do ograniczenia spadku wytrzymałości mechanicznej materiału w zakresie temperatur do 1000°C.

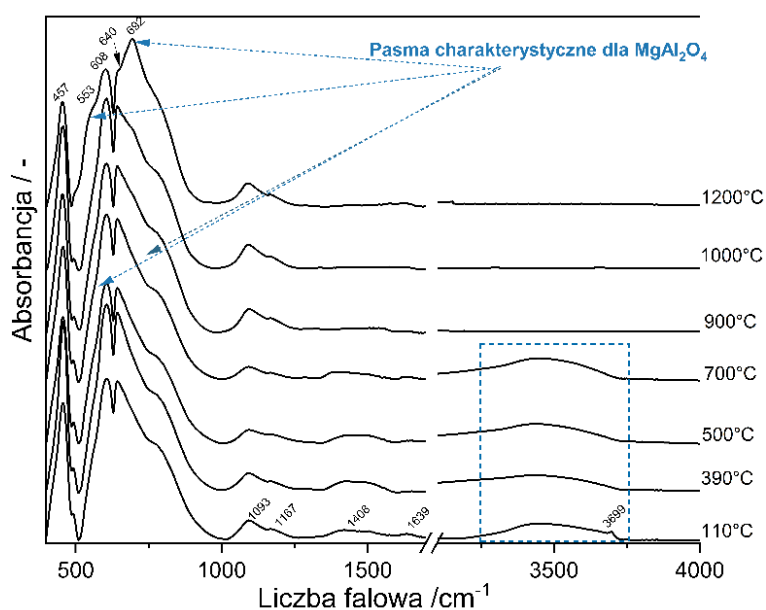


Rys. 10. Zdjęcie mikrostruktury otrzymanego betonu bezcementowego poddanego obróbce cieplnej w temperaturze 900°C [10.3].

Dodatkowo dla betonu poddanego obróbce cieplnej w temperaturach w zakresie 500-700°C stwierdzono zjawisko ponownej hydratacji składników osnowy. Analiza spektroskopii w podczerwieni matrycy betonu (Rysunek 12) poddanego obróbce cieplnej w temperaturach do 700°C wykazała obecność pasm w położeniu $3000-3700\text{ cm}^{-1}$, które związane były z drganiem grup hydroksylowych. Obecność ww. pasm w materiałach wypalonych do 425°C związana była z występowaniem w osnowie sieci hydratów tworzącą wiązanie hydrauliczne. Natomiast, w przypadku materiałów poddanych obróbce cieplnej w temperaturach 500-700°C jest to wynik niespotykany wcześniej w dostępnej literaturze naukowej.



Rys. 11. Wynik analizy XRD matrycy otrzymanego betonu bezcementowego poddanego obróbce cieplnej w wybranych temperaturach [10.3].



Rys. 12. Wynik analizy FTIR matrycy otrzymanego betonu bezcementowego poddanego obróbce cieplnej w wybranych temperaturach [10.3].

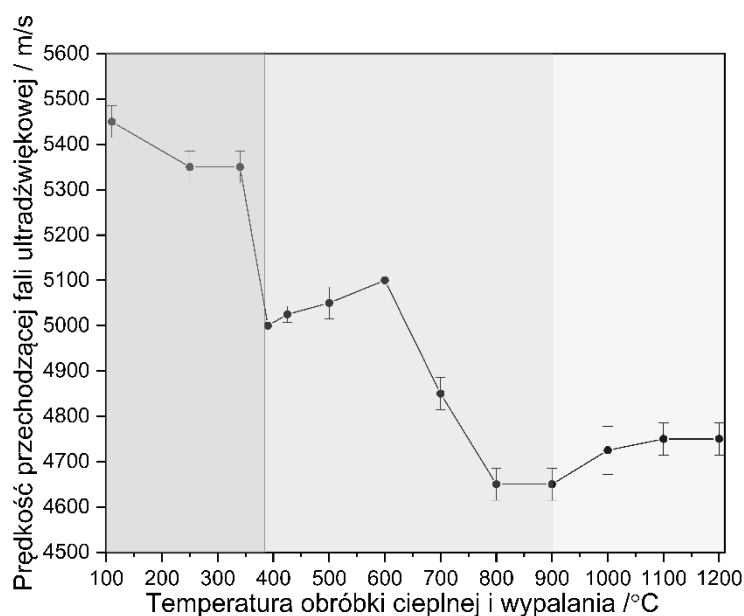
Uzyskane wyniki w połączeniu z bardzo zwartą mikrostrukturą otrzymanych materiałów dowodzą, że w trakcie obróbki cieplnej betonu, nastąpiła ponowna hydratacja składników osnowy na skutek wytworzenia się warunków zbliżonych do hydrotermalnych [10.3]. Tym samym, wyniki badań wskazały, że przeobrażenie wiązania hydraulicznego w wiązanie ceramiczne nie zaszło w sposób gwałtowny, tylko następowało w kilku etapach, które wzajemnie się na siebie nakładały, co w rezultacie przyczyniło się do utrzymania wytrzymałości mechanicznej betonu. Potwierdzają to

wyniki badania wytrzymałości na zginanie oraz ściskanie, zgodnie z którymi zaobserwowano stopniowy przyrost wytrzymałości mechanicznej w temperaturach 300-1200°C, a podsumowanie uzyskanych wartości przedstawiono w Tabeli 5:

Tabela 5 Podsumowanie wytrzymałości na zginanie oraz ściskanie bezcementowego betonu korundowo-spinelowego poddanego obróbce cieplnej oraz wypalaniu [10.3].

Temperatura obróbki cieplnej oraz wypalania [°C]	Wytrzymałość na ściskanie [MPa]	Wytrzymałość na zginanie [MPa]
110	28,88	5,22
425	33,01	5,22
700	33,34	5,49
900	38,29	5,95
1200	55,15	9,87

W dotychczas publikowanych pracach naukowych dotyczących właściwości betonów zawierających jako spoiwo cement glinowo-wapniowy (betony LCC, ULCC) wykazywano spadek wytrzymałości mechanicznej w zakresie temperatur 300-1000°C [40-43, 46-49]. Przeprowadzono także pomiar prędkości przechodzącej fali ultradźwiękowej (Rysunek 13), który zestawiono z potwierdzonymi wcześniej zmianami strukturalnymi i mikrostrukturalnymi osnowy [10.3].



Rys. 13. Wynik pomiaru prędkości przechodzącej fali ultradźwiękowej przez prefabrykat betonowy otrzymany w wyniku obróbki cieplnej w wybranych temperaturach [10.3].

Wykazano, że właściwości betonów w zakresie temperatur do 1000°C zmieniały się w trzech zakresach, co znalazło swoje odzwierciedlenie w pomiarach prędkości

przechodzącej fali ultradźwiękowej. Rozpad wiązań hydraulicznych wynikający z usuwania wody związanej fizycznie oraz chemicznie (dehydratacja i dehydroksylacja do temperatury 390°C) prowadził do rozluźnienia tekstury materiału, czego dowodem był spadek prędkości przechodzącej fali ultradźwiękowej. Dalsza obróbka cieplna betonu do temperatury 600°C związana była ze zjawiskiem wstępnego zagęszczania mikrostruktury oraz wykazanymi wcześniej, rehydratacją składników osnowy i utworzeniem reaktywnych faz przejściowych [10.3], co potwierdził wzrost prędkości przechodzącej przez materiał fali. Ponowne rozluźnienie tekstury betonu wynikające z rekombinacji ww. faz przejściowych oraz ich reakcyjnego spiekania prowadzącego do syntezy spinelu magnezowo-glinowego w temperaturze powyżej 600°C, znalazło swoje odzwierciedlenie w gwałtownym spadku prędkości przechodzącej fali ultradźwiękowej. Natomiast, dalsze spiekanie i związane z nim zagęszczenie mikrostruktury oraz zintensyfikowana synteza fazy spinelowej, która zgodnie z literaturą [21] prowadzi do wzrostu porowatości materiału przełożyły się na stopniowy wzrost prędkości fali w temperaturach od 900°C [10.3].

Ostatni etap badań dotyczył wpływu ilości, rodzaju, składu fazy spinelowej i innych faz modyfikujących na mikrostrukturę oraz właściwości mechaniczne, termomechaniczne i odpornościowe prefabrykatu betonowego. W kontekście porównania technologii betonów bezcementowych (NCC) oraz ultra-niskocementowych (ULCC) zaprojektowano i otrzymano dwa rodzaje betonów: NCC zawierający wyłącznie spinel tworzący się wewnątrz materiału w trakcie wypalania oraz ULCC, stanowiący materiał odniesienia, zawierający kombinację spinelu tworzącego się w warunkach in situ oraz spinel syntetyczny. Porównanie właściwości mechanicznych i termomechanicznych prefabrykatów betonowych ULCC oraz NCC było możliwe dzięki utrzymaniu stałego składu ziarnowego betonów NCC_3M_SA, ULCC_3M_2Mw oraz ULCC_3M_1Mw. Prefabrykaty bezcementowe zawierały w różnej kombinacji spiekane MgO (SpM), mikrometryczny proszek SiO₂ (S) oraz wodną zawiesinę nanometrycznego proszku Al₂O₃ (A), co umożliwiło określenie roli fazy spinelowej i innych faz modyfikujących na właściwości materiału [10.4; 10.5]. Podsumowanie koncepcji technologicznych prefabrykatów betonowych wraz z nazwami próbek przedstawiono w Tabeli 6:

Tabela 6 Podsumowanie receptur wyjściowych prefabrykatów betonowych [10.4; 10.5].

Prefabrykat betonowy	SpM [% _{mas}]	A [% _{mas}]	S [% _{mas}]	CAC [% _{mas}]	AR90 [% _{mas}]
NCC_5M	5,00	-	-	-	-
NCC_5M_S	5,00	-	1,00	-	-
NCC_3M_SA	3,00	2,00	1,00	-	-
NCC_5M_SA	5,00	2,00	1,00	-	-
NCC_7M_SA	7,00	2,00	1,00	-	-
ULCC_3M_2Mw	2,01	-	1,12	3,16	10,53
ULCC_3M_1Mw	0,99	-	1,11	3,12	21,16

Opracowane betony ultra-niskocementowe zawierały łącznie 3%_{mas} MgO wprowadzonego zarówno w postaci surowca spiekanego (Mw) oraz syntetycznego spinelu magnezowo-glinowego. Sezonowanie mieszanek betonowych NCC zawierających wodną zawiesinę nanometrycznego proszku Al₂O₃ odbyło się z zachowaniem warunków umożliwiających otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego w wyniku hydratacji wewnątrz osnowy betonu [10.1; 10.2; 10.3]. Otrzymane w toku wypalania w temperaturze 1500°C prefabrykaty betonowe korundowo- spinelowe poddano badaniom istotnym w kontekście aplikacyjnym: wytrzymałości mechanicznej (wytrzymałość na zginanie oraz ściskanie), ogniotrwałości pod obciążeniem, odporności na pękanie, wytrzymałości na zginanie w temperaturze 1450°C oraz odporności na nagłe zmiany temperatury, a także badaniom mikrostrukturalnym SEM EDS. Ponadto, betony NCC scharakteryzowano pod względem właściwości fizycznych, tj. przeprowadzono badania: zwartości, rozszerzalności liniowej, wyznaczono współczynniki przewodności cieplnej i rozszerzalności liniowej, moduł Younga oraz liczbę Poissona. Zgodnie z przedstawionym studium literaturowym, ogniotrwałość pod obciążeniem oraz odporność na pękanie otrzymanych betonów oceniano na podstawie odpowiednio temperatury charakterystycznej T_{0,5} oraz szybkości pękania $\theta_3 \cdot \theta_4$. [87-90]. W przypadku betonów, dla których wartość T_{0,5} przekraczała 1500°C przedstawiono wartość teoretyczną. Natomiast, odporność na nagłe zmiany temperatury porównywano w oparciu o procentowy spadek prędkości przechodzącej fali ultradźwiękowej po 1, 3 oraz 5 cyklu grzania i chłodzenia. W Tabelach 7 oraz 8 przedstawiono podsumowanie uzyskanych wyników, a zdjęcia mikrostruktur wybranych prefabrykatów przedstawiono na Rysunkach 14 a-d.

Tabela 7 Zestawienie wybranych właściwości mechanicznych termomechanicznych i odpornościowych otrzymanych prefabrykatów betonowych NCC i ULCC [10.4, 10.5].

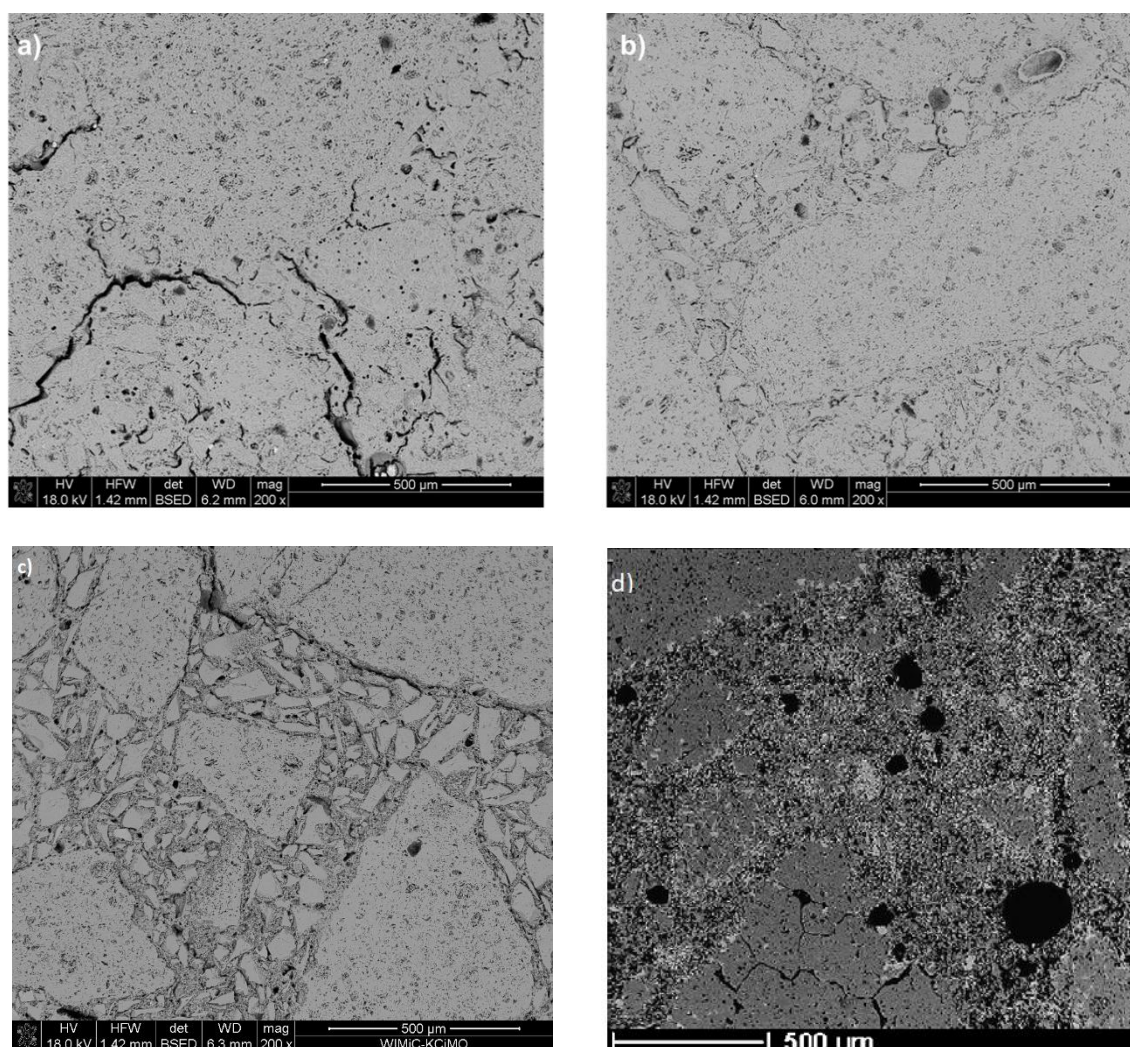
Beton	CMoR [MPa]	CCS [MPa]	HMoR [MPa]	RUL T _{0,5} [°C]	CIC $\theta_3 \cdot \theta_4$ [%/min]	OWT-1 [%]	OWT-3 [%]	OWT-5 [%]
NCC_5M	14,50	89,90	-	-	-	50,6	70,1	78,2
NCC_5M_S	34,20	249,00	-	1545	-	49,8	72,5	81,6
NCC_3M_SA	34,32	211,60	14,30	1658	$-5,37 \cdot 10^{-5}$	45,6	68,4	77,7
NCC_5M_SA	34,81	253,80	10,95	1604	$-4,20 \cdot 10^{-5}$	44,	72,4	80,0
NCC_7M_SA	34,50	226,80	7,52	1596	$-7,01 \cdot 10^{-5}$	50,5	77,8	82,0
ULCC_3M_2 Mw	47,91	185,73	6,26	1427	$-2,98 \cdot 10^{-4}$	50,5	70,3	77,4
ULCC_3M_1 Mw	47,99	198,83	6,79	1549	$-4,02 \cdot 10^{-4}$	47,9	69,0	74,4

Tabela 8 Zestawienie wybranych właściwości fizycznych otrzymanych prefabrykatów betonowych NCC [10.4, 10.5].

Beton	Porowatość pozorna [%]	α [1/K]	λ [W/mK]	Liczba Poissona ν [-]	Moduł Younga E [Pa]
NCC_5M	16,42	$6,55 \cdot 10^{-6}$	3,75	0,217	$1,51 \cdot 10^{11}$
NCC_5M_S	16,12	$6,93 \cdot 10^{-6}$	4,48	0,162	$1,55 \cdot 10^{11}$
NCC_3M_SA	15,07	$6,69 \cdot 10^{-6}$	4,38	0,203	$1,61 \cdot 10^{11}$
NCC_5M_SA	16,81	$6,99 \cdot 10^{-6}$	5,66	0,202	$1,58 \cdot 10^{11}$
NCC_7M_SA	17,59	$6,73 \cdot 10^{-6}$	4,86	0,194	$1,41 \cdot 10^{11}$

Otrzymane wyniki badań wykazały, że przez odpowiedni dobór kompozycji składu osnowy betonu, można kształtować mikrostrukturę, a tym samym determinować końcowe właściwości materiału. Zgodnie z aktualną literaturą naukową [25-37] oraz otrzymanymi rezultatami, z punktu widzenia właściwości mechanicznych i termomechanicznych korzystnym jest całkowite zastąpienie spoiwa cementowego, zastosowanie wodnej zawiesiny nanometrycznego proszku Al_2O_3 oraz mikrometrycznego proszku SiO_2 [10.4, 10.5]. W porównaniu z wynikami wytrzymałości na ściskanie przedstawionymi w [25-29], które dla betonów zawierających wyjściowo 3%_{mas} MgO lub odpowiadającą ilość spinelu syntetycznego, mieściły się w zakresie 100-190 MPa, prefabrykat NCC_3M_SA charakteryzował się zdecydowanie wyższą wytrzymałością na ściskanie. Wykazano, że wzrost udziału procentowego MgO w recepturze betonu prowadził do rozluźnienia tekstury materiałów bezcementowych

w trakcie wypalania, co potwierdził wzrost ich porowatości, a w konsekwencji, zaobserwowano pogorszenie właściwości termomechanicznych w obrębie betonów NCC. Analiza mikrostrukturalna SEM próbek betonów wykazała, iż betony zawierające w swojej kompozycji wyjściowej zol glinowy, charakteryzowały się ponadprzeciętnie zwartą mikrostrukturą po wypaleniu. Na uwagę zasługuje obecna w mikrostrukturze próbki zawierającej 3%_{mas} MgO sieć mikropęknięć (Rysunek 14a), która przyczyniła się do zwiększenia odporności na nagłe zmiany temperatury prefabrykatu betonowego NCC_3M_SA.



Rys. 14 Zdjęcie mikrostruktury betonów: NCC_3M_SA (a), NCC_5M_SA (b), NCC_5M (c), przykładowego betonu korundowo-spinelowego ULCC przedstawionego w [32](d)

Podobnie jak w [108, 109], zastosowanie SiO₂ wiązało się z pojawieniem się fazy ciekłej, której ilość oraz temperaturę pojawienia się jej pierwszej kropli przewidywano za pomocą programu FactSage 8.2, a wybrane wyniki przedstawiono w Tabeli 9. Symulacje termodynamiczne wykazały, że 1%_{mas} zawartość µSiO₂ w recepturze wyjściowej betonu

znacząco obniżał temperaturę pojawienia się pierwszej kropli fazy ciekłej, co w rezultacie obniżyło właściwości termomechaniczne materiału. Jednakże, z punktu widzenia właściwości mechanicznych oraz odporności na nagłe zmiany temperatury, a także aspektów technologicznych (poprawa reologii, możliwość zmniejszenia ilości wody zarobowej) jej obecność jest korzystna.

Tabela 9 Podsumowanie symulacji termodynamicznych przeprowadzonych w programie FactSage [10.4; 10.3].

Beton	Temperatura pojawienia się pierwszej kropli fazy ciekłej [°C]	Ilość fazy ciekłej w temperaturze 1500°C [%]	Ilość fazy ciekłej w temperaturze 1550°C [%]
NCC_5M	2005	0	0
NCC_5M_S	1471	2,43	2,67
NCC_3M_SA	1471	2,43	2,67
NCC_5M_SA	1471	2,43	2,67
NCC_7M_SA	1471	2,45	2,70
ULCC_3M_2Mw	1432	2,76	3,09
ULCC_3M_1Mw	1432	2,76	3,09

Występowanie fazy amorficznej, której przyczyną była faza ciekła powstała w trakcie wypalania wynikająca z obecności μSiO_2 w recepturze wyjściowej betonu, przyczyniła się do zwiększenia odporności na nagłe zmiany temperatury poprzez zwiększenie odporności na inicjację pęknięcia. Beton NCC_3M_SA spośród opracowanych materiałów stanowi najlepszy wariant technologiczny, a występująca w jego mikrostrukturze sieć mikropęknięć przyczyniła się do zwiększenia odporności na nagłe zmiany temperatury. Analizę eksperymentalną odporności na nagłe zmiany temperatury betonów połączono z teoretyczną oceną ww. odporności, w przypadku której na podstawie teorii wprowadzonych przez Kingery'ego i Hasselmana [88, 89], obliczono parametry R (R , R''' , R'''' , R_{st}) opisujące odporność materiału na inicjację i propagację pęknięcia. Zgodnie z otrzymanymi wynikami (Tabela 10) wspomniana sieć mikropęknięć zwiększała energię pęknięcia poprzez wydłużanie drogi pęknięcia, co zgodne jest z przeprowadzonymi obliczeniami teoretycznych parametrów R , które wykazały, że wraz ze wzrostem zawartości MgO w kompozycji wyjściowej beton był bardziej odporny na inicjację pęknięcia z jednoczesną mniejszą odpornością na jego propagację.

Tabela 10 Podsumowanie obliczonych parametrów R [88, 89] betonów NCC.

Beton	R (ΔT_c) [$^{\circ}\text{C}$]	R''' [Pa^{-1}]	R'''' [m]	R _{st} [mK^2]
NCC_5M	11,48	9,17E-04	0,163	5,243
NCC_5M_S	26,68	1,58E-04	0,054	6,773
NCC_3M_SA	22,53	1,47E-04	0,043	6,960
NCC_5M_SA	22,38	1,63E-04	0,052	5,739
NCC_7M_SA	30,15	1,47E-04	0,043	6,960

Oznacza to, że propagacja pęknięcia w materiale była utrudniona, o czym świadczyły wyniki pomiaru przechodzącej prędkości fali ultradźwiękowej po każdym cyklu grzania i chłodzenia, zgodnie z którymi procentowy spadek prędkości był mniejszy dla betonu o niższej zawartości MgO w kompozycji wyjściowej.

Podsumowując właściwości otrzymanych prefabrykatów betonowych NCC kształtowane były poprzez odpowiedni dobór receptury wyjściowej betonu, która determinowała m.in.: ilość, skład i rozkład faz ciekłych; ilość, wielkość cząstek i rozkład fazy spinelowej oraz porowatość, a także obecność fazy amorficznej.

12. Wnioski

W ramach pracy doktorskiej określono mechanizm formowania się więzby hydraulicznej betonu w wyniku hydratacji składników osnowy w temperaturach poniżej 50°C, a następnie więzby ceramicznej w materiałach ogniotrwałych bezcementowych i ultra-niskocementowych korundowo-spinelowych podczas ich obróbki cieplnej i wypalania w temperaturze do 1500°C. Hydratacja ukierunkowana była na otrzymanie podwójnego warstwowego wodorotlenku magnezowo-glinowego, którego obecność w matrycy betonu determinowała zachodzące w trakcie obróbki cieplnej zmiany strukturalne i mikrostrukturalne osnowy, co w konsekwencji decydowało o właściwościach materiału w temperaturach do 1000°C. W kontekście przyszłej aplikacji materiału określono rolę fazy spinelowej oraz innych faz modyfikujących w kształtowaniu właściwości mechanicznych, termomechanicznych i odpornościowych prefabrykatów betonowych, a także wybrano beton charakteryzujący się najwyższym potencjałem aplikacyjnym. Na podstawie otrzymanych wyników oraz obserwacji z przeprowadzonych badań wysunięto następujące wnioski:

1. Dobór warunków (temperatura, czas, zastosowane surowce) sezonowania betonu determinuje przebieg hydratacji mieszanin reakcyjnych $\text{MgO-Al}_2\text{O}_3$, jako składników osnowy, odpowiadających za formowanie więzby hydraulicznej materiału.
2. Kluczowymi warunkami w otrzymywaniu podwójnego warstwowego wodorotlenku magnezowo-glinowego jest zastosowanie nanometrycznego proszku Al_2O_3 oraz podwyższonej temperatury sezonowania (50°C).
3. Zastosowanie surowca magnezowego w formie topionego lub spiekanego proszku MgO w kombinacji z nanometrycznym proszkiem Al_2O_3 pozwala na uzyskanie zbliżonego efektu związanego z syntezą podwójnego warstwowego wodorotlenku magnezowo-glinowego w porównaniu do mieszanin zawierających nanometryczny proszek MgO .
4. Zachodzące w trakcie obróbki cieplnej betonu reakcje rozkładu termicznego składników osnowy betonu, w tym głównie podwójnego warstwowego wodorotlenku magnezowo-glinowego, rehydratacja, rekombinacje struktur przejściowych tj. tlenków mieszanych typu Mg(Al)O oraz faz przejściowych Al_2O_3 , a następnie ich reakcyjne spiekanie umożliwiły syntezę spinelu magnezowo-glinowego w temperaturze 700°C oraz przyczyniły się do stopniowego przyrostu wytrzymałości mechanicznej materiału.

5. Więżba ceramiczna betonu, który nie zawierał w recepturze wyjściowej cementu glinowo- wapniowego stanowiła efektywniejsze rozwiązanie pod względem siły wiązania gruboziarnistego szkieletu betonu w temperaturze 1450°C, co znalazło swoje odzwierciedlenie w wyższych właściwościach termomechanicznych betonów NCC w porównaniu do ULCC.
6. W betonie bezcementowym, który w recepturze wyjściowej zawierał 7%_{mas} MgO, rozluźnienie tekstury zachodzące na skutek syntezy fazy spinelowej w trakcie wypalania, prowadziło do obniżenia $T_{0,5}$, HMoR oraz odporności na nagłe zmiany temperatury w porównaniu do betonu zawierającego 3%_{mas} MgO.
7. Występowanie w mikrostrukturze sieci mikropęknięć oraz fazy amorficznej, której obecność i udział ilościowy wynikały z doboru surowców i składu recepturowego betonu, zwiększało odporność prefabrykatów betonowych na nagłe zmiany temperatury poprzez ograniczenie propagacji pęknięć.
8. Wariant technologiczny charakteryzujący się największym potencjałem aplikacyjnym stanowił beton bezcementowy zawierający w kompozycji wyjściowej 3%_{mas} MgO, nanometryczny proszek Al_2O_3 w postaci wodnej zawiesiny oraz mikrometryczny proszek SiO_2 .

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14. Spis rysunków

Rysunek 1. Diagram fazowy MgO-Al₂O₃ [21].

Rysunek 2. Wytrzymałość na ściskanie (a) oraz zginanie (b) prefabrykatów betonowych o różnej zawartości cementu glinowo-wapniowego, poddanych obróbce cieplnej w temperaturze: 300°C, 600°C, 800°C lub 1000°C [79].

Rysunek 3. Wynik analizy XRD próbek po określonym czasie hydratacji (50°C) oraz symulowany dyfraktogram Mg₆Al₂CO₃(OH)₁₆·4H₂O (JCPDS Card No. 00-022-0700) w zakresie od 5-90°: (od góry) nM_nA, μM_nA, SpM_nA, TopM_nA, SpM_nAs, SpM_nAs_S oraz nM_μA [10.1; 10.2; 10.3].

Rysunek 4. Wynik analizy XRD próbki nM_nA po określonym czasie od rozpoczęcia hydratacji (po 1h, 3h, 5h oraz 24h) w zakresie 10-44°(a) oraz 5-30° (b).

Rysunek 5. Wynik analizy FTIR próbki nM_nA po określonym czasie od rozpoczęcia hydratacji (po 1h, 3h, 5h, 24h oraz 98dn.).

Rysunek 6. Krzywe MS próbki nM_nA po 12 godzinach i 98 dniach od rozpoczęcia hydratacji oraz Mg(OH)₂ [10.1].

Rysunek 7. Krzywe mikrokalorymetryczne próbek SpM_nA, TopM_nA, MR66_5M oraz AR78_5M uzyskane w temperaturze 20°C oraz 50°C [10.2]

Rysunek 8. Wynik analizy XRD produktów otrzymanych w wyniku kalcynacji próbki nM_nA w wybranych temperaturach [10.3].

Rysunek 9. Wynik analizy ²⁷Al MAS NMR produktów otrzymanych w wyniku kalcynacji próbki nM_nA w wybranych temperaturach [10.3].

Rysunek 10. Zdjęcie mikrostruktury otrzymanego betonu bezcementowego poddanego obróbce cieplnej w temperaturze 900°C [10.3].

Rysunek 11. Wynik analizy XRD matrycy otrzymanego betonu bezcementowego poddanego obróbce cieplnej w wybranych temperaturach [10.3].

Rysunek 12. Wynik analizy FTIR matrycy otrzymanego betonu bezcementowego poddanego obróbce cieplnej w wybranych temperaturach [10.3].

Rysunek 13. Wynik pomiaru prędkości przechodzącej fali ultradźwiękowej przez prefabrykat betonowy otrzymany w wyniku obróbki cieplnej w wybranych temperaturach [10.3].

Rysunek 14. Zdjęcie mikrostruktury betonów: NCC_3M_SA (a), NCC_5M_SA (b), NCC_5M (c), przykładowego betonu korundowo-spinelowego ULCC przedstawionego w [32](d).

15. Spis tabel

Tabela 1. Podsumowanie opisywanych w literaturze przykładowych wariantów technologicznych betonów ogniotrwałych korundowo- spinelowych.

Tabela 2. Podsumowanie różnic w reaktywności zastosowanych proszków wyjściowych.

Tabela 3. Podsumowanie właściwości mechanicznych, termomechanicznych i odpornościowych otrzymanych betonów NCC oraz ULCC.

Tabela 4. Podsumowanie otrzymanych modelowych mieszanin reakcyjnych wraz z ich nazewnictwem.

Tabela 5. Podsumowanie wytrzymałości na zginanie oraz ściszenie bezcementowego betonu korundowo-spinelowego poddanego obróbce cieplnej oraz wypalaniu [10.3].

Tabela 6. Podsumowanie receptur wyjściowych prefabrykatów betonowych [10.4; 10.5].

Tabela 7. Zestawienie wybranych właściwości mechanicznych termomechanicznych i odpornościowych otrzymanych prefabrykatów betonowych NCC i ULCC [10.4, 10.5].

Tabela 8. Zestawienie wybranych właściwości fizycznych otrzymanych prefabrykatów betonowych NCC [10.4, 10.5].

Tabela 9. Podsumowanie symulacji termodynamicznych przeprowadzonych w programie FactSage [10.4; 10.3].

Tabela 10. Podsumowanie obliczonych parametrów R [88, 89] betonów NCC.

Publikacja 10.1



Research Paper

Effect of the particle size on the reactivity of MgO-Al₂O₃ hydrating mixtures: A long-term kinetic investigation of hydrotalcite synthesis

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ABSTRACT

Hydrotalcite-like compounds (HTlc) are commonly known anionic clay that may potentially be used as hydraulic binder component for refractory materials, ion exchangers, catalyst or carrier of bioactive molecules. According to current state of knowledge LDH (Layered Double Hydroxides) can be synthesized using various methods including mechanochemical synthesis, hydrothermal precipitation, sol-gel syntheses and coprecipitation method. Research on the synthesis of hydrotalcite in the mixture of oxide powders of Al₂O₃ and MgO cured under specific conditions is particularly important in case of the determination of the relationship between the type (susceptibility to hydration, grain size and specific surface area) of initial powders and reaction kinetics. As a result, the hydration of an equimolar mixture of magnesium and alumina oxides nano- or micro-powders has been proven to be an effective low temperature method of synthesis well crystallized Mg-Al LDH with highly ordered structures. This investigations clearly show that the kinetics of hydration is influenced only by properties of aluminium oxide as initial powder. The synthesis of Mg₆Al₂CO₃(OH)₁₆·4H₂O as a result of hydration is associated with composite matrix formation which firstly consist of partly reacted initial powders bonded by hydration products. The synthesis of Mg₆Al₂CO₃(OH)₁₆·4H₂O was discussed in terms of molar Gibbs free energy change of reactions within the MgO-Al₂O₃-CO₂-H₂O system. The calculated formation Gibbs energy was negative, when Mg(OH)₂ was formed as an intermediate product. The standard Gibbs free energies of hydrotalcite formation was estimated based on the simple mechanical mixture model that treats Mg₆Al₂CO₃(OH)₁₆·4H₂O as mixtures of simple oxides. Thermodynamic calculations were performed assuming an equilibrium state between aqueous solutions and corresponding precipitates after synthesis.

1. Introduction

Layered double hydroxides (LDH) or hydrotalcite-like compounds (HTLC) are commonly known anionic clays. There are many publications regarding the structure, properties and methods of LDH preparation (Alleman, Myiata, R.M. Taylor, Ross and Kodawa) (Myiata, 1975; Myiata and Okada, 1977; Taylor, 1984). According to the current state of knowledge the general formula of LDH is (M_{1-x}²⁺M_x³⁺(OH)₂)^{x+}(A_{x/m})^{m-}, where the divalent and trivalent ions can be: Mg²⁺, Ca²⁺, Zn²⁺, Cu²⁺, Co²⁺ or Ni²⁺ and Al³⁺, Fe³⁺ or Cr³⁺, respectively. The OH⁻, Cl⁻, NO₃⁻, CO₃²⁻ or SO₄²⁻ ions can be considered as compensation ions. The structure of these materials is similar to the structure of brucite Mg(OH)₂ and consists of neutral sheets and magnesium ions coordinated octahedrally by six OH⁻ ions (Perez et al., 2004). The schematic structure of Mg/Al hydrotalcite is shown in Fig. 1.

If the magnesium cation is replaced with an aluminium cation, the sheet receives a positive charge, which is proportional to the number of replaced divalent cations. To obtain an electrically neutral system, an appropriate number and kind of anions are built in between the positively charged sheets. The mineral Mg/Al hydrotalcite (Mg₆Al₂CO₃(OH)₁₆·4H₂O) consist of positively charged brucite-like layers [Mg_{1-x}Al_x(OH)₂]^{x+} with disordered opposite charged interlayers [(CO₃)_{x/2}·mH₂O]^{x-} (Myiata, 1983). According to Allmann et al. (Alleman, 1968; Myiata, 1983), the Mg and Al atoms are distributed at random octahedral positions. In addition, the magnesium ions dissolve in both Al(OH)₃ and AlO(OH). On the other hand some Al³⁺ ions dissolve in Mg(OH)₂. According to this, the double-hydroxide phase have a wide range of possible stoichiometries, as was also confirmed in the Mg(OH)₂-Al(OH)₃ system (Mascolo and Marino, 1980).

The recent findings from the literature reveal that the thermal

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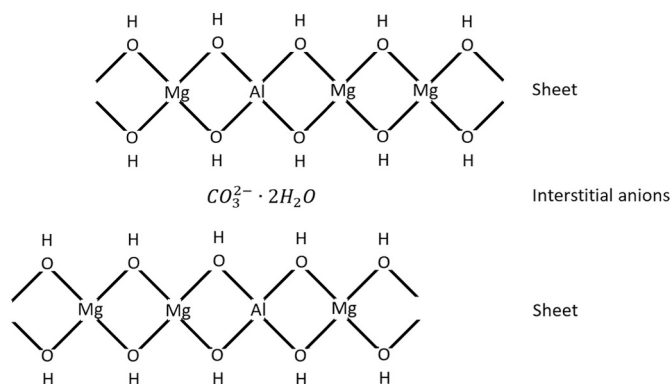


Fig. 1. Schematic structure of hydrotalcite reproduced according to (Reichle, 1986).

decomposition of Mg–Al hydrotalcite takes place in few steps. The first step is a release of physically adsorbed water and occurring at temperatures below 200 °C. Secondly, the interlamellar water is withdrawn (dehydration) between 150 and 250 °C. It is then followed by the loss of CO_2 at approximately 300 °C, which overlaps with the dehydroxylation process (Pesic et al., 1992; Forano et al., 2006). Interestingly, this effect can be associated with the elimination of CO_2 groups through the fine pores, which were generated on the surface of the hydrotalcite (Reichle et al., 1986). Above 300 °C, the dehydroxylation of hydroxide layers and the loss of exchange anions takes place. The thermal effects during thermal decomposition of Mg–Al LDH at the temperatures between 315 and 330 °C and between 350 and 370 °C are associated with the dehydroxylation of $(\text{Mg}_3)\text{-OH-}$ hydrotalcite sites and residues of magnesium hydroxides $(\text{Mg}_3)\text{-OH-}$ brucite-like sites, respectively. According to data summarized above, the thermal stability of hydroxyl groups within the $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]^{2+}$ brucite-like octahedral sheet may be placed: $(\text{Mg}_3)\text{-OH} < (\text{Mg}_2\text{Al})\text{-OH}$, as confirmed by other authors (Forano et al., 2006; Madej, 2018). At the temperatures above 1000 °C the decomposition of Mg–Al hydrotalcite takes place, leading to the mixture of MgAl_2O_4 and MgO as a final product (Valcheva-Traykova and Davidova, 1993).

The great interest of Mg–Al hydrotalcite is due to a good potential in various applications such as absorbents, CO_2 capture, ion exchangers, catalyst carrier of bioactive molecules, and catalyst support due to their structural stability, high surface area and phase purity (Forano et al., 2006). Layered double hydroxides can be used in a wide spectrum of organic reactions as either reagents or catalysts. On the other hand their application is limited due to the required high crystallinity, low impurity content and stable crystal structure (Wiyantoko et al., 2015).

The hydrotalcite can be synthesized using various methods including mechanochemical synthesis or hydrothermal precipitation (Xu and Lu, 2005; Zhang and Li, 2013). In case of hydrothermal precipitation, the two main reaction pathways based on the dissociation-deposition-diffusion mechanism were observed, depending on the synthesis conditions (Xu and Lu, 2005). Under basic pH conditions at 8.3, diffusion of $\text{Al}(\text{OH})_4^-$ ions onto the surface of $\text{Mg}(\text{OH})_2$ was observed. Under neutral pH conditions at pH 7.0 or 6.5, Mg^{2+} and OH^- ions diffused onto the surface of $\text{Al}(\text{OH})_3$. The residues were identified as MgO and $\text{Mg}(\text{OH})_2$ under basic and neutral conditions, respectively (Xu and Lu, 2005). According to Troczynski et al. (Ye and Troczynski, 2006) application of various forms of magnesia (reactive, deadburned or fused) is associated with significant difference in the hydration products. The authors showed that the hydration of reactive alumina in the presence of reactive magnesia leads to the hydrotalcite formation within the first 48 h at 20 °C, whereas in the mixtures containing deadburned magnesia and fused magnesia, hydrotalcite was not found under the same curing conditions. Additionally, a difference in product stoichiometry was observed depending on the used magnesia raw material (Ye and

Troczynski, 2006). It is also confirmed, that molar composition of mixture affects chemical properties of hydrotalcite (Xu and Lu, 2005). According to information presented above, the kinetics of the hydration is influenced by the specific surface area development, degree of homogenization, degree of packing, type and size of grains of MgO and Al_2O_3 in initial powders.

In the last decade, the nanomaterials draw more attention in comparison with micron size materials due to a higher specific surface area which leads to their specific properties (Dadkhah et al., 2014). The significant increase in the specific surface area of the involved nano-reactants results in enhancement in reactivity of nanoscale material (Valliappan et al., 2005). This is also associated with an increase in the number of contact points between the reactants (Shimizu and Saitou, 1990; Tomasi and Munir, 1999). The mechanism of highly exothermic reactions that occur with the participation of solid nanoreactants (simultaneous vaporization, melting, and decomposition of some of the participating reactants takes place) is also more complicated. Moreover nanopowders can improve strength and ductility of ceramic materials (Dadkhah et al., 2014). In addition to the grain size, the specific surface area is also affected by the grain shape and porosity of the powders, as well as the method of preparation. Nanoscale of MgO and Al_2O_3 powders may be obtained using sol-gel (Zeng et al., 1998) mechanical alloying (Panchula and Ying, 1997), hydrothermal and aqueous wet chemical methods (Panchula and Ying, 1997; Bhargava et al., 1998), flame spray pyrolysis (Ding et al., 2001) or chemical gas phase deposition (Matthews et al., 2000). Some of these methods require specific instrumentation and sometimes relatively meticulous experimental procedures. On the other hand these methods allow us to obtain e.g. nanosized MgO with controllable structure and morphology, narrow grain size distribution and large specific surface area. Hydrothermal method enables the control over: crystallite size, shape, and structure by applying appropriate solvents and reaction conditions (Ding et al., 2001). MgO synthesized by different routes has different surface morphologies, and thus the catalytic activity and selectivity may vary (Klabunde et al., 1996; Khairallah and Glisenti, 2007). Other parameters, such as treatment time, temperature, gelling agent, pH, and heating atmosphere affect the activity of the final product as well (Klabunde et al., 1996). Most of Al_2O_3 nanopowders were prepared through the sol-gel route which involves the precipitation of metal oxide particles from solution (Jiansirisomboon and MacKenzie, 2006). The most common precursors of aluminium oxide powder are boehmite (AlOOH), aluminium chloride, aluminium isopropylate and aluminium sulphate (Ibrahim et al., 1996; Varma et al., 1990;). Sol gel method enables obtaining of the boehmite (AlOOH) using e.g. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as raw material. The calcination of boehmite powders at temperatures between 500 and 1000 °C leads to the formation of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ nanopowders, respectively (Zeng et al., 1998; Jiansirisomboon and MacKenzie, 2006). Receiving $\alpha\text{-Al}_2\text{O}_3$ is also possible through high energy ball milling which results in the reduction of the average crystallite size of the material, and thereby increase of the sinterability of the powder (Panchula and Ying, 1997).

In this work, nano- and micro-powders of alumina mixed with several forms of magnesia, were hydrated under the specific conditions. The aim of this work was to determine the difference in the hydration products between the blended pastes which contain Mg–Al layered double hydroxide. Application of several forms of magnesia and alumina allows to determine the mechanism and kinetics of hydration. Kinetics was determined as the rate of loss of substrates.

2. Experimental

2.1. Sample preparation

MgO nano-powder (particle size <50 nm, Acros, 99.8% MgO), MgO micro-powder (Acros, 99.8% MgO), Al_2O_3 micro-powder (Almatis, RG4000, 99.8% Al_2O_3) and Al_2O_3 nano-powder (Aldrich, 99.8% Al_2O_3) were used as starting materials for the preparation of binary mixtures

with the MgO:Al₂O₃ molar ratio of 1:1. Three mixtures were composed of nano-MgO and nano-Al₂O₃, nano-MgO and micro-Al₂O₃, micro-MgO and nano-Al₂O₃ powders. For this purpose, dry powder mixtures were weighed with the referred to above Al₂O₃:MgO molar ratio of 1:1. Calculations of powders mass included purity of the initial powders and the amount of water bound physically or chemically by them. The content of water in starting materials was determined by thermogravimetry (TG). Each dry mixture of powders was homogenized for 30 min and then mixed with water. The adopted amount of water allowed obtaining homogeneous pastes in which no sedimentation was observed. The ratio between water and dry mix (w/s) is presented in the Table 1. Samples in the form of pastes were sealed in polyethylene bags and cured in a laboratory climatic chamber under conditions of relative humidity of 95% at 50 °C until the samples reacted completely. To obtain reference hydroxides, both MgO and Al₂O₃ nano- and micro- powders were mixed with water and stored under the same curing conditions for 42 days. After an appropriate time (12 h, 24 h, 3 days, 7 days, 14 days, 56 days and 98 days) samples were ground in acetone (Chempur, 96% solution) at ambient temperature to discontinue the hydration and remove free water from the blended pastes. Table 1 summarizes the nomenclature of both initial powders before and after hydration and obtained blended pastes.

According to techniques presented in 2.2 part, samples which contain only chemically bound water were investigated at any stage of hydration, hence "free" water was withdrawn using cold acetone.

2.2. Characterization techniques

Progress of hydration was investigated as rate of product formation and the disappearance of substrates, according to the methods presented below. The simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out in flowing synthetic air (50 mL·min⁻¹) using a Simultaneous Thermo Analyzer (STA) TG-DSC NETZSCH STA 449 F5 Jupiter coupled to mass spectrometry 403 D Aeolos. Empty α-Al₂O₃ crucible was used as a reference substance. 10 mg of each sample was heated from 20 to 1000 °C (a heating rate of 10 °C·min⁻¹) in corundum crucible.

Crystallographic structure and phase composition of the both initial powders before and after hydration and blended pastes were measured using X'Pert ProPANalytical X-ray diffractometer with Cu Kα radiation (λ = 1.54060 nm), with 0.02° per step and 3 s time per step (2θ: 5°–90°). The phases were identified using of HighScore Plus software (Panalytical) with the JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997). Crystallite size was calculated on the basis of the full width at half maximum (FWHM), by means of Scherrer equation (Zhang et al., 2013):

$$D_{XRD} = \frac{K \cdot \lambda}{\cos(\theta) \cdot FWHM} \quad (1)$$

Table 1
Nomenclature of initial powders and mixtures.

Starting powder	nano-MgO	micro-MgO	nano-Al ₂ O ₃	micro-Al ₂ O ₃
Designation of initial powder	nM	μM	nA	μA
Designation of initial powder hydrated counterparts	nMh	μMh	nAh	μAh
Binary mixtures of dry powders	nano-MgO + nano-Al ₂ O ₃	nano-MgO + micro-Al ₂ O ₃	micro-MgO + nano-Al ₂ O ₃	
w/s	3	0.6	1	
Designation of mixtures after hydration	nM_nA_h	nM_μA_h	μM_nA_h	

where D_{XRD} is the crystallite size (nm), K is a numerical factor referred as the crystallite-shape factor (0.90), λ is the wavelength of the radiation used [0.1540598 (nm)] and θ is the Bragg diffraction angle. For Rietveld amorphous quantification, blended pastes were mixed with 10% high-purity ZnO as an internal standard. Each mixtures were homogenized by hand milling in an agate mortar. Quantitative analysis of amorphous and crystalline phases was presented elsewhere e.g. by S. Kemethmüller et al. (2006).

The FT-IR spectra of initial powders and mixtures were recorded using the KBr pellets technique on a Fourier Transform Infrared Spectrometer from BRUKER (Vertex 70) in range of 4000–400 cm⁻¹.

The microstructure of both initial powders and hydrated blended pastes was investigated using a scanning electron microscope (SEM, FEI Nova Nano SEM 200). The chemical compositions of the samples were determined with electron-probe microanalysis using an energy-dispersive X-ray spectrometer (EDAX, Sapphire Si(Li) EDS detector).

The surface area of the initial powders was evaluated using the Brunauer–Emmett–Teller (BET) method. Multipoint nitrogen adsorption surface area measurements were performed at 77.35 K after drying of single samples at 200 °C for 24 h, using a Micromeritics ASAP 2000. The primary particle size D_{BET} was calculated using the following equation:

$$D_{BET} = \frac{6000}{d \cdot S_w} \quad (2)$$

where d is the theoretical density of the powder determined from the XRD (Winterer, 2002), S_w the specific surface area (Itatani et al., 1993; Osińska et al., 2016).

The surface zeta potential of the starting powders of nM, nA, μA, μM was determined with Zetasizer Nano ZS, Malvern Panalytical.

The pH of powders mixtures was determined with Sension+ MM 374, Hach.

3. Results

3.1. Characteristics of starting powders and their hydrated counterparts

Starting powders were tested for ability to form hydrates. Fig. 2a–d shows diffractograms of the initial powders (nA, nM, μA, μM) and their hydrated counterparts (nAh, nMh, μAh, μMh). Fig. 3(a–d) and Fig. 4(a–c) present the SEM image and zeta potential analysis result of the starting powders, respectively. As a result of 42 days of hydration hydrated counterparts of starting powders were obtained successfully. Due to the broad XRD peaks which are observed in Fig. 2a and b, it can be concluded that both nM and nA are definitely more poorly-crystalline than μM and μA samples, observed in Fig. 2c and d, respectively. The diffractograms obtained of hydrated counterparts nMh and μMh are similar despite the differences in the raised spectra background nM and μM. As can be seen in Fig. 2b and d, magnesium oxide (JCPDS Card No. 96–900-6786) is the predominant crystalline phase in both nM and μM samples. Magnesium hydroxide (JCPDS Card No. 96–900-6331) is also observed in nM and μM. Nevertheless, magnesium hydroxide is an impurity that results from the unwanted hydration of both nM and μM samples. XRD analysis of nMh and μMh samples revealed that MgO has fully transformed into Mg(OH)₂ after 42 days of hydration. In μA sample before and after hydration process only pure α-Al₂O₃ was identified (JCPDS Card No. 96–500-0093). Due to the lack of characteristic peak belonging to the Al(OH)₃ it can be concluded that μA has a poor ability to form hydrated counterparts. Nevertheless in nA sample there are two varieties of transition aluminas possible: γ-Al₂O₃ peak at 66.940° (JCPDS Card No. 96–101-0462) and θ-Al₂O₃ peak at 36.596° (JCPDS Card No. 96–120-0006) (Zhou and Synder, 1991; Boumaza et al., 2009). Moreover gamma alumina is a dominant phase in nA sample. In nAh sample both gibbsite (2θ = 18.2616°, JCPDS Card No. 96–900-8238) and bayerite (2θ = 18.7674°, JCPDS Card No. 96–100-0062) were observed. Presence of elevated background in XRD analysis of nAh

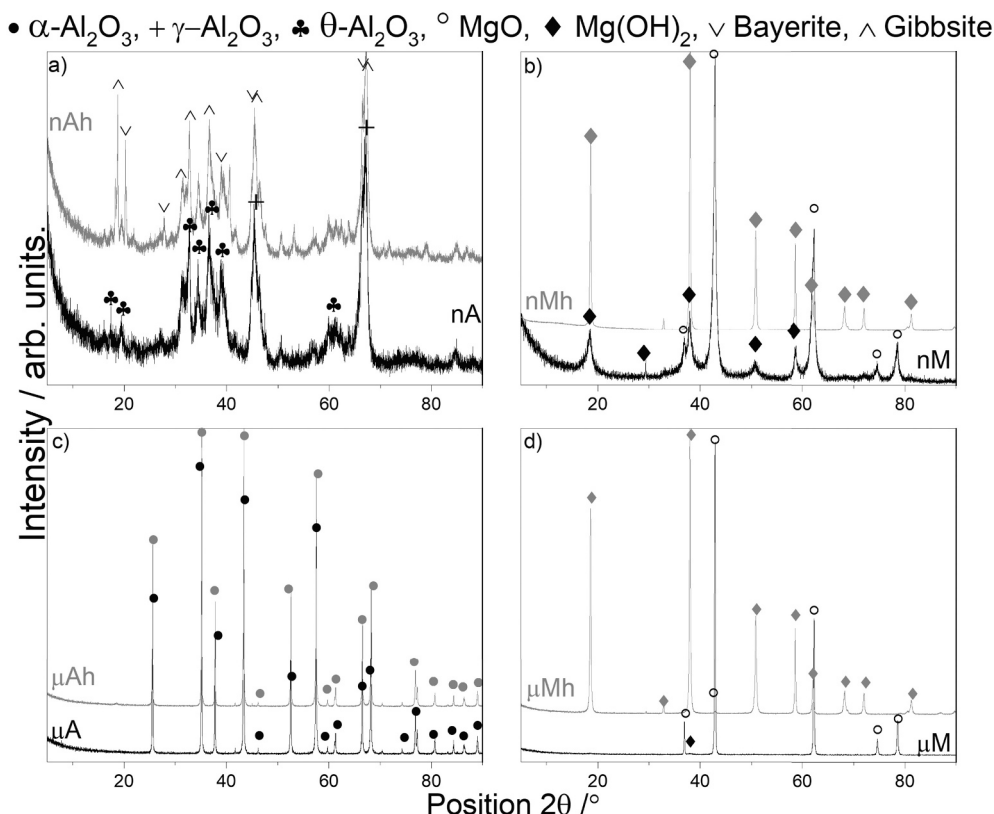


Fig. 2. X-ray diffraction pattern of: nA and nAh (a), nM and nMh (b), μA and μAh (c), μM and μMh (d). Diamond: $\text{Mg}(\text{OH})_2$ (JCPDS Card No. 96–900–6331), circle: $\alpha\text{-Al}_2\text{O}_3$ (JCPDS Card No. 96–500–0093), plus sign $\gamma\text{-Al}_2\text{O}_3$ (JCPDS Card No. 96–101–0462), clover $\theta\text{-Al}_2\text{O}_3$ (JCPDS Card No. 96–120–0006), degree sign MgO (JCPDS Card No. 96–900–6786), up arrowhead: Gibbsite (JCPDS Card No. 96–900–8238), down arrowhead: Bayerite (JCPDS Card No. 96–100–0062).

sample suggests significant amount of poorly-crystalline phase.

According to the Scherrer eq. (1) the average crystallite size of initial powders and their hydrated counterparts was calculated. Main diffraction peak was used to calculate the crystallite size. Based on eq. (2) the primary particle size was calculated. Additionally the degree of agglomeration $D_{\text{BET}}/D_{\text{XRD}}$ was calculated from the primary particle size D_{BET} determined from the specific surface area, and from the crystallite size D_{XRD} (Itatani et al., 1993; Alvarado et al., 2000). The characteristics of the initial powders and reference hydroxide samples are reassumed in Table 2.

The nanopowders are characterised by relatively high BET specific surface area, i.e. 28.2 and 56.6 $[\text{m}^2/\text{g}]$ for nM and nA, respectively (Table 2). These tests revealed a very large difference in the crystallite size of the both starting powders and reference samples. The degree of agglomeration lower than 1 indicates the low tendency to agglomeration (Itatani et al., 1993; Alvarado et al., 2000). The highest agglomeration degree, 5.07 was for nM and indicates the greatest tendency to agglomeration.

Fig. 3a-d present the representative SEM images of the nA, nM, μA and μM , respectively. The observation reveals significant differences between the microstructures of initial powders samples under the same magnification. The μA powder (Fig. 3c) is characterised by larger grain size and elongated shape, whereas both nM (Fig. 3b) and μM (Fig. 3d) powders consist of spherical, smaller grains. The SEM images of both nM and μM show generally the similar morphology of their powder particles and confirm the presence of agglomerates. The presence of agglomerates was also confirmed by previous measurements.

According to literature sources the value of the zeta potential indicates possible behavior of the dispersion. Generally, particles which have the zeta potential between -30 to 30 mV tend to agglomerate. The agglomeration is the most expressive at the isoelectric point, when the zeta potential equals zero mV (Marsalek, 2014). Due to the fact that

agglomeration can modify reactivity and mobility of nanoparticles (Henry et al., 2013) zeta potential as a function of pH and the initial pH values of the different MgO and Al_2O_3 mixtures were measured.

Fig. 4 presents the result of zeta potential analysis and mobility of initial powders as a function of pH and the results of pH measurement of the different MgO and Al_2O_3 mixtures. According to obtained results, zeta potential for nM and μM sample (Fig. 4a) over the entire measurement range is within the 0 to 25 mV. This indicates the tendency to the agglomeration and is in good agreement with previous studies. Additionally this measurement does not show significant differences between nM and μM initial powders. Analysing the results (Fig. 4b), it can be seen that nA sample has a positive surface charge over the entire pH range, which becomes progressively lower as the pH is increased. According to obtained results (Fig. 4c) pH of each blended mixtures aim to approximately 10.80. Comparing the Zeta potential analysis and pH measurement it can be suggest that in the presence of magnesium oxide, both μA and nA samples have the zeta potential approximately 10 and 20 mV, respectively, what indicate high tendency to agglomeration. Additionally the mobility of nA powder particles (1.55 umcm/VS), is almost twice higher than that of μA powder particles (0.75 umcm/VS). This results suggest that nA sample is characterised by slightly greater reactivity and stability than μA sample.

The TG and EGA curves obtained for the nMh, μMh , nAh and μAh samples are presented in Fig. 5a-b. This investigation makes it possible to compare the hydration ability of initial powders. According to thermogravimetric analysis results displayed as TG curves (Fig. 5a) the total mass loss due to decomposition of the hydrated counterparts of the initial powders within the temperature range 25°C to 1000°C was 0.66%, 4.99%, 31.29% and 31.97% of the initial mass of the μAh , nAh, μMh and nMh samples, respectively. The oxides contained in nM and nA samples are more susceptible to hydration than its μM and μA counterparts. This proves the greater reactivity of nMh and nAh samples and

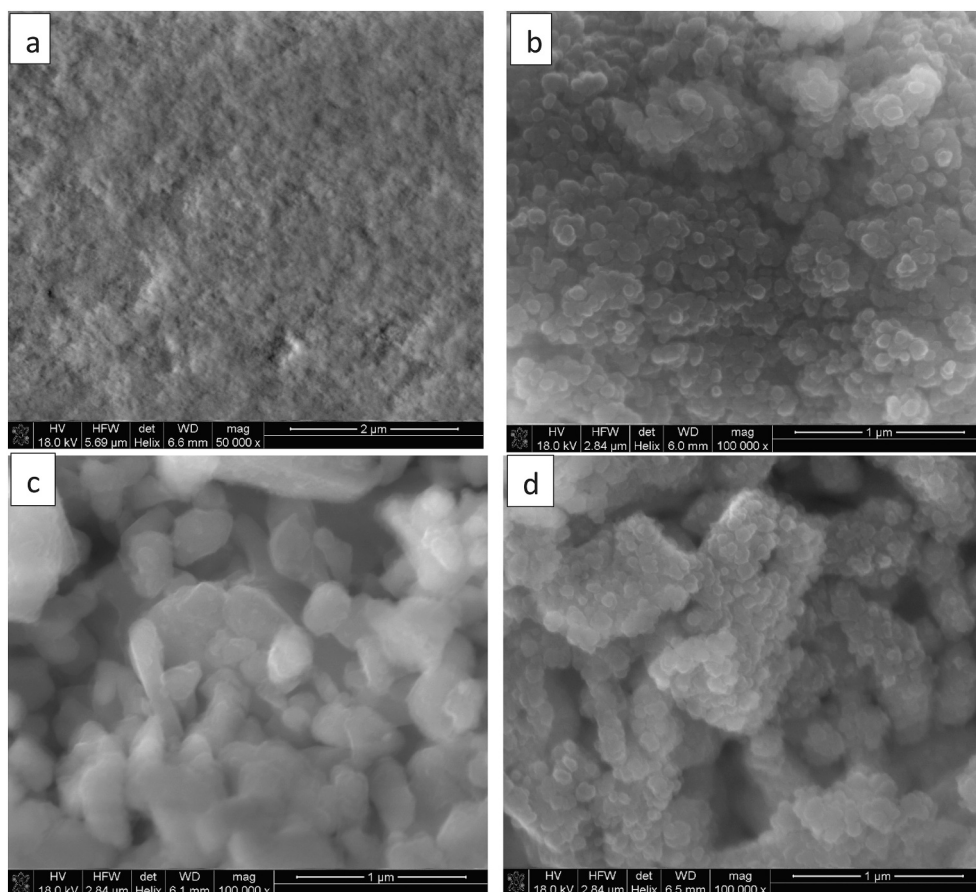


Fig. 3. SEM images of the nA (a), nM(b), μ A(c) and μ M(d) samples.

confirms the results of previous studies. Since no effects connected with H_2O release were observed in the ion current curve for $m/z = 18$ (H_2O^+) of the μ Ah sample, no $\text{Al}(\text{OH})_3$ was formed as it was already confirmed by XRD. According to the literature sources, peak at 253°C for nAh (Fig. 5b) can be assigned to the dehydration of bayerite or gibbsite (Carrier et al., 2007; Zhu et al., 2010). This also confirms the significant differences between nA and μ A hydration ability and indicates higher reactivity of nA than μ A initial powder. However, in the case of magnesium hydroxide identified in nMh and μ Mh samples, thermal decomposition takes place at 377 and 398°C , respectively and is consistent with the literature data (Pan and Zhao, 2015; Pimminger et al., 2016). According to the literature, lower decomposition temperature of magnesium hydroxide in nMh than μ Mh sample is probably associated with lower crystallite size and lower degree of crystallinity.

Fig. 6 presents FTIR spectra and band assignments of the initial powders and their hydrated counterparts from 4000 to 400 cm^{-1} . The infrared spectrum of μ A sample shows the characteristic bands for $\alpha\text{-Al}_2\text{O}_3$ at 453 , 602 and 640 cm^{-1} (Al—O bonds) (Zhou and Synder, 1991; Boumaza et al., 2009). After the curing period of 42 days, no band related to Al—OH is seen in the μ A sample spectrum, indicating no alumina hydroxides were formed, as shown in Fig. 6. The outline IR spectrum of nA sample was similar to the spectrum characteristic for $\gamma\text{-Al}_2\text{O}_3$ presented in (Boumaza et al., 2009; Barton and Quintard, 1982). We can observe wide, unresolved band in the range from 430 to 1000 cm^{-1} with the maximum absorbance positions at 548 and 818 cm^{-1} (AlO_6 and AlO_4 stretching, respectively) (Boumaza et al., 2009). According to the other literature sources the $\Theta\text{-Al}_2\text{O}_3$ phase infrared spectrum has better resolved bands with the maximum absorbance at: 560 , 620 , 760 , and 820 cm^{-1} (Boumaza et al., 2009). The characteristic bands related to $\Theta\text{-Al}_2\text{O}_3$ are highly overlapped and hidden in spectrum.

The outline spectrum of nA sample is close to the $\gamma\text{-Al}_2\text{O}_3$ which confirms that the gamma aluminium oxide is the dominant phase in the nA sample.

Due to its greater reactivity in contact with water, presence of gamma transition alumina is favourable (Tsuchida et al., 1975). Furthermore, as regards band at 431 cm^{-1} confirms the presence of Mg—O vibrations (Kumar et al., 2015). Additionally the FTIR spectra of nM, nMh, μ M and μ Mh samples indicate in all case the presence of Mg ($\text{OH})_2$ (band at around 3701 cm^{-1}) and this is consistent with the XRD analysis results reported in Fig. 2 (Kniizinger et al., 1993; Forano et al., 2006; Madej et al., 2018).

Based on the conducted research of initial powders and their hydrated counterparts, it can be concluded that nA sample is characterised by greater reactivity than μ A sample. Additionally, slight differences between nM and μ M samples can suggest that the reactivity and kinetics of binary mixtures will be probably affected by type of used alumina powder. The given results will be useful for further monitoring of the compositional changes within the obtained MgO— Al_2O_3 blended pastes.

3.2. XRD analysis of binary MgO— Al_2O_3 blended pastes

The low temperature X-ray diffraction and infrared spectroscopy measurements within the MgO— Al_2O_3 systems provided insights into the mechanism of hydrotalcite formation. Fig. 7 presents the overview of the XRD patterns of the examined blended pastes μ M_nA_h (a), nM_μA_h (b), nM_nA_h (c) and depicts the evolution over time for all blended pastes after the selected (12 h, 3 days, 7 days, 14 days, 56 days and 98 days) hydration time. Fig. 8 a-c presents the same diffractogram of the examined blended pastes within the narrower range 2θ of $10.0\text{--}44.0^\circ$. The course of the reaction was monitored based on the

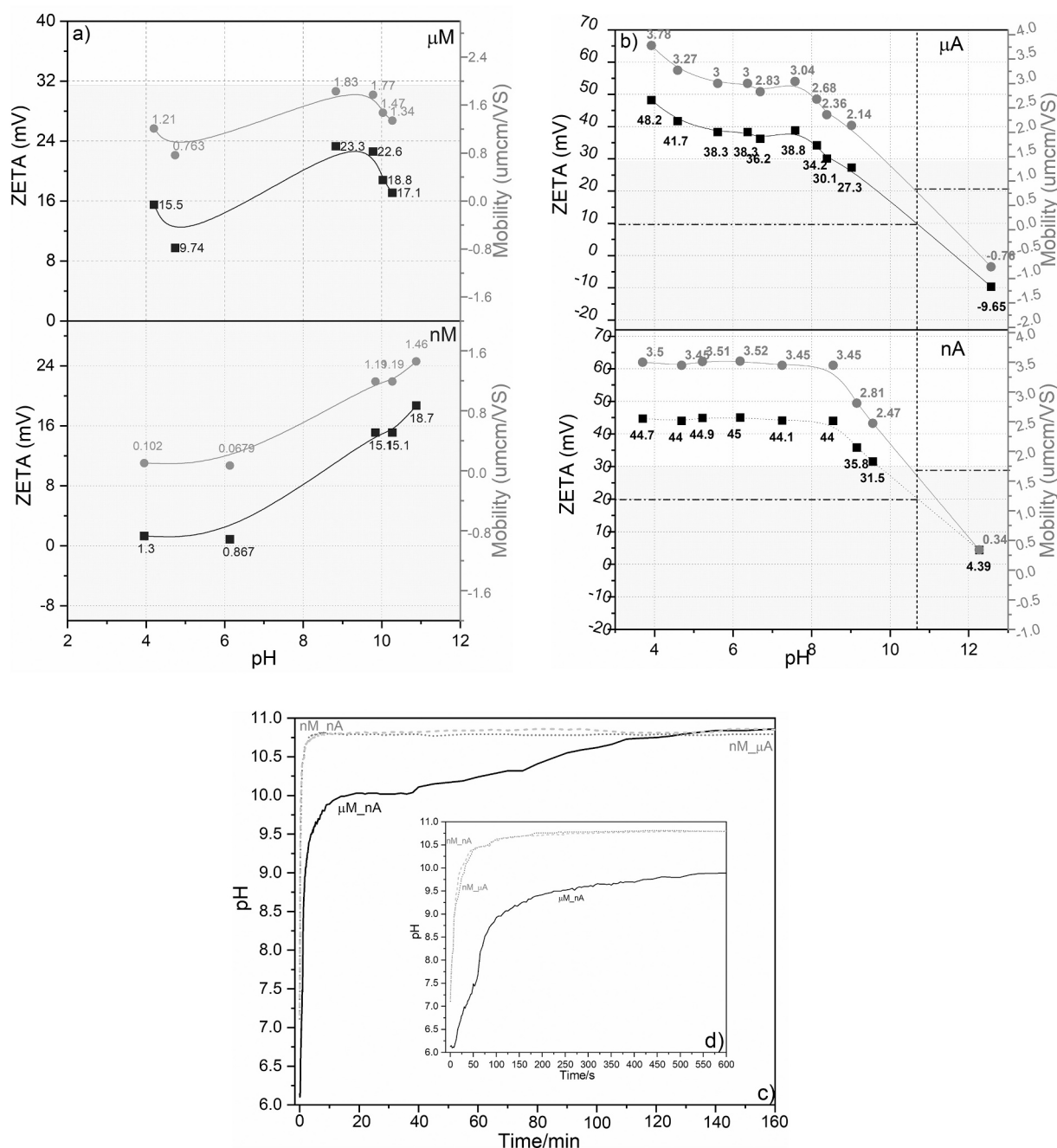


Fig. 4. Zeta potential and mobility of μM , nM (a) and μA , nA (b), the results of pH measurement of the different MgO and Al_2O_3 mixtures (c), and the insert graph with pH measurement of 10 min (d). The light grey range indicate the area where the initial powders have a tendency to agglomeration.

presence of hydrotalcite according to simulated XRD patterns of $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00-014-0191) and consumption of both magnesium oxide and magnesium hydroxide. Magnesium hydroxide peak (characteristic diffraction peak $2\theta = 37.966^\circ$, (JCPDS Card No 96-900-6331) occurs during first 12 h of hydration in all samples. Since no peak at $2\theta = 42.888^\circ$ (JCPDS Card No 96-900-6786) associated with MgO was observed after 14 days ($\text{nM}_\mu\text{A}_\text{h}$ (Fig. 8b), $\text{nM}_\text{nA}_\text{h}$ (Fig. 8c) samples) and 7 days ($\mu\text{M}_\text{nA}_\text{h}$ (Fig. 8a) sample) of curing, magnesium oxide has fully converted into either brucite or hydrotalcite. It is worth noting that in $\text{nM}_\mu\text{A}_\text{h}$ sample after 56 days of hydration there is a large amount of unreacted $\text{Mg}(\text{OH})_2$ (Fig. 8b). After extended hydration time reaching 98 days, no both starting MgO and intermediate product $\text{Mg}(\text{OH})_2$ were found in $\mu\text{M}_\text{nA}_\text{h}$ sample (Fig. 8a), hence fully-reacted blended paste was

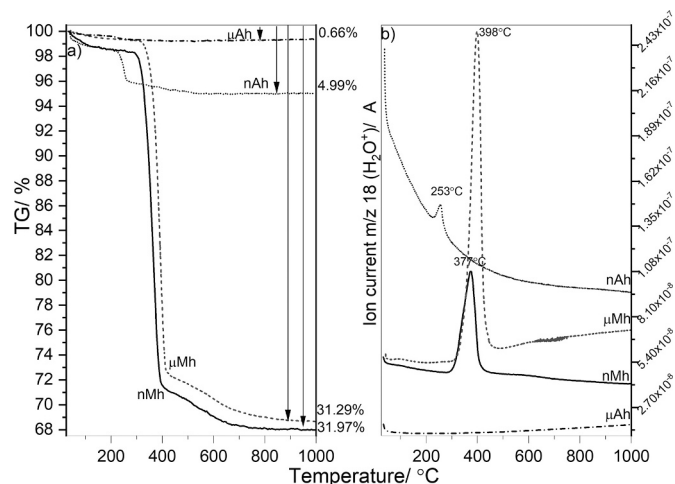
obtained.

The samples were prepared from binary mixtures with the MgO : Al_2O_3 molar ratio of 1:1. This means that the starting Mg/Al molar ratio was 0.5 while in the precipitated hydrotalcite described by the formula $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ it is about 3. The molar composition of the binary mixtures directly affect the chemical composition of the samples after hydration. The quantitative analysis (Table 3) showed that a greater amount of hydrotalcite was obtained in the $\text{nM}_\text{nA}_\text{h}$ 98d sample (58.6 wt%). In both samples approximately 35 wt% unreacted nano-metric Al_2O_3 powder was still present. Additionally, according to Rietveld quantity analysis (Table 3) traces amount of magnesium hydroxide (1.7 wt%) were found in $\text{nM}_\text{nA}_\text{h}$ 98d sample. The amorphous phase in the $\mu\text{M}_\text{nA}_\text{h}$ 98d sample reached over 20 wt% and probably mainly consisted of AH_3 -gel, nano-metric Al_2O_3 and certain quantities of

Table 2

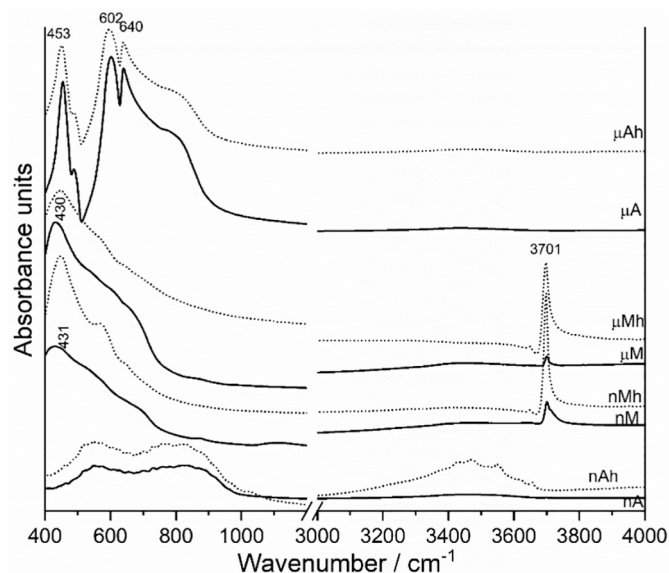
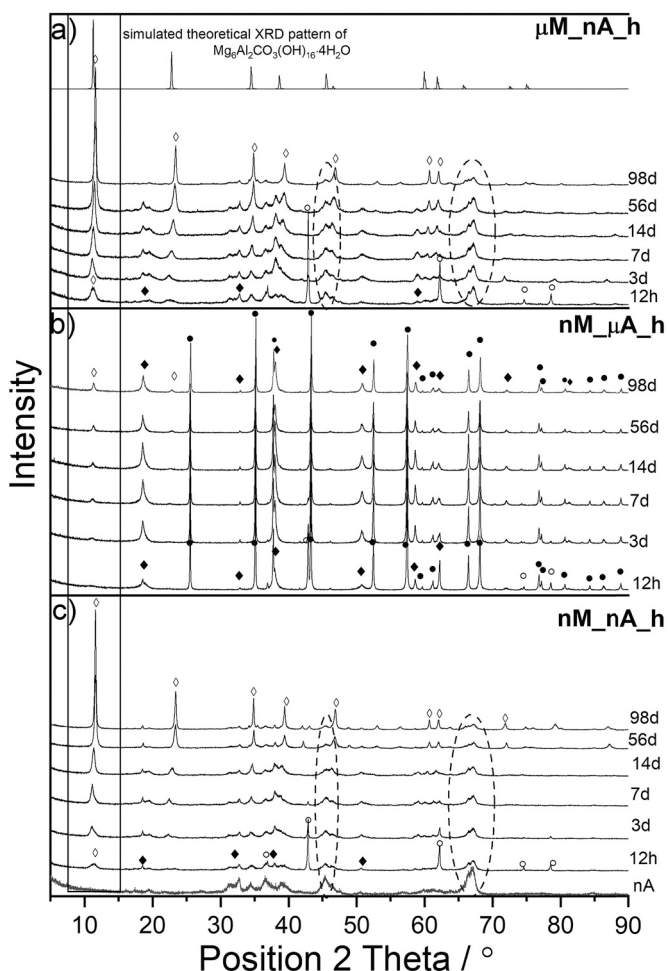
Characteristics of the starting powders and reference samples.

Sample	nM	μM	μA	nA
Identified major phase	MgO	MgO	Al ₂ O ₃	Al ₂ O ₃
FWHM [°]	0.7265	0.1895	0.1311	1.4428
2θ [°]	42.9118	42.9118	43.3467	66.8232
Crystallite size of starting powder	11.75	45.05	65.23	6.66
D _{XRD} [nm]				
Theoretical density [g/cm ³]	3.58	3.58	3.99	3.61
BET surface area [m ² /g]	28.2	10.9	6.6	56.6
Primary particle size D _{BET} [nm]	59.54	153.86	227.94	29.03
Agglomeration degree	5.07	3.42	3.48	4.41
Sample	nMh	μMh	μAh	nAh
Identified major phase	Mg(OH) ₂	Mg(OH) ₂	Al ₂ O ₃	Al(OH) ₃
FWHM [°]	0.2244	0.1152	0.1311	0.1756
2θ [°]	38.02338	38.0175	43.3467	18.7509
Crystallite size of hydrated powder [nm]	37.45	72.94	65.23	45.84
			(bayerite)	(gibbsite)

**Fig. 5.** TG curves (a) and evolution of the MS profile of the gaseous product ($m/z = 18$ (H_2O^+)) (b) characteristic for the reference Mg and Al hydroxides obtained via hydration of MgO and Al₂O₃ nano- and micro-powders.

hydroxide. It should be noticed, that crystalline products with higher ordered arrangement of elements was obtained from the substrates in less crystalline form (nM and nA). This suggests that the amorphous phase can be considered as a precursor of crystalline hydroxide.

Comparing the obtained results with the simulated XRD pattern of hydroxide, it can be seen, that the hydration of nM_nA_h (Fig. 7c) and μM_nA_h (Fig. 7a) samples leads to Mg–Al hydroxide formation within the first 12 h whereas in the nM_μA_h (Fig. 7b) trace amount of hydroxide was found after 3 days. This suggests that the hydroxide formation is determined by the reactivity of alumina. Due to the fastest hydroxide formation the nM_nA_h and μM_nA_h mixtures are characterised by the greatest reactivity. The gradual increase in XRD peak intensities along with increase in the curing time (Fig. 8a–c) is associated with an increase in both hydroxide content and probably crystalline degree. The characteristic peak belonging to the stoichiometric Mg–Al hydroxide described by the formula $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (Fig. 8a–c) shifts towards to higher 2 theta value ($2\theta = 11.6322^\circ$ and 11.6169° for μM_nA_h and nM_nA_h samples, respectively) what probably indicates different stoichiometry in relation to theoretical X-ray

**Fig. 6.** FT-IR spectra of initial powders and their hydrated counterparts in the range of 400–4000 cm^{-1} .**Fig. 7.** Overview of the low-temperature XRD patterns of samples μM_nA_h (a), nM_μA_h (b) and nM_nA_h (c) after the selected (12 h, 3 days, 7 days, 14 days, 56 days and 98 days) hydration time and nA starting powder. Black diamond: Mg(OH)₂ (JCPDS Card No. 96–900–6331), degree sign: MgO (JCPDS Card No. 96–900–6786), white diamond: $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00–014–0191), black filled circle: α-Al₂O₃ (JCPDS Card No. 96–500–0093).

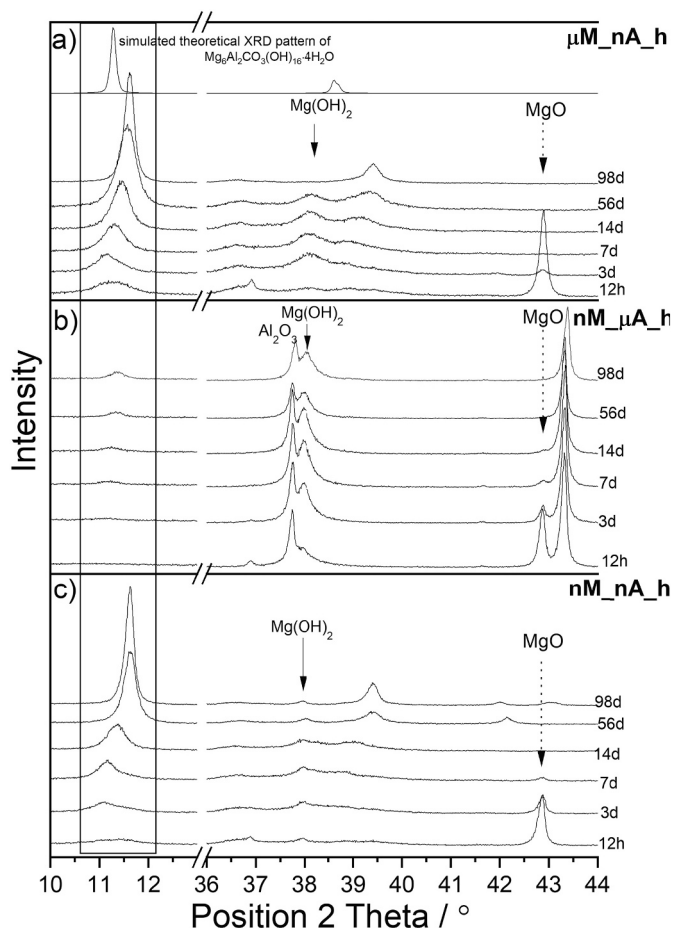


Fig. 8. X-Ray diffraction patterns of the samples $\mu\text{M_nA_h}$ (a), $\text{nM_}\mu\text{A_h}$ (b) and nM_nA_h (c) after the selected (12 h, 3 days, 7 days, 14 days, 56 days and 98 days) hydration time and simulated XRD pattern of $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00-022-0700) in the range of $10\text{--}44^\circ$.

Table 3

The quantitative phase composition of the samples nM_nA_h_98d and $\mu\text{M_nA_h_98d}$ by the Rietveld method.

Phase	Sample	
	nM_nA_h_98d	$\mu\text{M_nA_h_98d}$
	wt% according to Rietveld method	
Hydrotalcite	58.6	41.4
$\gamma\text{-Al}_2\text{O}_3$	20.6	13.6
$\Theta\text{-Al}_2\text{O}_3$	13.4	21.7
$\text{Mg}(\text{OH})_2$	1.7	–
Amorphous phase	5.7	23.3

Table 4

XRD data and structural parameters of hydrotalcite-like compound.

Sample	nM_nA_h_98d	nM_nA_h_56d	nM_nA_h_14d	$\mu\text{M_nA_h_98d}$	$\mu\text{M_nA_h_56d}$	$\mu\text{M_nA_h_14d}$
FWHM $[\circ]$	0.2339	0.3400	0.42	0.2677	0.4266	0.4515
2θ $[\circ]$	11.6169	11.6276	11.47	11.6122	11.5705	11.4432
Crystallite size in the direction c [nm]	34.15	23.48	18.90	29.83	18.72	17.68
FWHM $[\circ]$	0.1536	0.2304	0.3405	0.1728	0.3072	0.2882
2θ $[\circ]$	60.7912	60.7718	60.4140	60.7687	60.7554	60.5357
Crystallite size in the direction a [nm]	59.96	39.97	26.99	53.29	29.98	27.57

diffraction pattern of hydrotalcite. According to other literature sources this shift is connected with enrichment of hydrotalcite with a larger amount of the smaller Al^{3+} ions (Madej et al., 2018).

According to the Scherrer eq. (1), the average crystallite size was calculated and result of the hydrotalcite compound formed in nM_nA_h and $\mu\text{M_nA_h}$ blended pastes are shown in Table 4. Over time in the samples, we can observe a decrease in the FWHM value and increase in the size of crystallites. The hydrotalcite-like compound formed in the Mg–Al blended pastes are all in nanoscale structures. In nM_nA_h sample a tendency to form hydrotalcite of larger sizes was observed.

3.3. FTIR spectra analysis of binary $\text{MgO-Al}_2\text{O}_3$ blended pastes

The progress of formation of the Mg–Al– CO_3 hydrotalcite-like phase was also confirmed by the FTIR test result, which is shown in Fig. 9. Fig. 9a–c present infrared spectrum of $\mu\text{M_nA_h}$, $\text{nM_}\mu\text{A_h}$ and nM_nA_h after 12 h, 3 days, 7 days, 14 days, 56 days and 98 days of hydration.

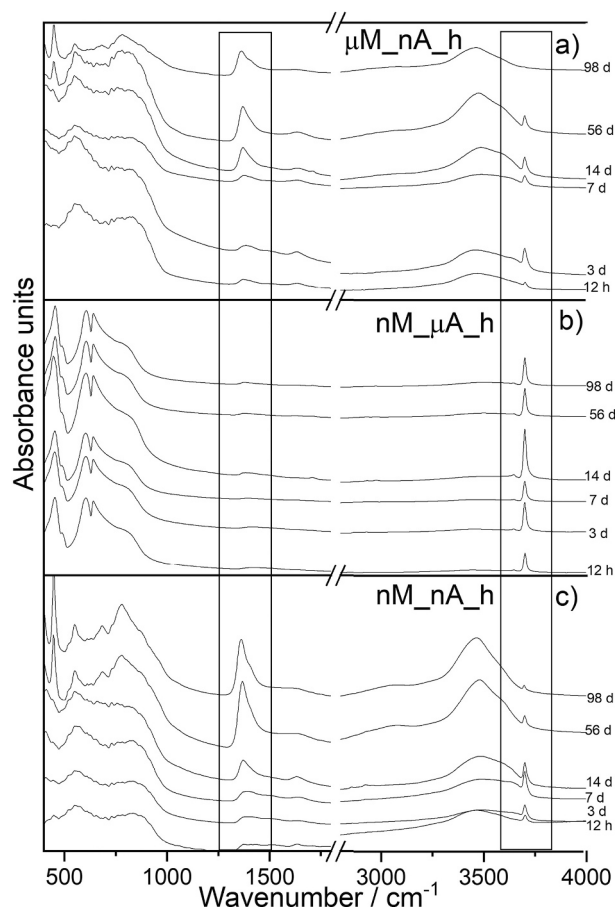


Fig. 9. FT-IR spectra of the $\mu\text{M_nA_h}$ (a), $\text{nM_}\mu\text{A_h}$ (b) and nM_nA_h (c) sample cured between 12 h and 98 days.

According to research, the outline IR spectrum of nM μ A_h sample was close to μ A (Fig. 5) through the analysed hydration period. Samples containing nanometric Al₂O₃: μ M_nA_h and nM_nA_h after 56 days of hydration exhibited bands characteristic for hydrotalcite, which indicates hydrotalcite as the main phase formed in the samples. In the range below 1000 cm⁻¹ we can identify bands which are associated with M–O stretching and M–OH bending vibrations (M = Mg and Al) in the octahedral host layers near 550 and 447 cm⁻¹, respectively. Other absorptions near 679 cm⁻¹ and 779 cm⁻¹ correspond to antisymmetric deformation mode (ν_4) and strong out-of-plane symmetric deformation mode (ν_2) of hydrotalcite CO₃²⁻ ions, respectively (Forano et al., 2006). During formation of hydrotalcite, Mg²⁺ ions are replaced with Al³⁺ ions, which requires compensation of charges by incorporation of carbonate anions into interlayer spaces. The incorporation of CO₃²⁻ ions is observed as a band at about 1360 cm⁻¹ which is attributed to the antisymmetric stretching vibration (ν_3) (Madej et al., 2018). The progress of the reaction is proved by the disappearance of the sharp and narrow band at about 3699 cm⁻¹. This band belongs to the magnesium hydroxide (O–H stretching vibration) which was formed in the initial reaction phase. It was confirmed by measurement of starting materials and other literature sources (Kniizinger et al., 1993). The disappearance of this band is the result of the consumption of initially formed Mg(OH)₂ and is associated with the appearance of a wide band in the range of about 3200 cm⁻¹ to about 3700 cm⁻¹ which is characteristic for hydrotalcite. As is well known, this broad band consists of the following bands: stretching vibrations of hydroxyl –OH groups attached to Mg OH–Mg₃: 3575 cm⁻¹, stretching vibrations of hydroxyl –OH groups attached to both Mg and Al: OH–Mg₂Al: 3454 cm⁻¹, CO₃²⁻–H₂O bridging: 3252 cm⁻¹ and H-bonded modes: 3069 cm⁻¹ (Valcheva-Traykova and Davidova, 1993; Madej et al., 2018). These changes in the spectrum were observed for both nM_nA_h and μ M_nA_h samples. After 98 days no magnesium hydroxide band was identified in the μ M_nA_h sample, which confirms the fully-reacted blended paste. In the spectrum of nM μ A_h wide band at around 3700 cm⁻¹ is not observed, which indicates a much slower Mg–Al hydrotalcite synthesis reaction. Based on the obtained results, it can be concluded that the presence of nanometric alumina oxide in the binary mixture definitely accelerates the transformation of MgO firstly to Mg(OH)₂ and finally to Mg–Al hydrotalcite.

3.4. Thermal analysis of binary MgO–Al₂O₃ blended pastes

Fig. 10a–c shows the gas evolution curves which were obtained during thermal analysis (DSC–TG–EGA–MS) for representative mass spectroscopic ion fragments of H₂O ($m/z = 18$) vapour during the thermal decomposition of the Mg–Al blended pastes which were obtained via different curing time (12 h, 14 and 56 days), whereas the Fig. 11 presents the results of DSC, TG and EGA (MS) of the nM_nA sample after 98 days of curing. Due to the greater precision/accuracy in analysing the thermal effects associated with dehydroxylation and dehydration EGA (MS) curves are presented instead of DSC curves for studying the reaction progress in the intermediate steps. As it can be seen in all EGA–H₂O profiles, the main difference between hydrated phases formed in the Mg–Al blended pastes obtained from various precursors is the thermal stability of interlayer water and hydroxyl groups within the structure of LDH minerals thus affects structural diversity of these phases. In the nM_nA_h (Fig. 10c) sample the measurement result confirms previous arrangements. Four effects are observed in sample after 56 days of curing, at temperatures, which are associated with: elimination of interlayer water (223 °C), dehydroxylation of OH–(Mg₃) hydrotalcite layers (313 °C), dehydroxylation of residue magnesium hydroxide/dehydroxylation of brucite-like layers (358 °C) and dehydroxylation of OH–(Mg₂Al) hydrotalcite layers (398 °C) (Madej, 2018). Whereas in the nM μ A_h (Fig. 10b) sample present wide effect associated with dehydroxylation of both magnesium hydroxide and hydrotalcite with a maximum at 375 °C and 185 °C, respectively. The sample is dominated by magnesium hydroxide and traces amount of

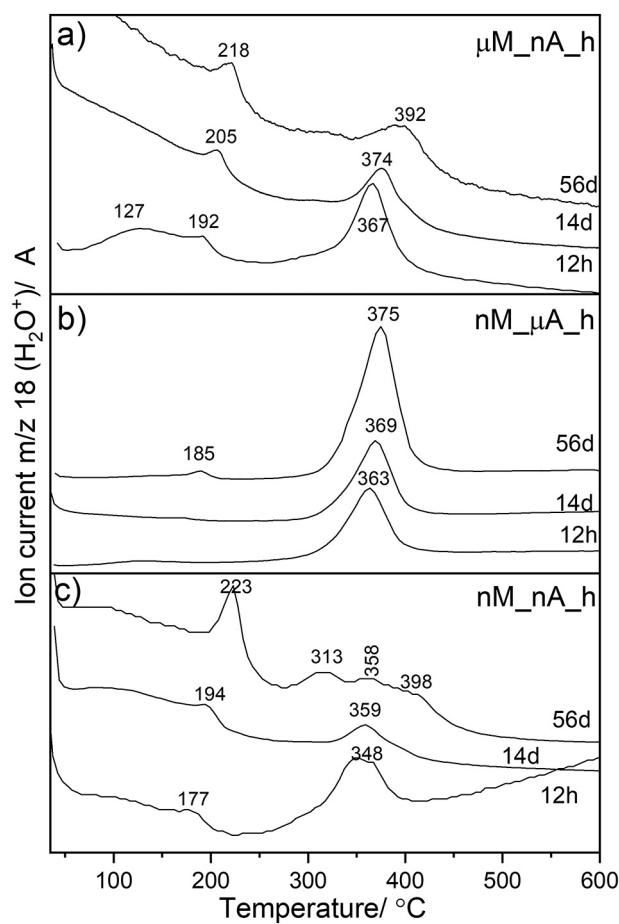


Fig. 10. Evolution of the MS profile of the gaseous product ($m/z = 18$ (H_2O^+)) characteristic for the $\mu\text{M}_\text{nA}_\text{h}$ (a), nM μ A_h (b) and nM_nA_h (c) blended pastes decomposition vs. the temperature for different curing times (12 h, 14 days and 56 days).

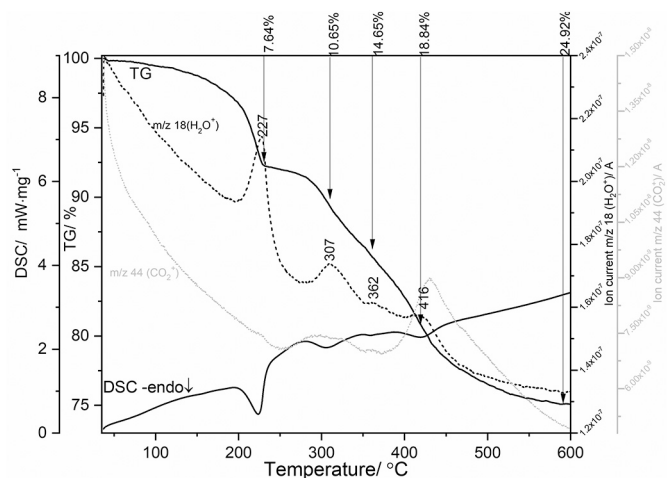


Fig. 11. TG–DTA profiles and gas evolution curves for representative mass spectroscopic ion fragments of CO₂⁺ ($m/z = 44$) and H₂O⁺ ($m/z = 18$) vapours during the thermal decomposition of the nM_nA_h sample after 98 days of hydration.

hydrotalcite. It is worth noting that the presence of nanometric alumina powder in the sample contributed to the shift of the decomposition temperature of magnesium hydroxide towards lower temperatures. This shift indicates change in thermal stability of structural hydroxyl groups.

Fig. 11 illustrates results of DSC-TG-EGA analysis which characterize the thermal behavior of the nM_nA_h blended paste after 98 days of curing as a reference sample. During heating in the temperature range between room temperature and 600 °C, the sample lost 24.92% of its weight. The theoretical weight loss for a hydrotalcite sample with Mg/Al = 3 is about 45% (Millange et al., 2000). This suggests that the sample is not a pure hydrotalcite phase and is consistent with the XRD analysis results reported in Fig. 7 and quantitative analysis. Additionally, it should be noticed, that the obtained mass loss result is in a good agreement with the theoretical weight loss based on hydrotalcite content evaluated by the Rietveld method (58.6%) and the expected weight loss of 45% for a sample with $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$. Indeed hydrotalcite content evaluated by the Rietveld method multiplied by the expected weight loss for mentioned sample is 26.4% which is close to the obtained value of 24.92%. At temperature below 227 °C the dehydration of amorphous gel products and physically adsorbed water molecules takes place. Due to the high surface area of components of blended paste, the high tendency to CO_2 adsorption is observed during both curing of blended pastes and sample preparation via quenching with acetone. At temperatures below 227 °C the EGA (MS) profile of released CO_2^+ ($m/z = 44$) is slightly raised which indicates the CO_2 desorption. The TG profile depicts that the mass loss at temperature of 227 °C is associated with removal of interlamellar water (the EGA (MS) profile of released H_2O ($m/z = 18$)). The decarbonisation process takes place at temperatures above 307 °C and 430 °C (the EGA (MS) profile of released CO_2^+ ($m/z = 44$)). Comparing the EGA- H_2O profiles presented in Fig. 10c and Fig. 11 slight shifts of effects associated with dehydration and dehydroxylation towards higher temperatures can be observed. The appearance of the indicated thermal effects confirms the presence of hydrotalcite in the sample.

3.5. SEM EDS studies of binary $\text{MgO-Al}_2\text{O}_3$ blended pastes

Fig. 12 a-c presents the representative SEM images and results of EDS analysis of the Mg—Al blended pastes. Fig. 12(a) and (b) show the SEM image of both nM_nA_h and $\mu\text{M}_\text{nA}_\text{h}$ samples, respectively, from which it can be clearly seen that the hydrotalcite is composed of many nearly monodispersed hexagonal plate-like structure. Hexagonal plate-like structure in the nM_nA_h sample is significantly larger than which we observe in the $\mu\text{M}_\text{nA}_\text{h}$ sample. According to EDS analysis molar weight ratio of Mg:Al element is different in the $\mu\text{M}_\text{nA}_\text{h}$ and nM_nA_h samples and may indicate different stoichiometry of the hydrotalcite. This confirms previous results of the XRD analysis. The morphology of nM_μA_h (Fig. 12c) is definitely different from the others. It can be noticed that the unreacted Al_2O_3 powder and well crystallized brucite are present. In the upper right corner of the Fig. 12b can be observed surface-reacted initial powders in the form of clusters which is confirmed by the SEM analysis. The results of the SEM analysis indicate a faster crystallization

process and growth of hydrotalcite crystals in the samples where nA have been presented. The SEM EDS observations is in good agreement with both XRD and FTIR results.

4. Discussion

The XRD and FTIR analysis reveal significant differences between Al_2O_3 -bearing raw materials while MgO -bearing raw materials are quite similar. The nM and μM samples differ from each other in grain size and tendency to agglomeration what was confirmed by SEM and BET analysis. The nA initial powder is characterised by greater reactivity due to the smaller grain size and better mobility determined from Brunauer–Emmett–Teller (BET) method and zeta potential investigation, respectively. Additionally in the alkaline environment the nA sample exhibits lower tendency to agglomeration than μA sample. It can be expected that the nA and μA may behave differently in the presence of MgO powder in terms of kinetics. This suggest that the reactivity and kinetics of binary mixtures is probably affected by type of used alumina powder. According to XRD and FTIR analysis, it can be concluded that applications of μA as initial powder leads to slower hydrotalcite formation.

In order to understand and modelled the mechanisms of hydrotalcite formation within the hydrating mixtures of $\text{MgO-Al}_2\text{O}_3$ powders with different sized grains, the equilibrium of systems must be considered with the help of thermodynamic data issued from the literature (Allada et al., 2005, 2006; Costa et al., 2010). Generally, many difficulties in the thermodynamic data determination for hydrotalcite arised from its structure which exhibits wide compositional variations, disordering and readily exchange anions. Additionally, in the consideration presented in this work, the accurate prediction of the feasibilities of reactions in the $\text{MgO-Al}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ system requires reliable values for standard enthalpies of formation for a wide range of compounds belonging to layered double hydroxides (LDH) or hydrotalcite-like compounds (HTLC), magnesium hydroxide and aluminium hydroxide in both the amorphous and crystalline states and also aqueous ions. Since, at each of the individual stages of reaction within the system composed of micrometric- and nanometric-sized powders of MgO and Al_2O_3 the structural inhomogeneity, as indicated by differences in phase composition and varying with time phase composition was detected, the determination of thermodynamic properties of the hydrating paste containing carbonate-bearing hydrotalcite, magnesium hydroxide and aluminium hydroxide, aqueous ions and starting materials is a difficult task. Moreover, the thermodynamic equilibrium can not be assumed in this system due to an excess of unconsumed Al_2O_3 .

Being aware of these limitations, simple thermodynamic calculations were performed assuming an equilibrium state between aqueous solutions and corresponding precipitated phases after synthesis via novel synthesis method of hydrotalcite-like compound of formula

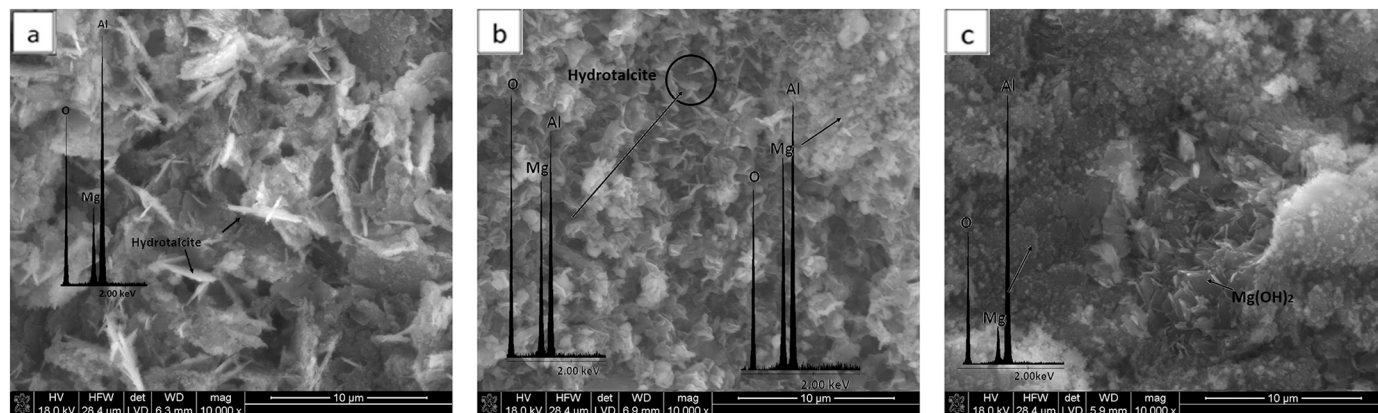


Fig. 12. SEM images and EDS analysis of the nM_nA_h (a), $\mu\text{M}_\text{nA}_\text{h}$ (b) and nM_μA_h (c) after 212 days of hydration.

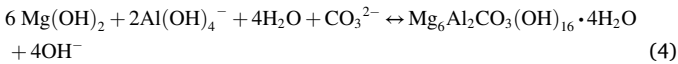
$Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$. For this purpose, the model adopted for the estimation of the thermodynamic properties of formation of hydrotalcite based on the combinations of simple compounds in this clay mineral structure is a combination of the compounds MgO , Al_2O_3 , CO_2 and H_2O . In order to estimate the Gibbs free energy of $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ formation, we adopted a very simple approach presented previously (Tardy and Uplay, 1992). The standard molar Gibbs free energy of formation from the elements of hydrotalcite $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ is estimated as equal to the weighted sum of the standard molar Gibbs free energies of formation from the oxides:

$$\Delta G_f^0[Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O] = 6\Delta G_f^0[MgO] + \Delta G_f^0[Al_2O_3] + \Delta G_f^0[CO_2] + 12\Delta G_f^0[H_2O] \quad (3)$$

The value of the standard Gibbs free energies of hydrotalcite formation ($\Delta G_f^0[Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O]$) using Eq. (3) and data listed in the Table 5 was estimated as -8236.98 kJ/mol.

In the next stage, we illustrate the effect of the substrates on our final thermodynamic data by examining the energetic difference between formation of $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ from magnesium oxide, aluminium tetrahydroxy ion, liquid water and carbonate ion (Eq. 4–5) and from magnesium ion, aluminium ion, liquid water and carbonate ion (Eq. 6–7) in calculation of the free energy of reaction (Eq. 8). The relevant standard Gibbs free energies of formation (ΔG_f^0 , kJ/mol) oxides, hydroxides and aqueous ions were previously presented in the Table 5.

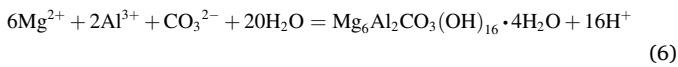
The reaction of formation of $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ from the hydroxides was formulated as:



$$\Delta G_{reaction} = [\Delta G_f^0[Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O] + 4\Delta G_f^0[OH^-]] - [6\Delta G_f^0[Mg(OH)_2] + 2\Delta G_f^0[Al(OH)_4^-] + 4\Delta G_f^0[H_2O] + \Delta G_f^0[CO_3^{2-}]] \quad (5)$$

and,

the reaction of formation of $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ from the aqueous species was formulated as:



$$\Delta_r G_{reaction} = [\Delta G_f^0[Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O] + 16\Delta G_f^0[H^+]] - [\Delta G_f^0[Mg^{2+}] + 2\Delta G_f^0[Al^{3+}] + 20\Delta G_f^0[H_2O] + \Delta G_f^0[CO_3^{2-}]] \quad (7)$$

where,

$$\Delta_r G_{reaction} = \sum \Delta G_f^0 \text{ products} - \Delta G_f^0 \text{ substrates} \quad (8)$$

In the first case:

- the free energy of reaction (Eq. 4 and 5) $\Delta_r G$ was calculated as

Table 5
Standard Gibbs free energies of formation (ΔG_f^0 , kJ/mol) oxides, hydroxides and aqueous ions.

Oxides and ions	(ΔG_f^0 , kJ/mol)	References
MgO (periclase)	-569.2	Tardy and Uplay, 1992
Al_2O_3 (corundum)	-1582.2	Tardy and Uplay, 1992
CO_2	-394.38	Ahmad and Upadhyayula, 2019
H_2O	-237.1	Tardy and Uplay, 1992
$Mg^{2+}_{(aq)}$	-453.99	Curtius et al., 2013
$Al^{3+}_{(aq)}$	-483.71	Curtius et al., 2013
$OH^-_{(aq)}$	-157.27	Curtius et al., 2013
$H^+_{(aq)}$	0	Chang, 1982; Allada et al., 2006
CO_3^{2-}	-528.1	Allada et al., 2006
$Al(OH)_4^-$	-1305.3	Chang, 1982
$Mg(OH)_2$	-832.3	Xiong, 2008

-214.84 kJ/mol.

Whereas in the second case:

- the free energy of reaction (Eq. 6 and 7) $\Delta_r G$ was calculated as $+724.48$ kJ/mol.

Hence, based on the thermodynamic modeling presented here, it can be concluded that the process of hydrotalcite formation in the $MgO-Al_2O_3-CO_2-H_2O$ system is becoming more thermodynamically feasible when magnesium hydroxide is formed as an intermediate product.

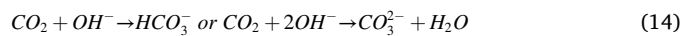
The $Mg(OH)_2$ formation as a starting product of hydration in each of analysed ternary system was confirmed by XRD and FTIR analysis (Figs. 8 and 9). According to the obtained results and literature sources it can be concluded that on the surface of the solid particles, before and during hydrotalcite formation and development hydration of MgO described as follows occurs:



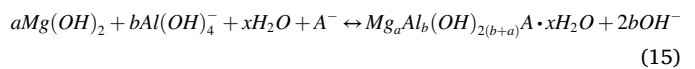
The magnesium oxide is a donor of the electron for proton from water. MgO crystallites acquire a positive surface charge according to eq. (9). Negative OH^- ions are adsorbed at the positively charged surface (eq. 10). According to the eq. (11), the complex adsorbed on the surface of the magnesium oxide is dissolved in the aqueous medium. In this process, magnesium hydroxide precipitates as a layered structure on the surface of magnesium oxide (Eliseev et al., 2002; Szczerba et al., 2013). Noticeably, these reactions are all related with hydroxide anion (OH^-) and thus affected by the environment pH. It is why the lower tendency of alumina oxide powder to the agglomeration in an alkaline environment is important. The release of $Al(OH)_4^-$ ions occurs in the $MgO-Al_2O_3-H_2O$ system due to the surface hydration of Al_2O_3 at a small extent also. A small amount of hydrate gel is formed



When the saturation level is reached, the nucleation phase begins and the hydrotalcite precipitate. The precipitation of the hydrotalcite causes a decrease in the ion concentration which leads to further reactions described above. Aluminium ions substitute magnesium ions in the brucite structure and to obtain an electrically neutral system the CO_3^{2-} ions are incorporated into the structure. CO_2 have been absorbed at the surface of $Mg-Al$ hydrotalcite from air and a reaction occurs:



through which compensation anions (A^-) for charge compensation are delivered. The incorporation of carbonate ions is observed as a band associated with the antisymmetric stretching vibration (ν_3) (1360 cm^{-1}), what present Fig. 9 (Madej et al., 2018). The total reaction of forming hydrotalcite is as follows and is associated with an increase in pH:



It is worthwhile noting that analogous reactions are observed during crystallization of many LDH phases, for example, $Li-Al$ LDH (Edelstein and Cammarata, 2002). According to Table 4, the crystallite sizes increase with hydration time. This indicates an increase in size of precipitated hydrotalcite crystals, which mesh and bond of hydrotalcite crystallites with each other. Fig. 13 is a schematic summary of hydrotalcite formation through the hydration process.

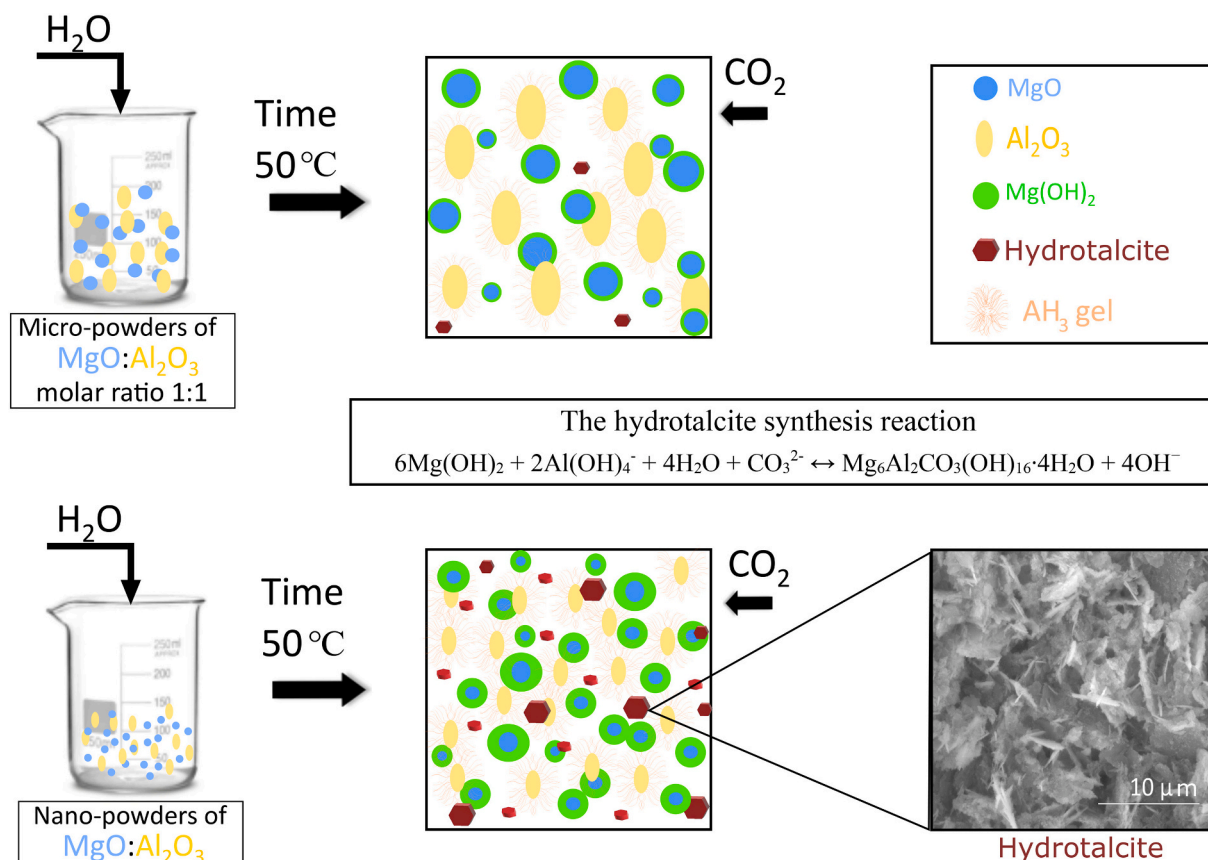


Fig. 13. Proposed mechanism of hydrotalcite synthesis through the hydration process.

5. Summary and conclusions

According to the current research, few certain conclusions can be drawn:

1. The reactivity of initial powders were analysed based on X-ray diffraction, infrared spectroscopy, SEM morphology, zeta potential analysis and DSC-TG-EGA measurement. This measurements confirm that nanometric Al_2O_3 powder presents a greater ability to hydration than micrometric Al_2O_3 initial powder, while nano- and micrometric MgO starting powders showed similar reactivity.
2. A blended pastes containing hydrotalcite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ was developed through the hydration of binary mixtures with the $\text{MgO}:\text{Al}_2\text{O}_3$ molar ratio of 1:1. For this purpose three mixtures which consist of nano- MgO and nano- Al_2O_3 , nano- MgO and micro- Al_2O_3 , micro- MgO and nano- Al_2O_3 powders were prepared.
3. Since, no both starting MgO and intermediate product $\text{Mg}(\text{OH})_2$ were found in $\mu\text{M_nA_h}$ sample after 98 days of hydration, fully reacted blended pastes were obtained successfully. Both nM_nA_h and $\mu\text{M_nA_h}$ blended pastes after hydration contained $\text{Mg}-\text{Al}$ hydrotalcite-like phase as the main product. Nevertheless $\mu\text{M_nA_h}$ sample contains the larger amount of amorphous phase than nM_nA_h sample.
4. Kinetics of the hydration was influenced by the type, grain size and specific surface area of alumina powder. The type of magnesium oxide does not significantly affect the kinetics of reactions.
5. According to the thermodynamic modeling, it can be concluded that the process of hydrotalcite formation in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{CO}_2-\text{H}_2\text{O}$ system is becoming more thermodynamically feasible when magnesium hydroxide is formed as an intermediate product.

6. Based on the hydration analysis of blended pastes, it can be concluded that the synthesis of hydrotalcite takes place in several stages and forms through a disappearance of initially formed $\text{Mg}(\text{OH})_2$. Firstly, magnesium hydroxide is precipitated as a layered structure on the surface of magnesium oxide and slightly dissolved. The release of $\text{Al}(\text{OH})_4^-$ ions occurs also. Secondly, the nucleation phase begins and precipitation of the hydrotalcite takes place.
7. The $\text{Mg}-\text{Al}$ hydrotalcite synthesis through hydration of binary mixtures which contain nanometric alumina powder is a simple and effective method of obtaining high purity $\text{Mg}-\text{Al}$ LDH and is characterised by high degree of conversion.

Author contributions

Karina Warmuz: methodology, writing-original draft preparation, visualization, data curation, investigation, software; Dominika Madej: conceptualization, methodology, validation, formal analysis, resources, writing-review and editing, supervision, project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Publikacja 10.2



Comparison of the CAC-containing and CAC-free hydraulic binders in term of the hydrated matrix formation within refractory castables designed for the fast drying procedure

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Abstract

In this work, two types of cement-free and CAC-containing binders were designed, prepared, and studied. The main purpose of this work was to demonstrate an alternative route to elaborate CAC-free hydraulic binder systems designed for monolithic refractories, e.g., castables. The fundamental research presented in this paper was focused on comparing CAC-containing and CAC-free (mixtures of simple oxides such as MgO and Al₂O₃) hydraulic binders in terms of hydrated matrix formation within refractory castables designed for fast-drying. Complete structural (XRD, FTIR) and thermal (D(TA-TG-EGA(MS))) characterizations of the hydration products of the mixtures allowed us to determine their reactivity. The effects sample composition and temperature on the hydration behavior of binders were explored by using the TAM Air isothermal calorimetry system at two temperatures (20 °C and 50 °C). It has been proven that the main hydrate in the cement-free system was hydrotalcite Mg₆Al₂CO₃(OH)₁₆·4H₂O, which was confirmed by the presence of a characteristic diffraction line at $2\theta = 11.498^\circ$. Mg–Al hydrotalcite was not synthesized in samples with CAC. Additionally, CAC-containing binders that contain free MgO introduced with spinel raw material were characterized by greater reactivity than the second CAC-containing sample because they contained larger amounts of hydrated phases. The findings obtained for the CAC-based binder showed that elevated temperature induced alterations in the calorimetric curve that were the same as those observed for the MgO–Al₂O₃-type cement-free sample. The induction period was shortened, and only one exothermic peak was detected.

Keywords Heat flow calorimetry · Thermal analysis · Mg–Al hydrotalcite · Hydraulic binder

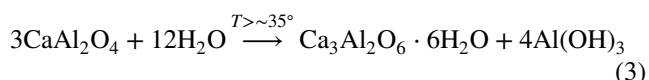
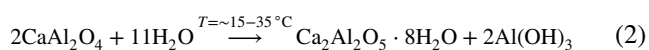
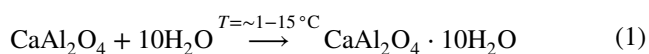
Introduction

Three types of calcium cements (CACs) are available: dark, gray, and white and they present significant differences in their chemical compositions. White CACs are mainly composed of three main clinker phases: calcium monoaluminate (CA, CaAl₂O₄ or CaO·Al₂O₃) and calcium dialuminate (CA₂, CaAl₄O₇ or CaO·2Al₂O₃). However, dark and gray CACs consist of CA, dodecacalcium hepta-aluminate (C₁₂A₇, Ca₁₂Al₁₄O₃₃ or 12CaO·7Al₂O₃), melilite (gehlenite C₂AS-alkermanite C₂MS₂ solid solution) and belite (larnite) β-C₂S, [1]. It has been confirmed that hydration

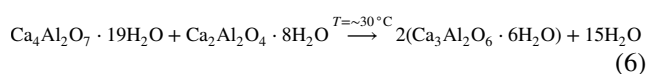
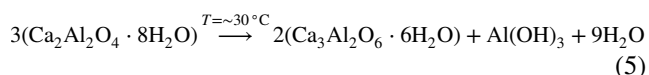
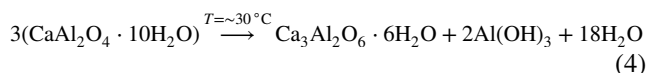
of CAC depends on the conditions (temperature, humidity, time and water-to-binder ratio) [2]. According to literature data obtained at low temperature (0–15 °C) the metastable phase CAH₁₀ can be formed. When the hydration temperature is raised above 15 °C, CAH₁₀ can coexist with C₂AH₈ and AH₃. The major crystalline products formed from CA at intermediate temperatures (between 27 and 35 °C) are C₂AH₈, AH₃ and C₃AH₆, with AH₃ forms at higher temperatures (from 35 °C) [3–5]. Other literature sources [6] claimed that in the temperature ranges 15–30 °C and above 30 °C the predominant phases were C₂AH₈ with AH₃ and C₃AH₆ with AH₃, respectively. In the prior work, it was suggested that the temperature ranges should be considered approximate due to the self-heating that occurred, since this influenced the formation of hydrates [6]. The reactions involved in CA hydration depend on temperature and are presented in Eqs. (1)–(3):

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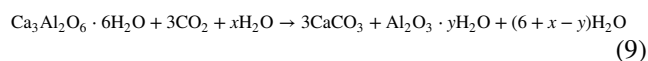
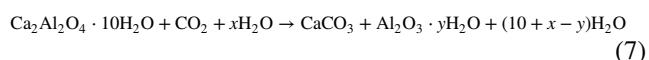
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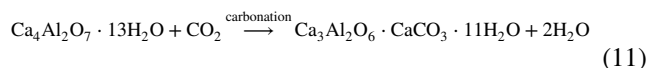
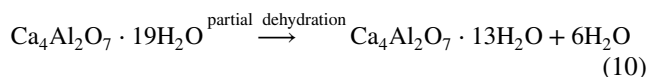
With the passage of time or at elevated temperature, the metastable phases convert into C_3AH_6 according to the Equations below:



CACs are multipurpose cements, and they cover a wide market in civil engineering or the refractory industry due to their unique properties; these include rapid strength development, high-temperature resistance and refractory performance, and resistance to chemically aggressive environments [6–9]. The added advantages of the CAC bonding system for the refractory industry are suitable working, curing and demolding times, availability, and price [10–12]. However, application of cement is associated with the formation of low-melting phases formation, such as anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) or gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) [13]. This leads to deterioration of important refractory castable properties such as thermal shock resistance, hot modulus of rupture, refractoriness, and refractoriness under load [15, 16]. Additionally, CAC affect the mechanism of MgO hydration [10, 16]. Hydration of MgO depends on the content of the binder used in the castable composition. According to literature data, the amount of CAC in MgO-based refractory materials influences the apparent volumetric expansion generated by magnesium oxide hydration, which leads to microcrack formation [17]. Therefore, inappropriate selection of amount of calcium aluminate cement could result in a decrease in green mechanical strength for refractory castables [11, 17]. On the other hand, changes in the mechanical properties of refractory castables caused by CAC binder can also be associated with carbonization [17]. During calcium alumina cement carbonation hydrates (CAH_{10} , C_2AH_8 and C_3AH_6) react with CO_2 and calcium carbonate and aluminum hydroxide are formed according to the Equations below [18]:



Additionally, $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 19\text{H}_2\text{O}$ can be partially dehydrated and then carbonated. According to Eqs. 10 and 11 as a result of the aforementioned reactions $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ may be formed [19]:



Calcium aluminates in CACs are inherently hydraulic i.e., capable of reacting with water to form crystalline hydrates, and these reactions are rather fast. On the other hand, the rates of reaction within $\text{MgO}-\text{Al}_2\text{O}_3$ powders can be increased by increasing the surface areas of these two substrates through use of a fine powder. Hence, formation of the ternary hydration products from the $\text{MgO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system is rather slow, and these hydrates can occur in amorphous, semicrystalline or crystalline forms. This is associated with lower amounts of chemically bound water and gradual water removal. Additionally, bonding through the amorphous hydrates decomposes at lower temperatures than that for crystalline hydrates.

There is currently increasing interest in modern supplementary binders, which are environmentally friendly alternatives to CAC. The combination of Al_2O_3 and MgO powders mixed with water gives a cement-free binding system based on the M–A–H phase designed for refractory corundum castables. Hydration of MgO and Al_2O_3 powder mixtures leads to $\text{Mg}-\text{Al}$ hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) formation. In our recent paper [20], we showed that the type, grain size and specific surface area of alumina powder affect the kinetics of hydrotalcite synthesis. Additionally, the properties of both magnesium and aluminum oxides also determine hydraulic (cementitious) activities. This kind of binder has an additional advantage associated with low-temperature in situ spinel synthesis, which exhibits very good mechanical properties, a high melting point and good chemical resistance to alkaline substances. On the other hand, it is becoming common to use a binder combination of MgO and Al_2O_3 powders combined with CAC. The sintering process for these components leads to MgAl_2O_4 spinel and CA_6 formation within the fine-grained matrix in refractory corundum castables.

Based on the results described above, the two most important aspects of CAC-based and CAC-free hydrated

binders were investigated in our work. First, the mechanism for hydration of the calcium aluminates depends on a congruent dissolution of the material and formation of hydrate crystallization nuclei. Hence, CAC-based binders generate high green mechanical strength in refractory castables in a short period of time. Nevertheless, optimization of the castable composition to improve the drying and high temperature behavior of refractory castables must be done. On the other hand, CAC-free binders, especially MgO-containing binders, are capable of forming magnesita-alumina-hydrates within alumina-based castables designed for fast drying. This can result from progressive dehydration behavior occurring over a wide temperature range during the heating stage, whereas dehydration of calcium aluminate hydrates occurs within a narrow temperature range.

Hence, the main aim of this work was to compare the formation of hydrated mixtures designed for fast drying, i.e., mixtures for which dehydration is possible at low temperature, within mixtures of simple oxides such as like MgO and Al_2O_3 and mixtures containing CAC modified with MgO powder. Additionally, the influence of MgO on CAC hydration was analyzed.

*Cement chemists abbreviation notation is used; thus, C=CaO, A= Al_2O_3 , H= H_2O , M=MgO.

Preparation of cement-free and CAC-containing binders

In this work, two types of cement-free and CAC-containing samples were subjected to thermal analyses and structural investigations. Binder samples were prepared with and without addition of calcium aluminate cement, and they constitute excellent simulations of modern ULCC and NCC refractory castables matrixes. The magnesita-alumina-based binders were prepared by mixing fused MgO (98% MgO) or dead-burned MgO (98% MgO) and Al_2O_3 nanopowder (Sigma-Aldrich, 99.8% Al_2O_3) with a MgO/ Al_2O_3 molar ratio of 1:1. Binders with ultra-low levels of calcium aluminate cement content were prepared by mixing: calcium aluminate cement (Górkal G70, 30% CaO), reactive Al_2O_3 (Almatis, CTC40, 99.8% Al_2O_3), Al-rich magnesium alumina spinel (Almatis, AR78) or Mg-rich

magnesium alumina spinel (Almatis, MR66). Compositions of the samples were selected so that the total amount of magnesium oxide (both in free and spinel form) was kept constant. Therefore, dead-burned MgO was added to the sample containing Al-rich spinel. Four mixtures were prepared: dead-burned MgO mixed with nanopowder Al_2O_3 (SpM_nA), fused MgO mixed with nanopowder Al_2O_3 (TopM_nA), Mg-rich spinel and CAC mixed with reactive Al_2O_3 (MR66_5M), Al-rich spinel, CAC and dead-burned MgO mixed with reactive Al_2O_3 (AR78_5M). Table 1 summarizes the nomenclature and composition of each sample.

Dry raw materials were weighed and prehomogenized for 30 min. The SpM_nA and TopM_nA mixtures were prepared with a water–solid material ratio (abbreviated w/s) of 1.5:1, while both the MR66_5M and AR78_5M mixtures were prepared with w/s = 0.5. The difference in the amount of water added was related to the presence of nanometric alumina oxide powder. Each dry mixture of powders was mixed by hand in a glass beaker until the water and powders were uniformly distributed. Mixtures were placed in a sealed polyethylene bag in a laboratory climatic chamber with the relative humidity maintained at 95% and the temperature of 20 °C and 50 °C. After an appropriate time of hydration (12 h, 24 h, and 72 h) the hydration process was stopped by grinding the samples in acetone (Chempur, 96% solution) at ambient temperature.

Characterization

The samples for XRD, FTIR and TG–DSC–EGA investigations were obtained by grinding the hardened binders with acetone after an appropriate curing time. Thermal decomposition data for hydrated mixtures after selected hydration times (72 h) were obtained by using simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC) and evolved gas analysis-mass spectrometry (EGA-MS) with the help of NETZSCH STA 449 F5 Jupiter coupled to a QMS 403 D Aeolos. The TG–DSC–EGA (MS) analyses were carried out with a sample mass of 10–15 mg in alumina crucibles in flowing synthetic air ($50 \text{ mL} \cdot \text{min}^{-1}$) at a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. An empty α - Al_2O_3 crucible was used as a reference substance. The crystalline phases in hydrated

Table 1 Nomenclature and composition of binary mixtures cement-free and CAC-containing samples

Designation of sample	SpM_nA	TopM_nA	MR66_5M	AR66_5M
Composition of sample	28.3 mass % dead-burned MgO nanometric 71.7 mass % Al_2O_3 powder	28.3 mass % fused MgO 71.7 mass % nanometric Al_2O_3 powder	59.8 mass % Mg-rich spinel 28.4 mass % reactive Al_2O_3 11.8 mass % CAC	54.9 mass % Al-rich spinel 4.9 mass % dead-burned MgO 28.4 mass % reactive Al_2O_3 11.8 mass % CAC
w/s	1.5	1.5	0.5	0.5

cementitious mixtures were identified by X-ray detection (XRD). X-ray analyses were carried out with an X'Pert ProPANalytical X-ray diffractometer with Cu K α radiation ($\lambda = 1.54060$ nm), with 0.02° per step and 3 s time per step (2θ : $5\text{--}70^\circ$). The phases present in samples after the hydration time were identified using HighScore Plus software (Panalytical) with the JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997), and the PDF-2 database supported by ICDD was used for data analyses. The FT-IR spectra of the binary mixtures of MgO and Al $_2$ O $_3$ powders and CAC-containing samples were recorded on a Fourier Transform Infrared Spectrometer from BRUKER (Vertex 70), and KBr pellets were studied in the range $400\text{--}4000$ cm $^{-1}$.

The evolution of hydration heat for mixtures containing dead-burned or fused MgO and nanometric Al $_2$ O $_3$ powders with an MgO/Al $_2$ O $_3$ molar ratio of 1:1 and the CAC-containing binders was determined with a TAM Air microcalorimeter (TA Instruments) at 20°C and 50°C (40-h hydration process) by integrating the continuous heat flow signal. In all cases, the mass of each substrate was calculated in such a way that the heat capacity of the sample was equal to heat capacity of the reference sample. Each mixture was introduced into the calorimeter after preliminary homogenization of the dry powders, but before mixing with water and an isothermal environment was obtained. After inserting the ampoule into the calorimeter, the powders were mixed with water (in situ mixing procedure). Better stability of the baseline (before and during measurement) was obtained due to the application of a second glass vial that contained sand as an inert reference in the twin channel of the calorimeter.

The specific surface area of fused and dead-burned magnesium oxide were evaluated using the Brunauer–Emmett–Teller (BET) method. Multipoint nitrogen adsorption surface area measurement was performed with a Micromeritics ASAP 2000 at 77.35 K after drying single samples at 200°C for 24 h. Additionally, grain size distributions of the powders and CAC were determined with a Mastersizer 2000.

Results and discussion

Characteristics of starting powders

The aim of this work was to compare the hydration of simple oxide mixtures such as MgO and Al $_2$ O $_3$ with those of hydratable compounds based on CAC. Therefore, it was necessary to highlight the differences between the raw materials used. Material type, specific surface area, grain size distribution or varieties of transition phases present may have a significant influence on reactivity in the presence of water and the ability to form hydrates. General information on the chemical compositions of the selected starting materials is presented in Table 2.

It is worth noting the differences between the raw materials used. Two kinds of spinel, both alumina and magnesium oxide, were used. Mg-rich spinel has a higher content of magnesium oxide than Al-rich spinel. Almais spinel MR 66 contains a certain amount of free magnesia. This free magnesium oxide reacts during sintering with aluminum oxide to form secondary spinel. Additionally, free MgO can also be used as a setting agent. Both Mg-rich and Al-rich spinel should be considered inert; however due to the presence of free MgO in spinel MR66 partial hydration could be expected.

α -Al $_2$ O $_3$ is the dominant phase in reactive alumina (CTC40). According to our previous work [18] nanometric aluminum oxide is composed of two transition aluminas, γ -Al $_2$ O $_3$ and θ -Al $_2$ O $_3$. Moreover, high BET specific surface area and great susceptibility to hydration indicate high reactivity. It is commonly known that the presence of transition aluminas is favorable and leads to greater reactivity than that seen for α -Al $_2$ O $_3$ alone.

Two types of magnesium oxide dead-burned and fused, were used. The average grain sizes in the dead-burned and fused magnesia samples ranged between $2.507\text{--}64.694$ μm ($d_{0.5} = 17.353$ μm) and $2.438\text{--}66.879$ μm ($d_{0.5} = 17.605$ μm), respectively. Dead-burned MgO exhibited a higher specific BET surface area (0.9077 m 2 g $^{-1}$)

Table 2 Typical chemical compositions of raw materials [21–24]

Chemical composition [mass %]	Mg-rich spinel (MR66)	Al-rich spinel (AR78)	CAC (G70)	Dead-burned MgO	Fused MgO	Al $_2$ O $_3$ (CTC 40)	Nanometric Al $_2$ O $_3$
Al $_2$ O $_3$	> 63.00	> 74.00	69.00–71.00	< 1.80	< 0.80	> 99.80	> 99.80
SiO $_2$	0.09–0.15	0.10–0.15	0.50	< 5.00	< 2.50	0.03–0.07	–
MgO	33.0–35.0	22.05–24.00	–	> 90.00	> 96.00	–	–
CaO	0.39–0.60	0.24–0.30	28.0–30.0	< 2.50	< 2.50	0.03–0.07	–
Na $_2$ O	0.03–0.20	0.09–0.32	0.50	–	–	0.08–0.12	–
Fe $_2$ O $_3$	0.20–0.30	0.15–0.25	0.30	< 1.30	< 1.00	0.03	–

than fused MgO ($0.8770 \text{ m}^2 \text{ g}^{-1}$). The results of both measurements indicated that dead-burned MgO has a greater ability to form hydrated counterparts.

GÓRKAL 70 is a hydraulic binder with a high Al_2O_3 content. According to the product data sheet, setting times within the range 160–240 min can be used for various refractory products. Additionally, the average grain sizes in the CAC samples ranged between 1.992 and $47.686 \mu\text{m}$ ($d_{0.5} = 16.968 \mu\text{m}$).

X-ray diffraction characterization of cement-free and CAC-containing samples

The XRD method was used to analyze the progress of hydration for both Mg–Al cementitious matrixes and cement binders. All results from X-ray analyses are presented in Fig. 1a–d. These figures present diffractograms illustrating phase evolution after 12 h, 24 h, and 72 h hydration at 20 °C or 50 °C. Since the peak at $2\theta = 37.966^\circ$ (JCPDS Card No.

96-900-6331), which is associated with $\text{Mg}(\text{OH})_2$, was not observed in either SpM_nA or TopM_nA, magnesium oxide was converted only into Mg–Al hydrotalcite. Nevertheless, the process of hydrotalcite formation through hydration is thermodynamically preferred when magnesium hydroxide is formed as an intermediate product [20]. This suggests that $\text{Mg}(\text{OH})_2$ was formed in the investigated CAC-free binders simultaneously consumed for $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ synthesis. The intensity of the characteristic diffraction peak belonging to the $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00-014-0191, $2\theta = 11.498^\circ$) indicated that at each stage of hydration, more hydrotalcite was present in SpM_nA than in TopM_nA. In comparing the results obtained for the mentioned Mg–Al cementitious matrixes, it is clear that the SpM_nA sample at 50 °C exhibited the highest degree of magnesium oxide conversion directly into Mg–Al hydrotalcite. Additionally, hydration of the SpM_nA sample (Fig. 1b) led to Mg–Al hydrotalcite formation within the first 12 h whereas in the TopM_nA sample, a

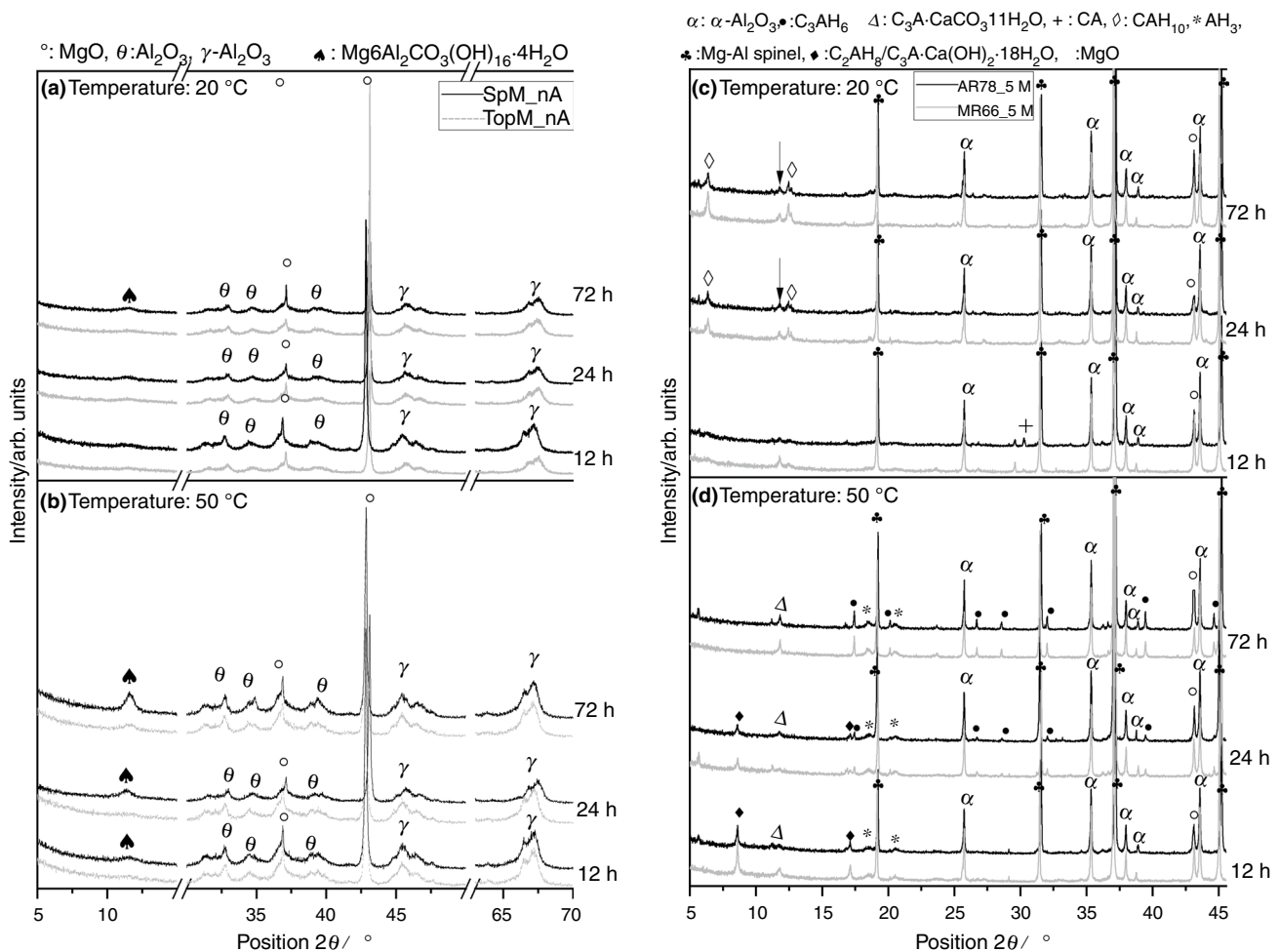


Fig. 1 a–d X-ray diffraction patterns of the both cement-free (SpM_nA and TopM_nA) and CAC-containing (AR78_5M and MR66_5M) samples after 12 h, 24 h and 72 h of curing at 50 °C and 20 °C in the range of 5–70° and 5–45°, respectively

trace amount of hydrotalcite was found after 72 h. According to the results obtained after 72 h of hydration at both temperatures, MgO, Mg–Al hydrotalcite, γ - Al_2O_3 and θ - Al_2O_3 were present in all samples. The presence of MgO, γ - Al_2O_3 , $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ and θ - Al_2O_3 were confirmed by peaks at 2θ : 42.888° (ICDD Card No. 01-087-0651), 66.940° (JCPDS Card No. 96-101-0462), 11.489° (JCPDS Card No. 00-014-0191) and 36.596° (JCPDS Card No. 96-120-0006), respectively.

Figure 1c, d presents diffractograms for the examined cementitious mixtures within the 2θ range 5–45°. X-ray diffraction analyses allowed us to determine the effects of hydration temperature and time on the phase compositions of the obtained mixtures. As noted above, cementitious samples contain prefabricated spinel and CAC in addition to both Al_2O_3 and MgO introduced as free or with spinel. The Mg-rich spinel MR66 contain the free magnesium oxide introduced with Mg-rich spinel. Therefore, a different compositions of the MR66_5M and AR78_5M samples before and after hydration should be expected.

The X-ray diffraction measurements of MR66_5M and AR78_5M revealed differences between hydration processes run at different temperature. It was clearly seen that, after 12 h of hydration at 20 °C (Fig. 1c), both the MR66_5M and AR78_5M samples contained MgO (ICDD Card No. 01-087-0651, $2\theta = 42.888^\circ$), α - Al_2O_3 (JCPDS Card No. 96-900-9674, $2\theta = 43.537^\circ$), CaAl_2O_4 (ICDS Card No. 98-018-0997, $2\theta = 30.043^\circ$) and Mg–Al spinel (JCPDS Card No. 96-900-2168, $2\theta = 37.070$ – 37.206°). The intensity of the characteristic peak observed for CA after 12 h of curing was definitely higher in the diffractogram for AR78_5M than in that for MR66_5M. Identification of only starting substrates in both samples suggested that curing for 12 h led to the formation of amorphous hydration products, which should be confirmed by FTIR measurements. Extending the curing time to 24 h led to crystallization of hydration products, which were initially considered amorphous. X-ray diffraction patterns for powders obtained after 24 h of hydration at 20 °C confirmed the presence of hydration products and consumption of the CA during hydration. After 24 h of hydration, the following phases were formed: CAH_{10} (ICOD Card No. 00-011-0204, $2\theta = 6.176^\circ$) and $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ (JCPDS card No. 01-087-0493, $2\theta = 11.706^\circ$). The presence of $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ resulted from an unwanted carbonization process, which probably took place during grinding of the samples in acetone. With the passage of time, the intensity of the characteristic peak belonging to CAH_{10} constantly increased. Since the peak at $2\theta = 39.21^\circ$ associated with C_3AH_6 (JCPDS Card No. 96-900-1773) was not observed after 72 h of curing at 20 °C, it appeared that metastable hydrate dominated and there was no conversion into C_3AH_6 . Additionally, XRD measurements did not reveal the presence of AH_3 (JCPDS Card No. 98-024-5301, $2\theta = 18.268^\circ$).

After 12 h of curing at 50 °C (Fig. 1d), the peak associated with CA was not observed. This suggests that elevated temperature accelerated hydration. Additionally, X-ray diffraction patterns for samples cured at 50 °C for 12 h confirmed the presence of crystalline hydration products. The diffraction peak centered at a specific angle $2\theta = 8.170$ – 8.180° was in good agreement with JCPDS cards No. 00-014-628 and No. 00-045-0564 for C_4AH_{19} and C_2AH_8 , respectively. Nevertheless, the X-ray diffraction patterns of C_2AH_8 and C_4AH_{19} are very close, so a clear distinction between these two hydration products is not possible. Although C_3AH_6 formation at 50 °C is more thermodynamically preferred, the aforementioned metastable phases were formed. Additionally, AH_3 and MgO were observed. According to these results, further hydration of the MR66_5M and AR78_5M samples led to a decrease in the intensity of the diffraction line for both C_4AH_{19} and C_2AH_8 , which is associated with conversion of the mentioned metastable phases into C_3AH_6 . Formation of C_3AH_6 was indicated by the appearance of a characteristic diffraction peak at $2\theta = 39.21^\circ$.

It is worth noting that after each stage of hydration at both temperatures, the characteristic peak for $\text{Mg}(\text{OH})_2$ was not observed. Additionally, the intensities of the diffraction peaks belonging to the hydrates were higher in MR66_5M than in AR78_5M, which indicated greater reactivity of the MR66_5M cementitious binder. In the MR66_5M sample, magnesium oxide was enclosed inside inert spinel grains. This suggests that all added water was consumed for calcium aluminate hydrate formation. On the other hand, magnesium hydroxide was not found in the AR78_5M sample, although MgO was added as a separate component. Most likely, the cement prevented the MgO from undergoing hydration.

FTIR analyses of cement-free and CAC-containing samples

FTIR spectra for the SpM_nA, TopM_nA, MR66_5M and AR78_5M samples are shown in Fig. 2a–d. The FTIR spectra of the SpM_nA and TopM_nA samples (Fig. 2a, b) confirmed previous findings. The absence of a characteristic sharp and narrow band at approximately 3700 cm^{-1} (O–H stretching vibration) confirmed the lack of $\text{Mg}(\text{OH})_2$, which indicated consumption for Mg–Al LDH synthesis [20]. Additionally, the higher temperature of the hydration process and the application of dead-burned magnesium oxide, accelerated the synthesis of hydrotalcite. This was also confirmed by the presence of a band at approximately 1360 cm^{-1} , which was related to the antisymmetric stretching vibration (ν_3) of CO_3^{2-} ions incorporated into the structure of hydrotalcite. This incorporation of carbonate anions into the hydrotalcite structure resulted from the replacement of Mg^{2+} ions by Al^{3+} ions, which required charge compensation. The IR spectra of both the SpM_nA

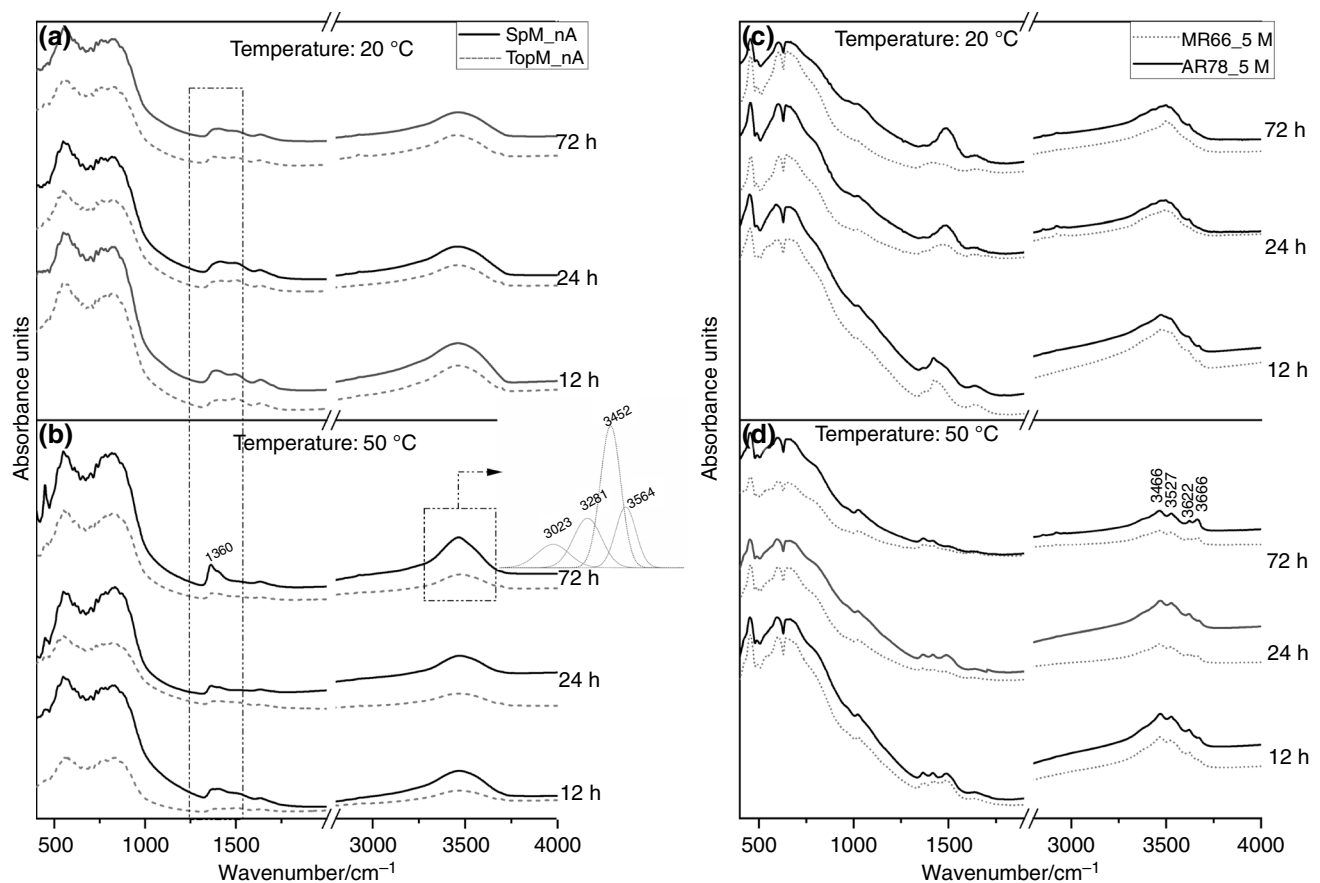


Fig. 2 a–d FTIR spectrum of the TopM_nA, SpM_nA, AR78_5M and MR66_5M samples after 12 h, 24 h and 72 h of curing at 20 °C and 50 °C in the range of 400–4000 cm^{-1}

and TopM_nA samples were similar to that of $\gamma\text{-Al}_2\text{O}_3$ throughout the hydration period. This suggests that $\gamma\text{-Al}_2\text{O}_3$ was the dominant phase in the nanometric aluminum oxide powder used. The most characteristic band for the hydrotalcite-like phase can be found in the range of approximately 3200 cm^{-1} to approximately 3700 cm^{-1} . This broad band consists of a few bands: H- bonded modes (3023 cm^{-1}), $\text{CO}_3^{2-}\text{-H}_2\text{O}$ bridging (3281 cm^{-1}), stretching vibrations of hydroxyl –OH groups attached to both Mg and Al, $\text{HO-Mg}_2\text{Al}$ (3452 cm^{-1}), and stretching vibrations of hydroxyl –OH groups attached to Mg, HO-Mg_3 (3564 cm^{-1}) [25].

Figures 2c, d show FTIR spectra for the MR66_5M and AR78_5M samples hydrated at 20 °C and 50 °C, respectively. In the 400–1200 cm^{-1} region there is a very complex vibrational peak indicating presence of a few phases. Due to the preponderance of both magnesium aluminum spinel and $\alpha\text{-Al}_2\text{O}_3$ in the compositions of the samples, assignment of their characteristic bands was possible. The FTIR spectra of both the AR66_5M and MR66_5M samples (Fig. 2c, d) showed bands at 449, 592 and 655 cm^{-1} , which are characteristic of $\alpha\text{-Al}_2\text{O}_3$ (stretching vibrations of Al–O bonds

[26]). Moreover, bands at 549 and 692 cm^{-1} were assigned to MgAl_2O_4 .

The IR spectra of both the AR78_5M and MR66_5M samples hydrated at 20 °C presented a broad and intense band in the 3400–3650 cm^{-1} region, with maxima near 3500 cm^{-1} , arising from OH vibrations of water molecules. This band is associated with the presence of metastable calcium aluminate hydrates and amorphous AH_3 [17, 27]. Since no band was observed at approximately 3670 cm^{-1} , C_3AH_6 was not formed throughout the hydration period in samples hydrated at 20 °C. It is worth noting that a broad band was present after just 12 h of curing of both samples, and this confirmed previous XRD results indicating the absence of peaks belonging to hydrated phases. Thus, the hydration products obtained after 12 h of curing were amorphous rather than crystalline materials. The very weak band at approximately 1630–1650 cm^{-1} was related to the deformation mode of water [27]. Additionally, the IR spectra of the samples presented a broad strong ν_3 carbonate band between 1300 and 1600 cm^{-1} . This band was stronger for samples hydrated at 20 °C, thus confirming the results obtained by

XRD, which showed more carbonation of MR66_5M and AR78_5M hydrated at 20 °C than at 50 °C.

As with to the Mg–Al cementitious samples, elevated temperature accelerated the hydration process. According to XRD measurements for samples treated at 50 °C, the presence of C_3AH_6 and AH_3 was confirmed after 24 h of hydration. The FTIR spectra obtained for the MR66_5M and AR78_5M hydrated mixtures after 12 h of curing contained a very broad O–H stretching band in the 3300–3700 cm^{-1} region (Fig. 2d) which indicated the presence of amorphous hydrates. It is clearly seen that raising the temperature to 50 °C led to more crystalline hydration products, which were indicated by sharper bands with higher resolution in the mentioned range. These spectra have bands at 3466 and 3622 cm^{-1} due to OH vibrations of molecular water in C_2AH_8 , 3527 cm^{-1} due to the presence of AH_3 , and an OH-free absorption band at 3666 cm^{-1} due to C_3AH_6 [3].

Calorimetric studies of calcium aluminate cement (CAC)-containing and CAC-free hydrating mixtures

Isothermal calorimetry was used to evaluate the kinetics of CAC-containing and CAC-free binder hydration by measuring heat evolution. The continuous test results presented as hydration kinetics curves were used to compare these materials, which could be considered necessary precursors for formation of the hydrated castable matrix. Hence, hydration kinetics were represented by two types of curves: rate of hydration versus time, which was defined as the derivative curve (Figs. 3a, b and 4a–c), and total degree of hydration versus time, which was defined as the integral curve (Fig. 3c). Despite the fact that the temperature for mixing, installing, and curing refractory castables ranged from ca. 20 °C to 25 °C, calorimetric experiments were performed both at room and elevated temperatures. Hence, both the time- and temperature-dependent reaction curves are presented in Figs. 3a–c and 4a–c.

Hydration of the CAC-containing mixtures AR78_5M and MR66_5M at 20 °C was represented by two exothermic peaks and the dormant period, during which the rate of hydration occurring between the first and the second exothermic peaks slowed (Fig. 3a). During the first 24 h, free MgO which was added to the AR78_5M sample shortened the dormant period, whereas magnesium oxide introduced together with the spinel MR66 accelerated the initial hydration of the MR66_5M binder constituents, as indicated by increases in the intensities of the first and the second peaks of the heat evolution curve. The characteristic features of the calorimetry curves measured at 50 °C were also significantly affected by temperature (Fig. 3). As shown in Fig. 3a, b, heat release (one peak) was connected with both the initial wetting of cement-containing samples and the hydration reaction. Hence, over the course of ca. 1.5 h, the hydration

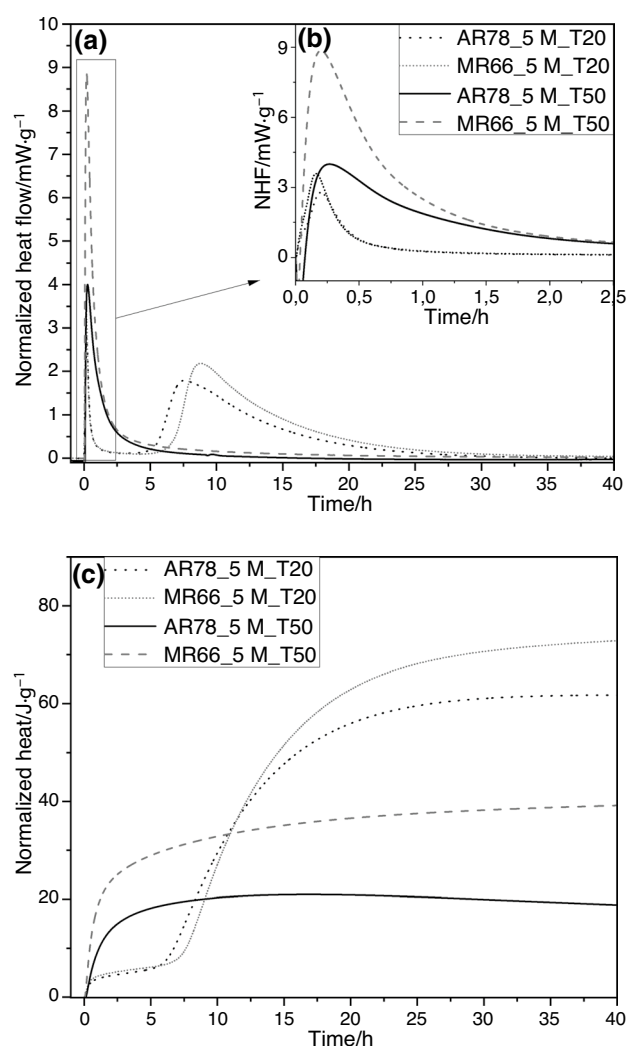


Fig. 3 a–c Heat flow curves (a, b) and cumulative heat release curves versus time (c) for cement binders hydrated at 20 and 50 °C and $w/c=0.5$ normalized to mass of dry powder (in situ mixing procedure)

reactions were diffusion controlled. According to the XRD and FTIR test results for CAC-containing samples the MR66_5M sample exhibited higher reactivity and elevated temperature accelerated the hydration process. There is an obvious relationship between the higher amount of hydrated compounds produced in the MR66_5M sample hydrated at both 20 °C and 50 °C, and the high intensities of both the first and the second peaks of the heat evolution curve.

Hydration of the CAC-free hydrating mixtures SpM_nA and TopM_nA at 20 °C and 50 °C was represented by one broad exothermic peak without any dormant period (Fig. 4a–c). As shown in Fig. 4, in the case of cement-free mixtures, the intensity of this peak was strongly reduced due to the elevated temperature. Similar observations from XRD, FTIR and calorimetric results, such as the highest intensity

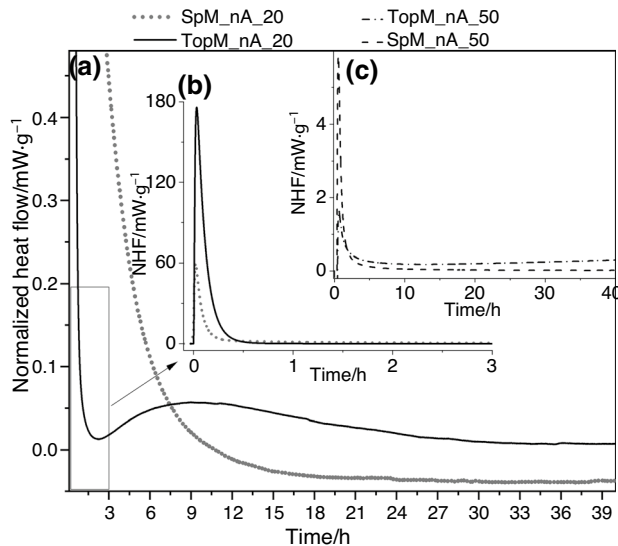


Fig. 4 a–c Heat flow curves (a–c) for no-cement binders hydrated at 20 and 50 °C and w/c = 1.5 normalized to mass of dry powder (in situ mixing procedure)

of the first exothermic peak of the heat evolution curve, generated similar interpretations concerning the higher amount of hydrated products generated in the SpM_nA sample cured at 50 °C.

Thermal analysis of CAC-free and calcium aluminate cement (CAC)-containing hydrating mixtures

Studies were undertaken to characterize the ability of both CAC-free and CAC-containing mixtures to form hydrated counterparts. Since physically bound water was removed from the SpM_nA, TopM_nA, MR66_5M and AR78_5M (Table 1) hydrating mixtures by acetone quenching, which was used to stop hydration at 12 h, 24 h and 72 h, the results of DSC-TG-EGA(MS) thermal analyses directly confirmed the amounts of chemically bound water and the presence of hydration products. Hence, both the decomposition temperature/steps characterized via DSC-TG and the gases evolved from samples in real-time, which were identified via mass spectrometry (MS), were helpful in comparing the ability of CAC-free and CAC-based binders to form hydrated products within the SpM_nA, TopM_nA, MR66_5M and AR78_5M samples. Moreover, MS can be considered a more sensitive tool than DSC in terms of peak detection.

Figure 5a, b shows TG-DSC-EGA(MS) data for acetone-treated CAC-containing mixtures (MR66_5M sample) heated from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹, whereas Fig. 6a, b presents TG-DSC-EGA(MS) data for acetone-treated cement-free binder (SpM_nA sample). The fragments with mass-to-charge ratios (m/z) 18 and 44 likely arose from H₂O and

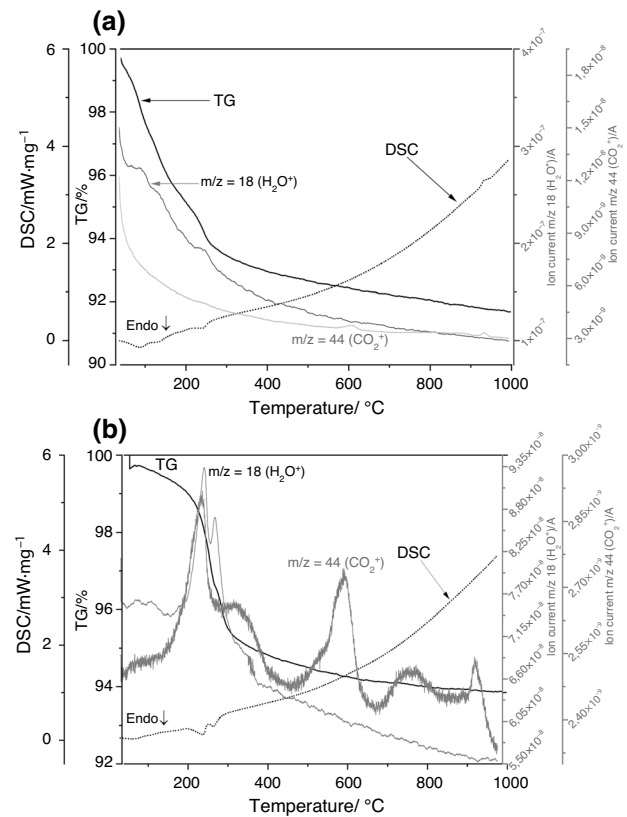


Fig. 5 a, b TG-DSC, fragment m/z = 18 (H₂O⁺) and fragment m/z = 44 (CO₂⁺) in the EGA-MS profiles of the MR66_5M sample at 72 h of curing at 20 °C (a) and 50 °C (b). Measured in air flow at the heating rate 10 °C·min⁻¹

CO₂, respectively. Some very important similarities can be noticed in the results presented i.e., the progress of hydration after 12 h and 72 h for both CAC-containing and cement-free binders mixed with water, which was measured as mass losses in the curves (TG). All reactions were accelerated at temperatures higher than room temperature especially in the cement-free samples. The amount of water chemically bound by the main binder constituents was indicated by the mass-loss behavior revealed by TG at 1000 °C, and the amount was greater for the CAC-based sample hydrated at room temperature than for the cement-free sample hydrated at two temperatures and the cement-containing sample hydrated at 50 °C for 72 h. However, this last point does not apply to the MR66_5M sample hydrated at 20 °C for 72 h, in which the the water-deficient calcium aluminate hydrate C₃AH₆ was identified by XRD.

In detail, the TG curves in Fig. 6a, b and in Fig. 5a, b showed multistage mass losses over a broad temperature range. The overall mass loss corresponded to the loss of water and carbon dioxide, as indicated by mass spectrometric (MS) detection of H₂O (m/z = 18) and CO₂ (m/z = 44). The DSC curves showed that all stages involving decomposition

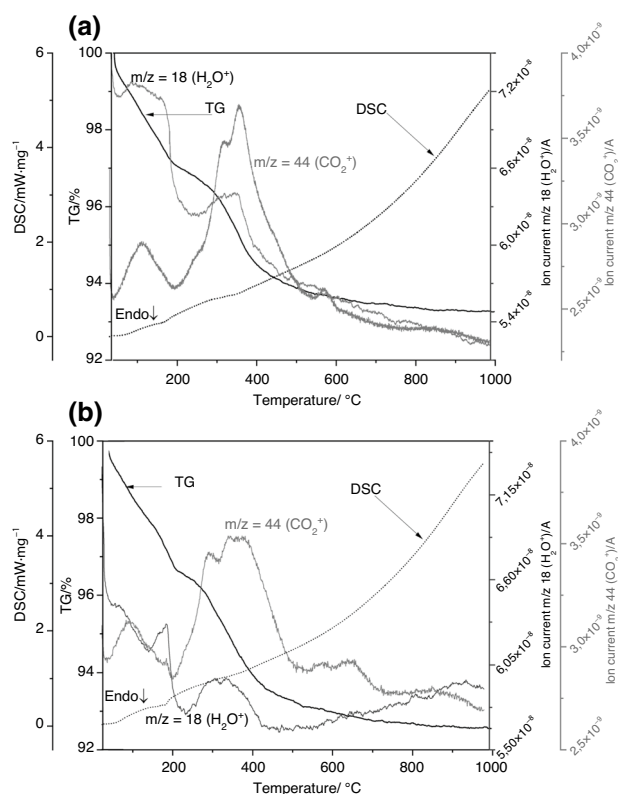


Fig. 6 a, b TG-DSC, fragment $m/z=18$ (H_2O^+) and fragment $m/z=44$ (CO_2^+) in the EGA-MS profiles of the SpM_nA sample at 72 h of curing at 20 °C (a) and 50 °C (b). Measured in air flow at the heating rate 10 °C·min⁻¹

reactions of hydrates and carbonated products were endothermic. Interestingly, EGA- H_2O revealed that during the first period of mass loss within the temperature range 40–250 °C and the second period within the temperature range 250–450 °C, large amounts of water were evolved from the CAC-free samples formed within 72 h of curing. This first step in thermal decomposition corresponded to the removal of physically adsorbed and interlayer water molecules (dehydration, removal of H_2O), whereas the second step corresponded to elimination of OH^- groups. These behaviors are mainly associated with decomposition of hydrotalcite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ [20, 28]. Generally, there were no significant changes in the thermal decomposition behavior of CAC-free samples cured at room temperature and at 50 °C since, there was also no qualitative change observed in the phase composition as a function of the curing temperature (Fig. 1a, b). The nature of the TG curve and the total mass loss for the SpM_nA sample hydrated at 20 °C (6.75%) were comparable with those of the SpM_nA sample (7.45%) hydrated at elevated temperature. The evolved gas analysis (EGA) curves for CO_2 vapor from the CAC-free samples (Fig. 6a, b) also showed peaks due to decarbonation of the hydrotalcite-like phase [20].

Well-defined DSC-TG-EGA(H_2O) curves for the MR66_5M sample cured at 50 °C for 72 h exhibited two consecutive decomposition within the temperature range 25–1000 °C (Fig. 5b). The first stage occurred in the temperature range 25–275 °C and the DSC-EGA(H_2O) peak at ca. 263 °C corresponded to a water mass loss of ca. 3.23% due primarily to decomposition of AH_3 -gel and $\text{Al}(\text{OH})_3$, and residual C_2AH_8 , $\text{C}_3\text{A}\cdot\text{Ca}(\text{OH})_2\cdot 18\text{H}_2\text{O}$ and $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ [30, 31]. The second stage occurred in the temperature range 275–1000 °C with a DSC-EGA(H_2O) peak at ca. 289 °C corresponding to a water mass loss of ca. 4.18% due primarily to decomposition of C_3AH_6 . The total mass loss from this sample at 1000 °C was 6.15%. Completely different thermal decomposition behavior was observed for the CAC-based binder (MR66_5M) cured at room temperature, for which the initially formed unstable hexagonal hydrates CAH_{10} and $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$, and AH_3 -gel dominated [31, 32]. The TG curve showed a mass loss of 5.96% at 250 °C with a broad and diffuse endothermic peaks and EGA- H_2O profiles and a total mass loss of 8.31% at 1000 °C. Here, no sharp temperature peaks for maximum water release were detected compared with the MR66_5M sample hydrated at 50 °C for 72 h. The evolved gas analysis (EGA) curves for CO_2 vapor from the CAC-containing samples (Fig. 5a, b) also showed peaks due to decarbonation of the $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ phase and other residual carbonated hydration products.

Conclusions

The main purpose of this study was to demonstrate an alternative route for elaborating the CAC-free hydraulic binder systems designed for monolithic refractories, e.g., castables. The fundamental research presented in this paper was focused on comparing CAC-containing and CAC-free hydraulic binders in terms of hydrated matrix formation within refractory castables designed for the fast drying procedure. Hence, two types of cement-free binary mixtures (dead-burned MgO mixed with nanopowder Al_2O_3 , fused MgO mixed with nanopowder Al_2O_3) and CAC-containing binders (Mg-rich spinel and CAC mixed with micropowder Al_2O_3 ; Al-rich spinel, CAC and dead-burned MgO mixed with micropowder Al_2O_3) were designed, prepared, and analyzed to determine the mechanism and capacity for formation hydrated mixtures. According to the obtained results, the following conclusions can be drawn:

1. Hydration of binary mixtures composed of MgO and Al_2O_3 led to $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ synthesis, while hydration in the presence of CAC did not lead to hydrotalcite formation.

2. Since the peak at $2\theta = 37.966^\circ$ associated with $\text{Mg}(\text{OH})_2$ was not observed in either CAC-free sample, $\text{Mg}(\text{OH})_2$ was probably formed and rapidly was consumed for $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ synthesis.
3. XRD and FTIR data for CAC-containing samples revealed that the sample containing MgO introduced with preformed spinel MR66 was characterized by higher reactivity than the sample that contained free MgO; this reflected the greater amount of hydrated products in the former. Additionally, an elevated temperature accelerated hydration of the CAC.
4. The findings obtained for the CAC-based binder showed that elevated temperature induced alterations in the calorimetric curve that were similar with those observed for the $\text{MgO}-\text{Al}_2\text{O}_3$ -type cement-free sample. The induction period was shortened, and only one exothermic peak was detected.
5. The remarkable feature is that the two exothermic peaks for CAC-based mixtures prepared at 20°C were integrated into one exothermic peak, which was attributed to the heat release from CAC-based binder prepared at 50°C . Then, the intensity of peak decreased and the outline of hydration vs. time, which was defined as the derivative curve, approached zero, indicating that hydration was diffusion controlled. This suggests that the hydration kinetics of the CAC-based mixture were similar to those of the CAC-free binder at elevated temperatures.

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Publikacja 10.3



Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures

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ABSTRACT

The mechanical properties of *in-situ* spinel (MgAl_2O_4)-forming alumina-based castables under intermediate temperatures are of critical importance before the refractory lining system reaches normal operating conditions. The objective of this study is to elucidate the role of the hydrotalcite formed within a fine-grained castables matrix, in which no strength loss of the MgO-bonded alumina-based castables without silica fume was observed. Numerous fundamental studies were conducted to examine the factors influencing hydrotalcite formation within the blended pastes composed of MgO and Al_2O_3 nanopowders; dead burned or fused magnesia and Al_2O_3 nanopowder; dead burned magnesia and water-dispersed sol of fumed alumina by using: XRD and DSC-TG-EGA (MS). The XRD, FTIR and ²⁷Al MAS NMR analysis of the hydrotalcite calcination products revealed that the spinel begins to form at temperatures as low as 700 °C. Finally, the physical properties, phase composition and microstructure of the refractory castables bonded with the hydrotalcite decomposition-routed nanostructured spinel were evaluated.

1. Introduction

Castable refractory materials are a type of unshaped monolithic refractory material composed of refractory grain, matrix components, bonding agents, admixtures, and water. As is well known, the type of binder and its properties have a significant influence on the workability, green mechanical strength, and both mechanical and thermomechanical properties of refractories. The use of ultrafine- SiO_2 and MgO particles ultrafine- Al_2O_3 and MgO particles, and superfine colloidal materials such as silica or alumina has expanded the horizons for refractory technologists [1]. High-alumina cement is a frequently used binder for refractory castables. Calcium oxide affects the hot properties of castables by forming CaO phases with low-melting points [1,2]. Additionally, calcium oxide can react with matrix components such as SiO_2 , Al_2O_3 , and MgO to form low-melting phases, such as gehlenite, anorthite, and monticellite, respectively, each of which has a melting point of: 1593 °C, 1553 °C and 1485 °C [3]. This results in a loss of refractoriness under load, thermal shock resistance, refractoriness and hot modulus of rupture [4,5]. Additionally, the mechanical strength of calcium alumina cement bonded castables degrades between 300 and 900 °C. This is due

to the dehydration process, which results in the destruction of the cement's hydrate network [6,7]. Correspondingly, the dehydration of $\text{CaAl}_2\text{O}_4 \cdot 10 \text{H}_2\text{O}$, $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8 \text{H}_2\text{O}$, $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6 \text{H}_2\text{O}$, and gibbsite has been reported at temperature of 120 °C, 170–195 °C, 240–370 °C, and 210–300 °C, respectively [8]. As some authors [9–13] have suggested, the decomposition of these hydration products may result in a reduction in the mechanical properties of CAC-bonded castables. Nonetheless, at temperatures between 700 °C and 900 °C, the decomposition reaction does not result in a significant decrease in the mechanical strength of these castables [6,7]. According to Zhang et al. [6] this can be attributed to the significant morphological difference between $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6 \text{H}_2\text{O}$ and gibbsite, as well as, their decomposition products.

Increasing the properties of the refractory castables in many cases is frequently associated with lowering the cement content. Low cement castables (LCC) and cement-free/ no-cement-content (NCC) containing *in situ* or pre-formed spinel (MgAl_2O_4) have developed rapidly in recent years and are now widely used for steel ladles. Due to the lower water content required for hydraulic bonding in comparison to conventional castables and the effective dewatering of castables, both physically absorbed and chemically bonded water is removed, thereby improving

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the mechanical, physical, and high-temperature properties of both NCC and LCC castables [2]. Additionally, it has been confirmed that in-situ spinel forming castables exhibit superior slag resistance to pre-formed spinel containing castables due to the finer and more evenly distributed spinel grains derived from the reaction between MgO and Al₂O₃ during sintering [2]. The most frequently used method for obtaining MgAl₂O₄ spinel is through ceramic-powder processing, specifically through the solid-state reaction of Al₂O₃ and MgO at 1600 °C [14]. Formation of spinel occurs by opposite directed diffusion of the magnesium (Mg²⁺) and aluminium (Al³⁺) ions through the rigid oxygen lattice of MgAl₂O₄ [15]. According to various sources of literature, the process of in-situ spinel formation results in a volume increase between 5 % and 7 %, which can result in an increase in the apparent porosity, as well as induce the formation of several microcracks in the microstructure [15]. Additionally, reaction sintering has several disadvantages including a limited degree of chemical homogeneity, a high-temperature reaction, and lack of sintering ability [15]. As a result, several novel methods for powder preparation have been developed in recent years, including spray-pyrolysis, freeze-drying, sol–gel, and pyrolysis of complex compounds [16–21]. These methods enable the production of powders with higher homogeneity, resulting in an increase in reactivity and sintering ability at low temperatures [14]. Unconventional methods for obtaining MgAl₂O₄ spinel, such as precipitation, aerosol method, and classical or modified sol–gel method by combining gelation and coprecipitation processes, also exist [22]. However, in the refractory industry, the cost and versatility of the chosen synthesis method are critical.

One of the possible methods of obtaining MgAl₂O₄ is through the synthesis of Mg–Al hydrotalcite. We have previously demonstrated [23] that the hydration of binary mixtures containing nanometric MgO and Al₂O₃ powders is a facile and effective approach for obtaining high purity Mg–Al hydrotalcite. Additionally, the use of hydrotalcite enables the low-temperature synthesis of spinel phase at temperatures as low as 600–700 °C. This indicates that the combination of powder hydration and calcination at 700 °C may be an interesting spinel synthesis route in the refractory industry. Thus, the purpose of the current study is to elucidate the role of hydrotalcite [Mg₆Al₂(OH)₁₆•4H₂O] formed within a fine-grained castable matrix, in which no strength loss of the MgO-bonded alumina-based castable in the absence of silica fume was demonstrated.

2. Experimental procedure

2.1. Samples preparation and characterisation techniques

2.1.1. Synthesis via natural curing and calcination of Mg–Al hydrotalcite

The Mg–Al hydrotalcite-like phase was formed by the hydration of three different types of magnesium oxides: the reactive MgO nanopowder (particle size <50 nm, Acros, 99.8 wt. % MgO), fused MgO (Denmag, 98 wt. % MgO), and dead-burned MgO (RHI Magnesita, 98 wt. % MgO), with Al₂O₃ nano-powder (Aldrich, 99.8 wt. % Al₂O₃) or Al₂O₃ sol (Evonik Aerodisp W 450 ZX). Correspondingly, four mixtures were designed. These include nanopowder MgO combined with nanopowder Al₂O₃, dead-burned MgO combined with nanopowder Al₂O₃, dead-burned-MgO combined with sol Al₂O₃, and fused-MgO mixed with nanopowder Al₂O₃. Dry powder mixtures were weighted with an Al₂O₃:MgO molar ratio of 1:1. Each dry powder mixture was homogenised for 30 min before being combined with water. The amount of water used resulted in the formation of pastes wherein no sedimentation was observed. Table 1 lists the nomenclature and other pertinent information concerning the binary mixtures that were analysed. Samples in the form of pastes were sealed in polyethylene bags and cured in a laboratory climatic chamber at a relative humidity of 95 % and a temperature of 50 °C. Following a period of 12 h, 24 h, 3 days, and 7 days of hydration, samples containing dead-burned or fused MgO were ground in acetone (Chempur, 96 % solution) at room temperature to stop the hydration and remove free water from the blended pastes. XRD analysis

Table 1

Nomenclature and details of binary mixtures.

Composition of binary mixtures	nanopowder MgO + nanopowder Al ₂ O ₃	dead-burned-MgO + nanopowder Al ₂ O ₃	fused-MgO + nano powder Al ₂ O ₃	dead-burned MgO + sol Al ₂ O ₃
w/s	3	1.5	1.5	1.5
Designation of mixtures	MA_0 (reference sample)	d-MA	f-MA	d-MAs
Curing time	110 days	12 h, 24 h, 3 days, 7 days		

was used to confirm the presence of Mg–Al hydrotalcite the in obtained samples. Additionally, after a 110-day curing period, reference sample (MA_0) was ground in acetone. A previous study [23] described the hydration mechanism and confirmed that after 98 days of hydration, a fully reacted blended paste consisting primarily of Mg–Al hydrotalcite with trace amounts of Mg(OH)₂ was obtained. As a result, the MA_0 sample was defined as the reference sample after 110 days of hydration. Thermal analysis techniques such as simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC), and evolved gas analysis-mass spectrometry (EGA-MS) were used to determine the thermal stability of the hydrotalcite structural groups. Following that, the sample containing the reference synthetic hydrotalcite was heated to 250, 340, 390, 425, 600, 700, 800, 900, and 1000 °C and maintained at the selected temperature for 2 h. Subsequently, XRD, FTIR, and ²⁷Al MAS NMR measurements were used to characterise the calcination products.

2.1.2. Alumina magnesia refractory castables sample preparation and gradual firing process

Vibratable no-cement castables were designed using the Dinger and Funk particle packing model ($q = 0.26$). The starting materials used in the experiment clude 80.6 wt. % of tabular alumina (grain size: 0–6 mm, Almatiss) as inert grains and 19.4 wt. % of matrix components. The castables matrix comprised 7 wt. % of dead-burned magnesia, reactive alumina (CTC 40, Almatiss) and some amount of Al₂O₃ sol. The binder components were magnesium oxide and alumina oxide in form of both powder and sol. Table 2 contains the general information about the selected raw materials. In the laboratory-scale mixer, the mixtures were dry-mixed for 5 min and then wet-mixed for 5 additional minutes. Subsequently, vibration was used to cast the mixed castables into 40 mm × 40 mm × 160 mm moulds. The castable samples were then de-moulded and cured for 5 days at 50 °C, 70 °C and 90 °C in a laboratory climatic chamber with a relative humidity of 95 %. The curing process was gradual. After 24 h of drying at 110 °C, the samples were partially fired for 2 h at temperatures ranging from 250 °C to 1200 °C.

After drying and firing at the following temperatures 250 °C, 340 °C, 390 °C, 425 °C, 500 °C, 600 °C, 700 °C 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C the sonic velocity along the longest direction of each specimen was measured. A section of the dried sample was cut to place in resin and cross-polish. After each firing temperature the cross-polish section was examined using a scanning electron microscope. Additionally, to obtain refractory castables matrix samples, portion of the sample was crushed and then inert corundum grains were separated from matrix components following heating at each temperature. The samples

Table 2

Typical chemical compositions of raw materials [24,25].

Chemical composition [wt. %]	Tabular alumina	Reactive alumina	Magnesium oxide
Al ₂ O ₃	99.50	99.80	0.30
SiO ₂	0.09	0.03	0.34
MgO	–	0.04	97.95
CaO	–	0.02	0.91
others	0.41	0.11	0.50

obtained in this manner were characterised by using XRD, FTIR and DSC-TG-MS (EGA) techniques. Further mechanical tests were conducted on samples fired at 425, 700, 900, and 1200 °C, based on the results of on the sonic velocity test. Additionally, the modulus of rupture (MOR) and cold crushing strength (CCS) of the castables after firing at the specified temperatures were determined at room temperature.

2.2. Detailed description of characterisation techniques

Three different types of samples were analysed in this work. The first type of sample consisted of blended pastes created by combining dry powders and water. These samples may provide an indirect indication of the matrix of refractory castables, from the time the substrates are mixed to the end of the curing process. Calcination of reference sample allowed for the generation of second type of sample. Additionally, the calcination of samples aided in the understanding of the reactions that occur within the matrix of refractory castables during the firing process. The third type of sample was castables matrix that had been separated from inert grains following each stage of the precast beam firing process. Table 3 lists the nomenclature of the samples used in this study.

The reference sample and the castables matrix were analysed by employing simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) in synthetic air (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ using a Simultaneous Thermo Analyzer (STA) [TG-DSC, NETZSCH STA 449 F5 Jupiter] coupled to a mass spectrometer 403 D Aeolos. An empty α -Al₂O₃ crucible was used as the reference substance. For the assessments, 10 mg of dried sample was heated from 20 to 1000 °C in corundum crucible.

The phase composition of the blended and dehydrated pastes, as well as the matrix of castables, was determined using an X'Pert ProP-Analytical X-ray diffractometer with Cu K α radiation ($\lambda = 1.54060$ nm), with 0.02 ° per step and 3 s time per step (2 θ : 5°–90 °). For data analysis, the phases were identified using HighScore Plus software (Panalytical) used in conjunction with the ICDD-supported PDF-2 database and the JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997). The crystallite size was determined using the Scherrer equation at full width and half maximum (FWHM) [26]:

$$D_{XRD} = \frac{K \cdot \lambda}{\cos(\theta) \cdot FWHM} \quad (1)$$

where D_{XRD} is the crystallite size (nm), K is a numerical factor referred as the crystallite-shape factor (0.90), λ is the wavelength of the radiation used (0.1540598 nm) and θ is the Bragg diffraction angle.

The FTIR spectra of reference hydrotalcite before and after calcination, as well as castables matrix after each firing stage, were recorded in the range of 4000–400 cm⁻¹ using the KBr pellets technique on a BRUKER (Vertex 70) Fourier Transform Infrared Spectrometer.

The ²⁷Al MAS NMR spectra of reference hydrotalcite sample before (MA_0) and after (MA_250, MA_340, MA_390, MA_425, MA_500,

MA_600, MA_700, MA_800, MA_900, MA_1000) calcination process were acquired using Bruker AV III 400WB (9.4 T) spectrometer, (BRUKER BioSpin, Rheinstetten, Germany).

The Vikasonic was used to determine the sonic velocity along the longest direction of each test specimen. Additionally, Young's modulus was calculated according to Panakkal and Ghosh [27,28] using the following equation:

$$E = \frac{V_i^2 \cdot \rho \cdot (1 + \mu) \cdot (1 - 2\mu)}{(1 - \mu)} \quad (2)$$

where: V_i - sonic velocity after testing [$\text{km} \cdot \text{s}^{-1}$], μ -dynamic Poisson's ratio and ρ - apparent density of specimen after testing. For refractory castables μ is about 0.16.

The bending strength of refractory castables was determined by a 3-point bending test using a specimen measuring 40 × 40 × 160 mm, with a span dimension of 100 mm, and a test speed of 50 N/s. To determine the cold crushing strength, half of each sample after the 3-point bending test, was placed in the compression testing equipment. The loading speed was 2.4 kN/s.

Bulk density and apparent porosity tests of refractory castables samples were done by standard methods, based on the Archimedes' principle, according to the PN-EN 993-1:2019-01 standard.

A scanning electron microscope (SEM, FEI Nova Nano SEM 200) was used to investigate the microstructure evolution of castables. Electron-probe microanalysis with an energy-dispersive X-ray spectrometer (EDAX, Sapphire Si(Li) EDS detector) was used to determine the chemical compositions of the samples. After drying at 110 °C, a representative sample of castables was ground and using a pressing force of 40 [N], a rotational speed of 300 RPM, and a continuous water wetting of the diamond surface disc. After polishing, the specimen was placed in an ultrasonic cleaner with isopropyl alcohol in a baker for approximately an hour. After microscopic examination, the sample was fired at the next selected temperature (250, 340, 390, 425, 500–1200 °C), gently polished and subjected to the SEM-EDS examination once more.

3. Results and discussion

3.1. Effect of the raw material type and the curing time on the synthesis of Mg-Al hydrotalcite within the mixtures of the powders of MgO and Al₂O₃ and water

The X-ray diffraction method was applied to analyse the degree of conversion of the substrates into Mg-Al hydrotalcite. The time interval between the appearance of Mg-Al hydrotalcite in the sample and the intensity of the characteristic diffraction peak (determined by the XRD patterns of stoichiometric hydrotalcite Mg₆Al₂CO₃(OH)₁₆•4H₂O, JCPDS Card No. 00-014-0191, 2 θ = 11.489 °) were used to determine the reaction rate and degree of MgO conversion, respectively. Additionally, the hydration kinetics analysis enabled the determination of the feasibility of using the selected raw materials in the refractory industry as Mg-Al layered double hydroxide-like phases. The XRD patterns of the binary mixtures d-MA, f-MA, and d-MAs after the selected hydration times (12 h, 24 h, 3 days, and 7 days) are shown in Fig. 1. In addition to the reference sample following 110 days of hydration. After 7 days of hydration, each sample contained MgO, Mg-Al hydrotalcite, γ -Al₂O₃ and θ -Al₂O₃. Both γ -Al₂O₃ and θ -Al₂O₃ were detected using peaks at 66.940 ° (JCPDS Card No. 96-101-0462) and 36.596 ° (JCPDS Card No. 96-120-0006), respectively. Due to the persistence of the peak at 2 θ = 42.888 ° (ICDD Card No. 01-087-0651) associated with MgO after 7 days of curing, fully reacted samples were not obtained. By comparing the obtained results to those obtained from the reference sample it can be seen, that the hydration of d-MA and f-MA samples results in the formation of trace amounts of hydrotalcite after 12 h whereas the presence of Mg-Al hydrotalcite was confirmed after 3 days in the d-MAs sample. This indicates that the hydration of a mixture composed of fused or dead-

Table 3
Summary of designation of samples.

Type of sample	Binary mixtures composed of dead-burned or fused MgO with Al ₂ O ₃ in the form of sol or powder	Nano-powder MgO + nanopowder Al ₂ O ₃ as reference sample	Reference sample after calcination process	Castables matrix separated from inert grains after firing process
Designation of sample	d-MA		MA_Calcination	C_Firing
	f-MA	MA_0	temperature	temperature
Example	d-MAs		MA_250	C_250

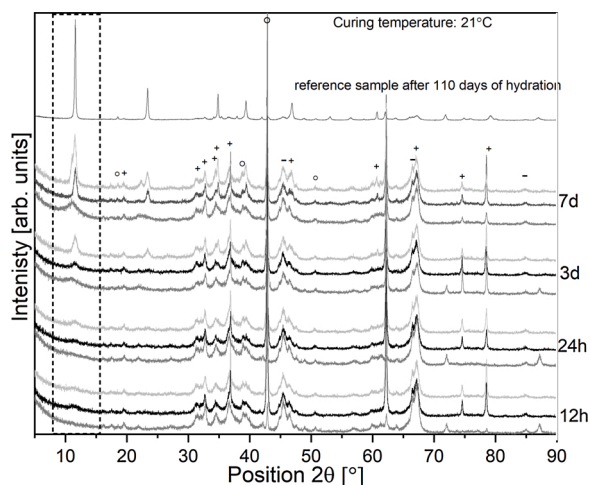


Fig. 1. Overview of the low-temperature XRD patterns of samples: d-MA (light grey curve), f-MA (black curve) and d-MAs (grey curve) after the selected (12 h, 24 h, 3 days and 7 days) hydration time and MA₀ sample. Degree sign: MgO (ICDD Card No. 01-087-0651), plus sign: θ -Al₂O₃ (JCPDS Card No. 96-120-0006), minus sign: γ -Al₂O₃ (JCPDS Card No. 96-101-0462).

burned magnesia and nano-metric aluminium oxide powder is a viable method for obtaining Mg-Al hydrotalcite. Additionally, when alumina is used in the form of a sol the reaction rate is reduced probably due to the presence of stabilisers in the sol. Moreover, it is clearly observed that, after 7 days of hydration, the intensity of the characteristic peak belonging to hydrotalcite is greater in the d-MA sample than in the f-MA or d-MAs samples. This demonstrates a higher concentration of Mg-Al hydrotalcite in the d-MA sample, as well as a higher degree of substrate conversion. Additionally, the main diffraction peak associated with $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ (JCPDS Card No. 00-014-0191, $2\theta = 11.489^\circ$) shifts towards a higher $2\theta =$ value (11.5242° and 11.5161°) for d-MA and f-MA samples, respectively, while simultaneously shifting towards a lower $2\theta =$ value (11.3162°) for d-MAs. This could indicate that the hydrotalcite synthesised in the examined samples had different stoichiometry. According to the obtained results, using the aforementioned raw materials as components of the castable matrix and curing at a temperature of 21°C for at least 12 h should most likely result in the formation of Mg-Al layered double hydroxide-like phases as the precursors for low-temperature synthesis of magnesium alumina spinel in the refractory castables at intermediate temperatures.

3.2. Fundamental research on evaluation of the low-temperature Mg-Al spinel formation via decomposition of hydrotalcite

Thermal analysis was performed on a reference sample composed primarily of Mg-Al hydrotalcite. Thermal analysis of the MA₀ sample enabled the thermal stability of hydroxyl groups and thus the calcination temperatures to be determined. The results of the DSC-TG-EGA analysis are presented in Fig. 2, and these characterise the thermal stability of the MA₀ blended paste after 110 days of curing. The total weight loss of the sample was 27.97 % during heating in the temperature range of 20 – 1000°C . The MA₀ sample was prepared from a binary mixture with a $\text{MgO}:\text{Al}_2\text{O}_3$ molar ratio of 1:1. The suggested molar ratio for the precipitated hydrotalcite sample ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) is approximately 3, whereas the starting Mg/Al molar ratio was 0.5 due to the sample preparation. The theoretical weight loss is approximately 45 % for a Mg-Al hydrotalcite sample with $\text{Mg}/\text{Al} = 3$ [29]. When the total and theoretical weight loss of the sample are compared, it is possible to infer the presence of other phases such as unreacted Al₂O₃. The mass loss is a result of hydrotalcite's dehydration, dihydroxylation, and decarbonisation processes. According to the obtained results and corresponding literature sources [30], it can be noticed that the removal of

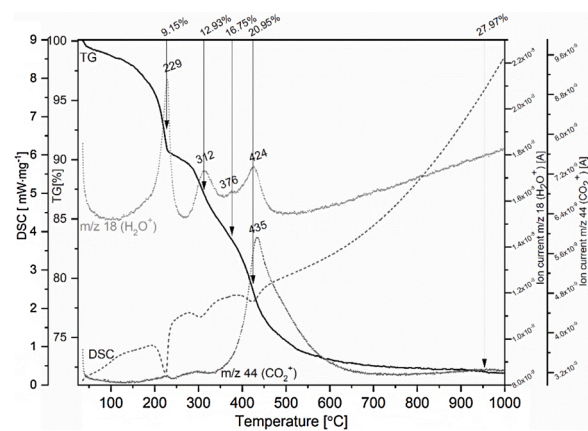


Fig. 2. TG–DSC profiles and gas evolution curves for representative mass spectroscopic ion fragments of CO_2^+ ($m/z = 44$) and H_2O^+ ($m/z = 18$) vapours during the thermal decomposition of the synthetic hydrotalcite.

interlayer water and the dehydroxylation of $\text{Mg}_3\text{-OH}$ hydrotalcite layers occur at 229°C at 312°C , respectively. Additionally, the weight loss at 376°C and 424°C may be assigned to dehydroxylation of residual magnesium hydroxide and dehydroxylation of the $\text{Mg}_2\text{Al-OH}$ hydrotalcite layers, respectively. The MS profile of CO_2 ($m/z = 44$) release indicates that the decarbonisation process occurs currently with dehydroxylation in the hydrotalcite structure and occurs at approximately 435°C . Following calcination temperatures of 250, 340, 390, 425, 500, 600, 700, 800, 900 and 1000°C were determined in the terms of further heat treatment of alumina- magnesia castables based on thermal analysis.

Thermal analysis of the MA₀ sample enables the calcination temperatures to be determined. The calcination products were analysed using XRD and FTIR to determine the progress of the low-temperature MgAl_2O_4 synthesis. Fig. 3a–e presents the low-temperature XRD patterns of the reference sample before and after calcination at the appropriate temperatures. The XRD analysis revealed that the major phase in the reference sample hydrated for 110 days was crystalline Mg-Al hydrotalcite. When the sample is heat-treated at 250°C the characteristic peak belonging to the Mg-Al hydrotalcite ($2\theta = 11.71^\circ$, JCPDS Card No. 00-014-0191) shifts to a higher 2θ value. Additionally, a significant broadening of this peak can be observed, in addition to the presence of amorphous hydrotalcite calcination products. This shift in the diffraction peak indicates structural changes as a result of interlayer water elimination [31]. At intermediate temperatures (340 , 390 , and 425°C), the calcination products exhibit a low degree of crystallinity. Due to the presence of amorphous calcination products, it was not possible to accurately identify all phases in the sample. As shown in Fig. 3c–d, the predominant phases in sample MA calcined at temperatures of 340 , 390 , 425 , 500 , and 600°C , are transition alumina type structures, $\text{Mg}(\text{Al})\text{O}$ mixed oxides or spinel nuclei; this was also confirmed in other studies [32–34]. Additionally, at the temperatures of 340 , 390 , and 425°C , there were no hydrotalcite-related diffraction peaks and no significant outline XRD changes were observed. The absence of diffraction peaks associated with the presence of Mg-Al hydrotalcite indicated that the layer structure had been completely destroyed during the dihydroxylation and decarbonisation processes of the brucite-like layers [29].

A trace amount of magnesium hydroxide (ICDD Card No. 01-083-0114) were detected only in the MA₂₅₀ sample, whereas the magnesium oxide peak (characteristic diffraction peak $2\theta = 42.94^\circ$, ICDD Card No 00-045-0946) does not appear until after calcination at 500°C . This indicates that the magnesium oxide was amorphous between 250°C and 500°C , or that the amount of MgO was less than the XRD detection threshold. At 600°C , a magnesium aluminate spinel peak (characteristic diffraction line $2\theta = 36.91^\circ$, JCPDS Card No. 96-900-3481) also appears. The average crystallite size was calculated using Scherrer's Eq. (1)

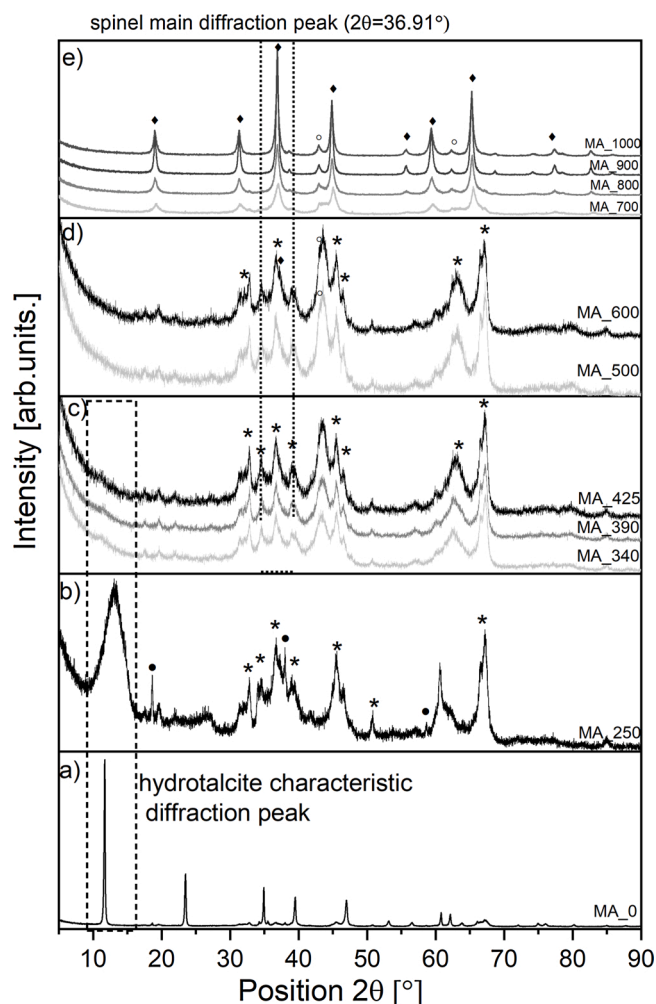


Fig. 3. Low-temperature XRD patterns of the MA sample before (a) and after calcination in the temperature range 250–1000 °C (a–e). Diamond: MgAl_2O_4 (JCPDS Card No. 96-900-3481), filled black circle: $\text{Mg}(\text{OH})_2$ (ICDD Card No. 01-083-0114), degree sign MgO (ICDD Card No. 00-045-0946), asterisk: transition alumina-type structures, $\text{Mg}(\text{Al})\text{O}$ mixed oxides or spinel nuclei.

and results of the spinel phase formed in samples calcined at temperatures ranging from 700 to 1000 °C are shown in Table 4. The half-width at half maximum of spinel's characteristic peaks decreases as the calcination temperature increases. This is due to an increase in the crystallinity or particle size of magnesium–alumina spinel, or a combination of the two. The increase in the intensity of the XRD diffraction line further indicates an increase in the spinel phase content of the sample as the firing temperature is increased.

Infrared spectroscopy is a method of research that complements X-ray diffraction. FTIR enables the investigation of functional group changes and tracking of CO_3^{2-} ions incorporated into the hydrotalcite structure. The FTIR spectrum of the reference sample is shown in Fig. 4

Table 4

XRD data and structural parameters of spinel formed in reference sample as a result of calcination process.

Sample	MA_700	MA_800	MA_900	MA_1000
FWHM [°]	1.0209	0.7353	0.5599	0.4261
2θ [°]	36.9723	36.8983	36.8768	36.8963
Crystallite size in the direction [nm]	8.2	11.4	15.0	19.7

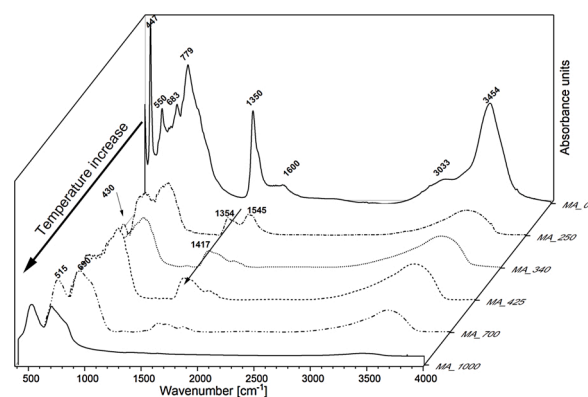


Fig. 4. FTIR spectra of the Mg-Al layered double hydroxide before and after calcination in the temperature range 250–1000 °C.

before and after calcination at the appropriate temperatures. The FTIR method confirmed previous XRD results by observing the progress of dehydration, decarbonisation and spinel formation in the MA_0 sample. The FTIR spectrum of the MA_0 sample reveals characteristic bands for Mg-Al hydrotalcite which contains CO_3^{2-} as the compensation ions. Additionally, the incorporation of interlayer ions is observed as a band at approximately 1350 cm^{-1} which corresponds to the antisymmetric stretching vibration (ν_3) [35]. Additionally, bands at 683 and 779 cm^{-1} are associated with ν_4 antisymmetric deformation mode and ν_2 strong out-of-plane symmetric deformation mode of hydrotalcite CO_3^{2-} ions, respectively [36]. Moreover, the first two bands (447 and 550 cm^{-1}) correspond to $\text{MO}-\text{H}$ bending vibrations and $\text{MO}-$ stretching in the octahedral host layers (where $\text{M} = \text{Mg}$ and Al). According to current knowledge hydrotalcite has a broad band in the range of approximately 3200–3700 cm^{-1} that consists of the following bands: H-bonded modes: 3069 cm^{-1} , $\text{CO}_3^{2-}-\text{H}_2\text{O}$ bridging mode: 3252 cm^{-1} , stretching vibrations of hydroxyl $-\text{OH}$ groups: 3454 cm^{-1} ($\text{OH}-\text{Mg}_2\text{Al}$) and 3575 cm^{-1} ($\text{OH}-\text{Mg}_3$). Additionally, at approximately 1600 cm^{-1} , a low band in the intermediate frequency region was observed, which is associated with the bending mode of interlayer water [35].

Calcination at 250 °C results in the separation of the carbonates' ν_3 band into two bands at 1354 cm^{-1} and 1554 cm^{-1} [29,37]. According to literature sources [38,39] this split occurs as a result of the carbonate rearrangement in the interlamellar space due to the interlamellar water release. At temperature below 250 °C, the carbonate groups are symmetrically coordinated to interlayer water. During interlamellar water release, the carbonate groups may coordinate with hydroxyl groups in the octahedral brucite-like layers. This results in the formation of new mono- or bidentate coordinations in the interlayer space between carbonates and structural hydroxyl groups [39]. According to Hibino et al. [37], these two split bands are in good agreement with those observed for bridged bidentate CO_3 complexes. This suggests that the carbonate exists as bridged bidentate ligands at temperatures of ~250 °C when interlayer water is lost. Simultaneously, the water-carbonate bridging mode (at about 3252 cm^{-1}) vanished, as did the water molecules' bending vibration ($\text{dOH}-$) [40,41]. Owing to the absence of both bands at 1600 cm^{-1} and 3252 cm^{-1} , the spectra indicate that interlayer water is completely removed at 250 °C. Additionally, MA_250 sample's FTIR spectrum contains a broad band at 430 cm^{-1} , which is probably associated with the vibrations of the oxides (MgO , Al_2O_3) [29].

At temperatures greater than 250 °C (i.e. 340–600 °C), FTIR spectra significantly differ from those obtained previously. These spectra are characterised by a broad band at 1417 cm^{-1} , which correspond to $\text{O}-\text{CO}-$ vibrations for non-interlayer carbonate, adsorbed on the surface of the calcination products [29,37]. As shown in Fig. 4, the spectra of the sample calcined at temperatures greater than 700 °C exhibit two distinct spinel bands at approximately 513 and 694 cm^{-1} [42]. This

demonstrates that spinel can be synthesised at low temperatures when hydrotalcite is used as a precursor.

Fig. 5 shows the ^{27}Al MAS NMR spectra of the sample before and after calcination at temperatures ranging from 250 to 1000 °C. The result of the ^{27}Al MAS NMR analysis result for the sample prior to calcination is a combination of resonance peaks derived from Mg-Al hydrotalcite and small amount of alumina oxide, whereas in samples after calcination at temperatures above 600 °C, Mg-Al spinel phase resonance peaks can also be found. As a result, precise the exact interpretation of results is extremely difficult.

The room temperature ^{27}Al MAS NMR spectrum of the uncalcined (MA_0) sample exhibits a prominent narrow resonance peak at a chemical shift, δ , of ~ 2 , corresponding to $\text{Al}(\text{OH})_6$ octahedral coordination. According to literature sources [43,44], when a sample is calcined at 250 °C, during interlamellar water release, Al^{3+} ions migrate from octahedral to tetrahedral coordination [45]. This is indicated by the appearance of an Al peak at approximately δ ca value of 40–80 ppm [46–48]. The ^{27}Al MAS NMR spectrum of the MA_250 sample reveals the presence of four-coordinate Al (peak at approximately δ ca. 57 ppm) and a much larger six-coordinate Al peak. Additionally, the ^{27}Al MAS NMR spectroscopy demonstrates that as hydroxyl groups are removed, tetrahedral resonance at 57 ppm continues to grow at the temperature range of 340 °C–390 °C. Calcination between 425 and 500 °C initially increases the intensity of both resonance peaks. However, upon further heating up to 800 °C a decrease in the intensity of aforementioned resonance peaks is observed. Additionally, calcination at temperatures of 900 °C and 1000 °C significantly increases the intensity of both resonance peaks, which is associated with an increase in intensified spinel synthesis.

Based on the XRD measurements, it is difficult to clearly identify the calcination products, when the calcination temperature reaches ~ 340 °C. The changes in the outline ^{27}Al MAS NMR spectra of samples calcined at 340–1000 °C are due to three overlapping processes. These include, the conversion of possible transition alumina polymorphs or transition alumina type-structures to the most stable $\alpha\text{-Al}_2\text{O}_3$, the migration of Al^{3+} ions in solid solution [unstable MgO-like phase or periclase $\text{Mg}(\text{Al})\text{O}$] from periclase structure and the primary and secondary spinel formation as a result of reactive sintering of MgO- Al_2O_3 mixed oxides (hydrotalcite calcination products).

3.3. SEM investigation of microstructural changes of MgO-fume bonded corundum castables versus temperature

SEM-EDS analysis was used to examine the microstructure evolution of no-cement corundum-spinel refractory castables during heat treatment at temperatures ranging from from 250 to 1200 °C. Figs. 6a–d, 7 a–c and 8 illustrate the microstructure, chemical composition analysis

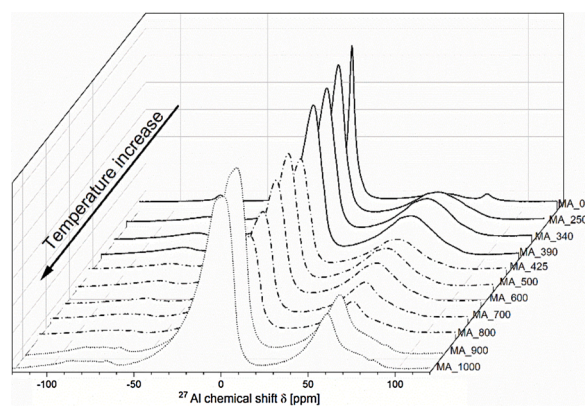


Fig. 5. The room-temperature ^{27}Al MAS-NMR spectra of the Mg-Al- CO_3 hydrotalcite-like phase formed in the reference MA sample and calcined in the temperature range 250–1000 °C.

in the microareas, and EDS line scan obtained by the SEM-EDS measurements of MgO-fume bonded corundum castables after heat treatment at various temperatures. Fig. 6a–e show the typical distribution of coarse tabular alumina grains imbibed in a fine-grained magnesia-alumina matrix. It is worth noting that the obtained castables have a significantly denser microstructure than conventional castables. This is almost certainly due to the presence of nanoparticles introduced previously via water-dispersed sol of the fumed alumina. For example, numerous authors [49] have confirmed that adding silica sol densifies the microstructure and accelerates the sintering process, allowing for the formation of mullite at lower temperatures. The obtained results, therefore, indicate that the application of nanoparticles from sol can similarly result in microstructure compacting at lower temperatures and intensifying the sintering process.

As illustrated in Fig. 7a–c, the majority of the microstructural changes observed in MgO-fume bonded corundum castables were associated with a fine-grained castables matrix. As previously stated and discussed in the 3.2 section, fine powders of MgO and Al_2O_3 in the presence of water were easily converted to magnesium hydroxide, aluminium hydroxide and Mg-Al-hydrotalcite in the presence of water, as confirmed by the XRD and FTIR measurements presented in the following section. Thus, the castables made from a blend of coarse, medium and fine grains exhibit excellent gains in green mechanical strength following demoulding. It can be assumed that crystalline Mg-Al-hydrotalcite formed in-situ in the MgO-fume containing corundum castables modifies and reinforces the nanostructure of the MgO- Al_2O_3 - H_2O matrix. As previously stated in the results section, Mg-Al-hydrotalcite thermally decomposes upon heating into several intermediate products, and then transforms into single-phase spinel and alumina via reactive sintering. This very brief summary of the structural of changes that occur in the Mg-Al-hydrotalcite-containing castables matrix during heat treatment at temperatures ranging from 25 to 1200 °C leads to the conclusion that the structural changes associated with these processes must have to find a corresponding consequence in the evolution of the microstructure. This, on the basis of evolution, clear evidence can be found based on more detailed microstructure observation at higher magnification, as illustrated in Fig. 7a–c. This detailed examination of the castables matrix following heat-treatment at 900 °C revealed that, in the case of the sample dried at 110 °C (Fig. 7a), the castables matrix's internal heterogeneous microstructure is rather dense. Additionally, numerous pores can be observed among the particles within the granular body during heating (Fig. 7b). Moreover, the sintering process began at higher temperature, and numerous connections between particles have also formed (Fig. 7c). Additionally, the reactive sintering of particles formed during the decomposition of the MgO- Al_2O_3 - H_2O matrix transforms and sinters them into a two-phase matrix of Al_2O_3 - MgAl_2O_4 . As shown in Fig. 9, the relative compositions of several elements (Mg, Al and O) were also determined using an EDS line scan across the dehydrated and reacted MgO- Al_2O_3 castables matrix.

The SEM EDS line scan enables the investigation of changes in fine-grained matrix microareas. Fig. 9 shows the line scan for the C_900 sample. As observed, spinel particles formed by the reactive sintering of mixed oxides $\text{Mg}(\text{Al})\text{O}$ exhibit a “single mountain” profile in the EDS Al K α , Mg K α and O K α intensity line scans. Additionally, it is clearly seen that magnesium aluminium spinel-like phase was formed during sintering as a result of recombination of the hydrotalcite calcination products. This is further confirmed by the concurrent increase in line scan intensity, which indicates the presence of Mg, Al, and O. Thus, the obtained results are consistent with the Al^{27} MAS NMR measurement.

3.4. XRD, FTIR and DSC-TG-EGA(MS) investigation of structural and phases changes of MgO-fume bonded corundum castables matrix versus temperature

Thermal analysis, XRD, and FTIR measurements were performed on

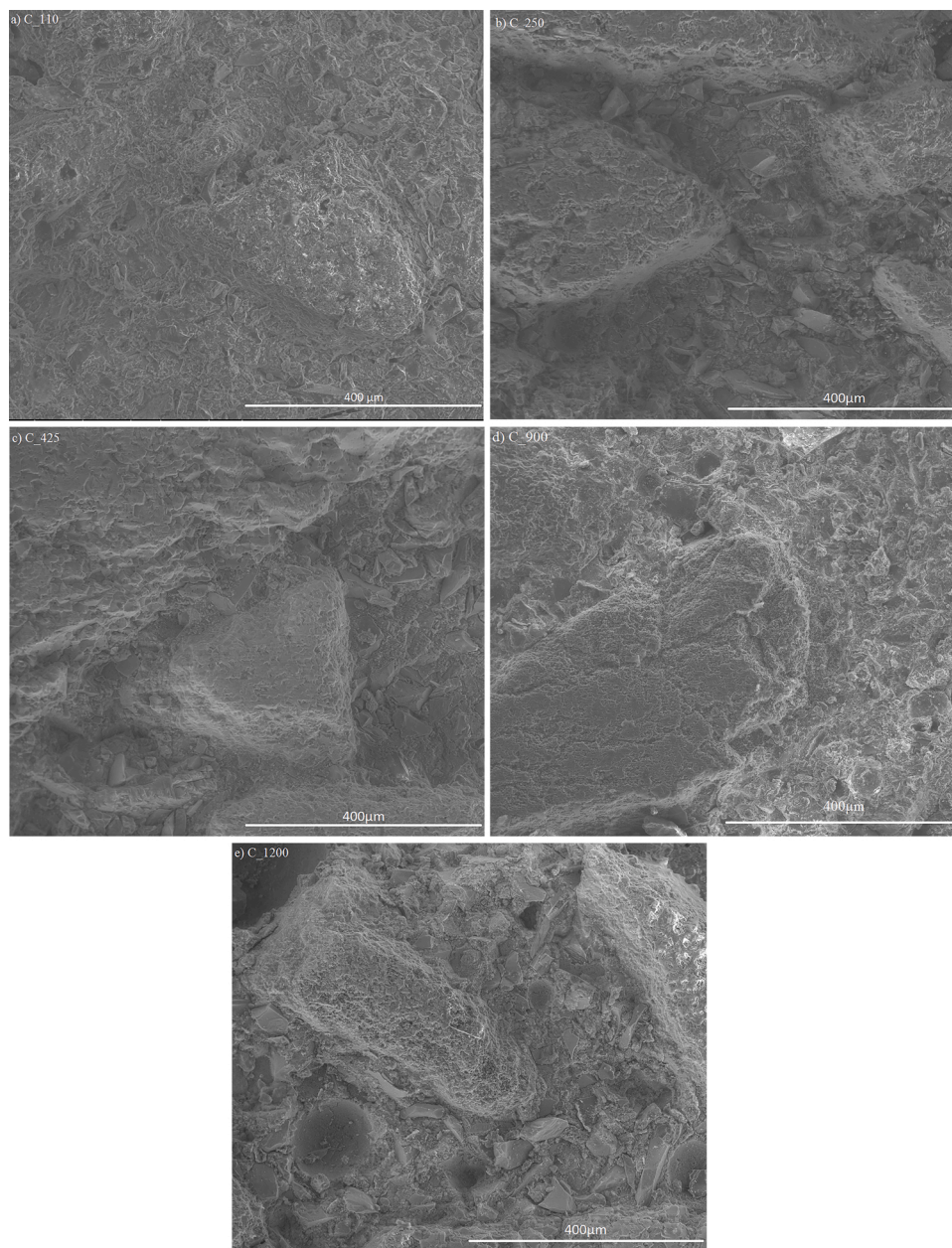


Fig. 6. a–e. Microstructure overview (SEM images with magnification of 350x) of the MgO-fume bonded corundum castables after heat treatment at 110, 250, 425, 900 and 1200 °C.

matrix samples obtained by crushing a piece of castables and separating the inert corundum grains. Fig. 9 illustrates the castables matrix's low-temperature XRD patterns following appropriate temperature firing. The XRD analysis revealed the presence of α - Al_2O_3 (JCPDS Card No. 96-900-9674) as the major phase and both β - Al_2O_3 (ICDD Card No. 01-084-0381) and MgO (ICDD Card No 00-045-0946) as minor phases in each sample. Additionally, the obtained results confirm the presence of spinel MgAl_2O_4 (JCPDS Card No. 96-900-3481) in both the C_1000 and C_1200 samples. Although, XRD analysis did not show the presence of MgAl_2O_4 in the castables matrix fired at temperatures lower than 1000 °C, it cannot be ruled out that the spinel was synthesised at lower temperatures. Spinel-like phases may exist in an amorphous state or may be undetectable due to the lower detection threshold of the equipment.

Fig. 10 shows the FTIR spectrum of the matrix samples after they have been heated to appropriate temperatures. The outline IR spectrum of the sample after drying (C_110 sample) in the range between 400 cm^{-1} and 1000 cm^{-1} was similar to that of α - Al_2O_3 described in both

[42] and [49]. Thus, we can confirm that the bands at: 457, 608, and 640 cm^{-1} in this range, are associated with Al-O bond stretching vibrations [50]. Additionally, the bands at 1093, 1167, and 1408 can be attributed to β - Al_2O_3 and H_2O deformation vibrations, respectively [51]. Moreover, the broad band in the range 3000–3750 cm^{-1} (C_110 sample) is most likely due to hydroxyl groups bonded to Al [30]. The obtained results, therefore, indicate that there are significant differences in the dehydration of samples when compared to conventional castables. With increasing heating temperature band associated with water deformation vibrations narrows, but completely vanishes at temperature above 700 °C. The SEM analysis confirms that the microstructure of the obtained castables was extremely dense, and as a result of this, it was possible that hydrothermal conditions were created in the castables sample during the firing process. This most likely results in the rehydration of Al_2O_3 . The results obtained are unprecedented of in the scientific literature. Additionally, the FTIR spectra of samples fired at 900 °C, 1000 °C, and 1200 °C show the presence of bands characteristic of MgAl_2O_4 (553 and

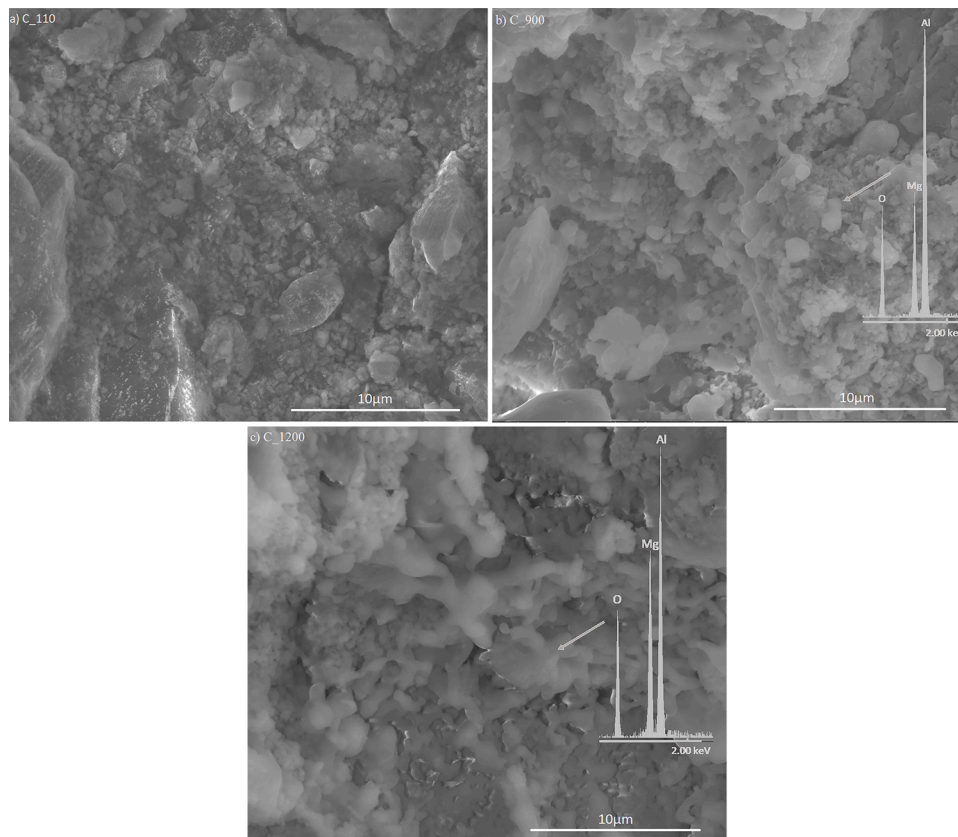


Fig. 7. a–c. Detailed microstructure analysis (SEM images with magnification of 10 000x) of the MgO-fume bonded corundum castables matrix after heat treatment at 110, 900 and 1200 °C and EDS analysis results.

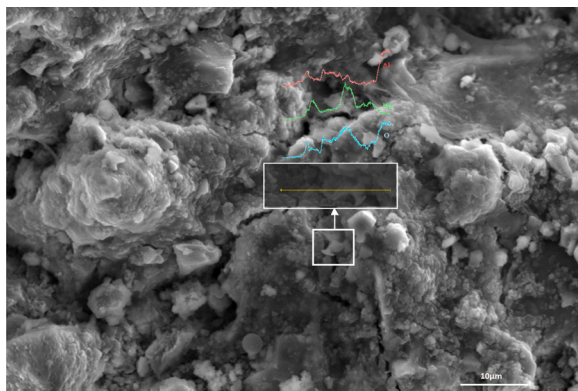


Fig. 8. Microstructure overview and SEM-EDS analysis in line-scan mode of the MgO-fume bonded corundum castables matrix after heat treatment at 900 °C.

692 cm^{-1}), which is consistent with the XRD results shown in Fig. 9. The presence of spinel bands in a sample fired at 900 °C further indicates that the spinel comprised amorphous MgAl_2O_4 which underwent crystallisation as its amount increased with the increase in temperature.

The thermal stability of a no-cement spinel-forming refractory castables matrix was determined at 110, 390, and 500 °C using simultaneous application of thermogravimetry (TG) and differential scanning calorimetry (DSC) in conjunction with coupled with mass spectrometry (EGA-MS). The analysis results are shown in Fig. 11. The black lines represent the weight loss of the samples mentioned above as a result of thermal decomposition. Additionally, the thermal decomposition of the castables matrix-based samples occur in a series of steps, even when the samples have been pre-heated. Consequently, the weight loss in the

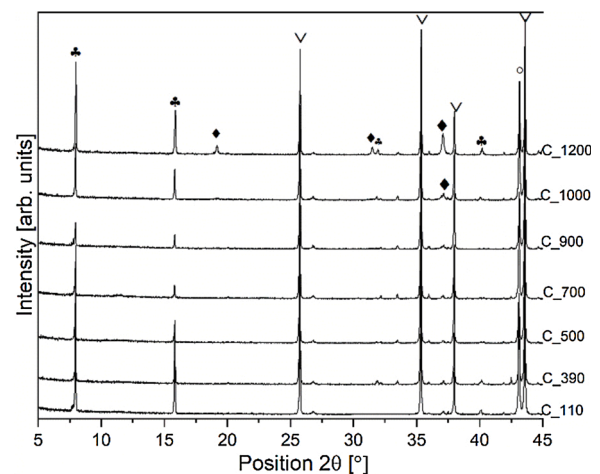


Fig. 9. Low-temperature XRD patterns of the castables matrix after heating in appropriate temperature in the range of 5–45 °. Down arrowheads: $\alpha\text{-Al}_2\text{O}_3$ (JCPDS Card No. 96-900-9674), clover: $\beta\text{-Al}_2\text{O}_3$ (ICDD Card No. 01-084-0381), degree sign: MgO (ICDD Card No 00-045-0946), diamond: MgAl_2O_4 (JCPDS Card No. 96-900-3481).

C_110 sample was attributed to thermal decomposition of $\text{Mg}(\text{OH})_2$ and various forms of hydrated aluminas, whereas weight loss in the C_390 and C_500 samples was attributed to thermal decomposition of hydrated aluminas. As a result, it can be assumed that the in-situ rehydration of the intermediate decomposition products occurred within the dense structure of nano-bonded MgO-containing castables. As a result, a improvements in the properties of castables at intermediate temperatures are expected. Moreover, the thermal decomposition of the hydraulically

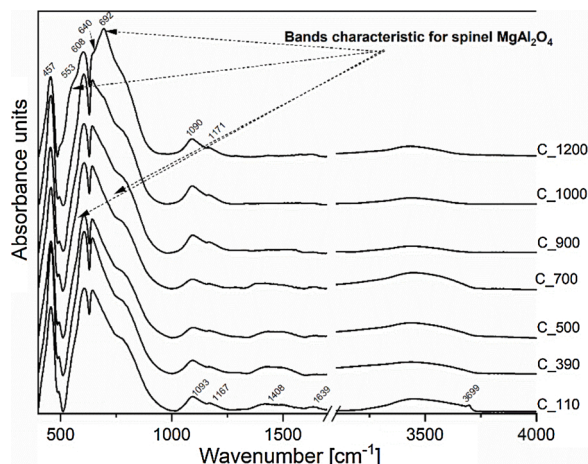


Fig. 10. FTIR spectra of the castables matrix after heating in appropriate temperatures.

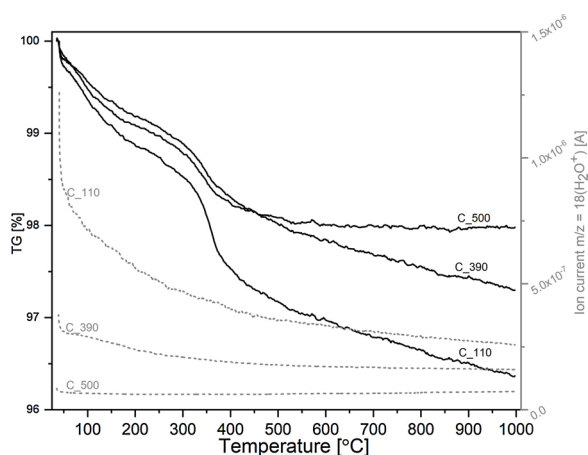


Fig. 11. Thermal analysis results of no-cement spinel-forming refractory castables matrix after heat-treatment at selected temperatures.

bonded castables was assumed to occur in a few steps. Up to ca. 250 °C, both physically bound water and zeolitic water were lost in the inter-layer regions. Additionally, more strongly bound water and the hydroxyl units found in the structure of hydrates were lost above ca. 250 °C.

3.5. Physical properties of the spinel forming refractory castables

The evolution of the microstructure and property changes of corundum-spinel refractory castables may be attributed to structural changes that occur within the matrix, as well as to the processes related to sintering. Based on the changes in sonic velocity following samples dried and fired at 425, 700, 900, and 1200 °C were chosen for further investigation. Subsequently, the refractory castable samples were subjected to both 3-point bending and compression tests. The results of the changes in sonic velocity and calculated Young's modulus (calculated using Eq. 2) vs. firing temperature, as well as the results of apparent density and porosity, cold crushing strength, and cold modulus of rupture are summarised in Figs. 12 and 13a, b, respectively.

According to the obtained results it can be seen that as firing temperature increased, the sonic velocity changed in three distinct stages. The primary stage comprised a reduction in sonic velocity (up to 390 °C firing temperature). The second stage involves a gradual increase up to 600 °C firing temperature followed by a decrease (up to 800 °C firing temperature). Finally, above 900 °C, the sonic velocity increases once again. The first sonic velocity change is almost certainly due to the

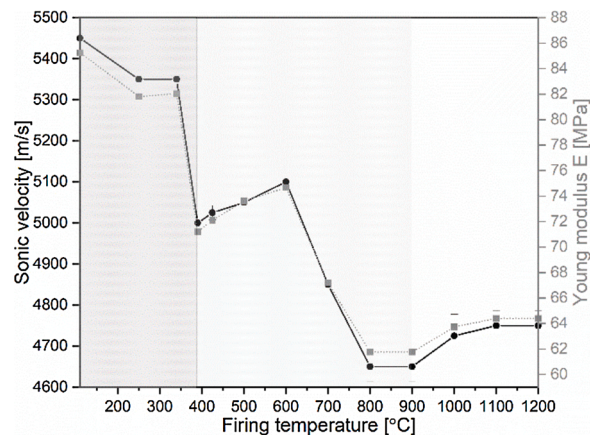


Fig. 12. Summary of the results of the changes in sonic velocity (black circle) and calculated Young's modulus (grey square) vs firing temperature.

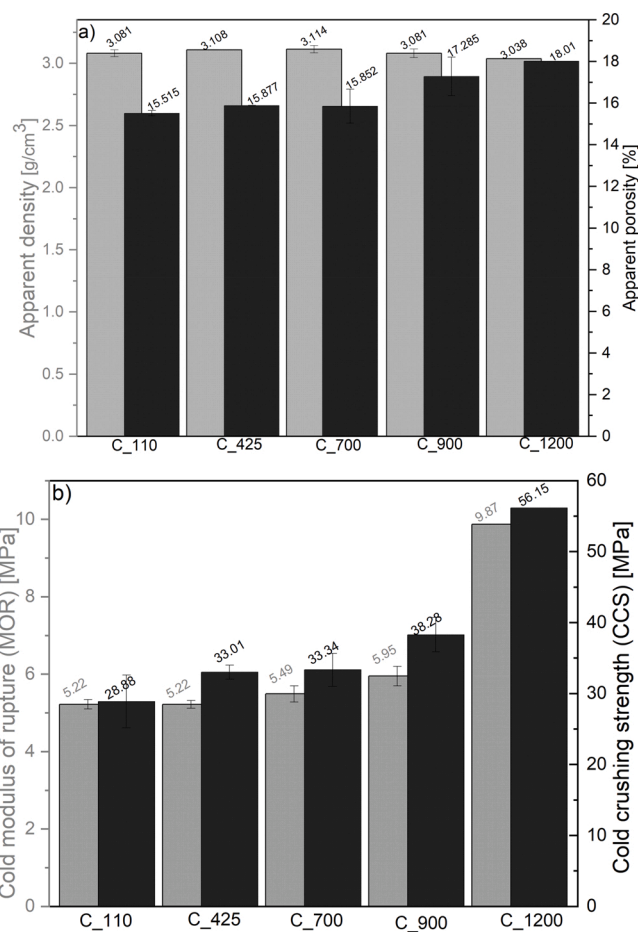


Fig. 13. Summary of the apparent porosity, apparent density (a) and mechanical properties (b) of dried (110 °C) and fired (250, 425, 700, 900 and 1200 °C) refractory castables.

elimination of physically and chemically bound water which results in the breakdown of hydraulic bonding in the matrix of refractory castables and a slight increase in apparent porosity. It is worth noting that heating above 425 °C results in an increase in sonic velocity. The increase in sonic velocity in samples heated at temperatures between 425 and 600 °C seems to have two overlapping reasons, one being is compacting of the castables microstructure due to the presence of nano-particles introduced previously with water-dispersed sol of fumed alumina, the

second being the rehydration of matrix components, which was confirmed by previous results. When the firing temperature reached 600 °C, the increase in sonic velocity was halted. According to previous findings, MgAl_2O_4 spinel can be synthesised at temperatures greater than 700 °C when Mg-Al hydrotalcite is used as a precursor. According to current knowledge, the process of in-situ spinel formation is associated with an increase in volume, which results in an increase in apparent porosity and the formation of a few microcracks in the microstructure. The decrease in sonic velocity and increase in apparent porosity of refractory castables fired above 600 °C may be attributed to the formation of fine crystalline spinel from Mg-Al hydrotalcite-like phases. Due to the small particle size of magnesium-alumina spinel, which was most likely synthesised from Mg-Al layered double hydroxides the increase in apparent porosity of castables fired to 900 °C is negligible. Sintering occurs at temperatures greater than 900 °C, resulting in the formation of a ceramic bond and an increase in cold crushing strength and cold modulus of rupture. On the other hand, a significant increase in apparent porosity can be observed as a result of increased magnesium alumina spinel synthesis. Due to the overlap of two processes (spinel synthesis and sintering), the increase in sonic velocity along the sample's longest direction at temperatures ranging from 900 to 1200 °C is negligible.

4. Summary and conclusions

First, the complete structural (XRD, FTIR and ^{27}Al MAS NMR) and thermal characterisations [DSC-TG-EGA(MS)] of hydrotalcite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ and its calcination and reactive sintering products were performed as a part of the fundamental research on the hardened blended paste initially composed of both MgO and Al_2O_3 nanopowders. This approach was used to simulate subsequent reactions that occur within the fine-grained matrix of the in-situ spinel-forming castables. From these findings it is clear that the calcination of hydrotalcite results in the formation of mixed oxides, which can be obtained via reactive sintering at relatively low temperatures to generate spinel.

Second, two commercially available magnesia raw materials, namely dead-burned and fused magnesium oxide micropowders, in combination with aluminum oxide nanopowder or aqueous dispersion of hydrophilic fumed aluminium oxide (Evonik Aerodisp W 450 ZX), were mixed with water, cured at 50 °C for up to 7 days, and evaluated for their ability to synthesise hydrotalcite in a time-dependent manner. After 12 h of hydration, structural investigations confirmed the trace amounts of $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ in the samples composed of fused or dead-burned MgO and nanometric Al_2O_3 powder. Additionally, the presence of nanometric alumina demonstrated an increased hydrotalcite formation efficiency. Moreover, due to the ease of distribution and lack of dusting, the Al_2O_3 was introduced into the castable matrix as a water-dispersed sol of fumed alumina.

Third, a fine-grained matrix of the in-situ spinel-forming castables was isolated directly from the precast beams and characterised using XRD, FTIR, and DSC-TG-EGA(MS). After firing at temperatures up to 700 °C, the FTIR spectrum of the castables matrix separated from the inert grains revealing the presence of a band at 1408 cm^{-1} associated with H_2O deformation vibration. Thermal analysis confirmed the presence of water as well. This indicates that the in-situ rehydration of the intermediate decomposition products occurred within the dense structure of the castables. According to the obtained results, after firing at 900 °C, a characteristic diffraction peak associated with the presence of MgAl_2O_4 appears. This confirmed the formation of spinel phase at low temperatures within the castable matrix.

Finally, both the results of the sonic velocity test and the mechanical investigation indicate that the castables exhibit improved properties at intermediate temperatures when compared to conventional castables. This is most likely due to two overlapping factors: the first one being is the extremely dense microstructure, which was confirmed by SEM-EDS analysis, and investigation, and the second being the rehydration of

matrix components. These findings, therefore, establish a direct link between the matrix structural changes and the properties of refractory castables.

Thus, several certain conclusions can be drawn from the obtained data:

- 1 Hydration of dead-burned or fused magnesium oxide mixed with nanometric alumina oxide in the form of powder or sol allows for the facile preparation of Mg-Al hydrotalcite.
- 2 The thermal decomposition of samples containing primarily $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ is associated with structural changes caused by the removal of interlayer water and the dehydroxylation process, which ultimately result in the formation of Mg-Al spinel and magnesium oxide.
- 3 The use of a water-dispersed sol of fumed alumina results in a significantly denser, which facilitates the in-situ rehydration of the castable matrix intermediate decomposition products.
- 4 By combining dead-burned or fused magnesium oxide with a water-dispersed sol of fumed alumina as a refractory castable matrix, properly selecting the curing conditions, and then firing at 900 °C, Mg-Al hydrotalcite is first formed, followed by low temperature spinel synthesis.
- 5 The results of sonic velocity tests and mechanical measurements of the smart refractory castables demonstrate the relationship between matrix structural changes (i.e., thermal decomposition of hydrotalcite, rehydration of intermediate decomposition products, low temperature spinel synthesis, and sintering) and properties of refractory castables.
- 6 It was demonstrated that compared to conventional CAC-containing castables, MgO -bonded alumina-based castables without silica fume exhibit no strength loss at intermediate temperatures.

Data availability

Raw data and other supplementary material are available at the following repository: osf.io/7zpcj.

No data was used for the research described in the article.

Data will be made available on request.

Author contributions

Karina Warmuz: methodology, writing-original draft preparation, visualization, data curation, investigation, software; Dominika Madej: conceptualization, methodology, validation, formal analysis, resources, writing-review and editing, supervision, project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Publikacja 10.4



Thermomechanical evaluation and thermodynamic simulation via FactSage of NCCs and ULCCs with different MgO content

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ABSTRACT

Thermomechanical properties are the most important for refractories and these give an idea about the bonding strength between the fine-grained matrix and the aggregates in the refractory body. Mentioned properties characterize the deformation of the refractories at high temperature, mainly due to the formation of the liquid phases of different quantity and viscosity. The objective of this study is to elucidate the role of the Mg-Al spinel content, stoichiometry and synthesis method on structural, microstructural, thermomechanical and other properties NCCs and ULCCs. The results show that the differences in thermomechanical performance of the ULCCs can be related to the CA_6 , Al_2O_3 and both pre-formed and in situ Al-excess Mg-Al spinel contents, whereas NCCs exhibit the best performance decreasing with an increasing the Al-rich spinel content. The thermodynamic simulation via FactSage 8.2 showed consistent results managing to indicate the effect of liquid phase on the thermomechanical properties of castables.

1. Introduction

According to current state of knowledge, castable refractory materials have found more and more applications in the last 20 years. The growing interest results mainly owing to their advantages in workability, energy-saving and cost efficiency [1,2]. In view of good thermomechanical properties and thermal shock resistance, high alumina refractory castables are one of the most popular within the various monolithics [3–5]. Nevertheless, the type of binder and its properties have a significant influence on the final properties of refractories such as green mechanical strength, mechanical properties, Refractoriness Under Load (RUL), creep in resistance (CIC), Hot Modulus of Rupture (HMoR) and Thermal Shock Resistance (TSR). Calcium aluminate cement (CAC) is widely used binder in the refractory industry due to its properties such as suitable working, curing and demolding times, good resistance to chemically aggressive environments, good high-temperature resistance and rapid strength development [1, 6–11]. In general, calcium hexaluminate (CA_6 , $CaO \cdot 6Al_2O_3$) is the main compound that forms at high temperatures in refractory systems based on calcium aluminate cements. It must be emphasized that an important aspect associated with calcium hexaluminate formation is its distribution within the refractory matrix. According to various literature sources [12–15], the CA_6 crystals

location in the refractory microstructure depends on both microsilica content and type of spinel (generated in situ or pre-formed). In refractory castables which contain SiO_2 , the presence of in situ Mg-Al spinel leads to CA_6 formation mainly at the border of the coarse alumina grains, while the presence of pre-formed spinel is associated with CA_6 formation within the matrix region [16,17]. The synthesis of CA_6 takes place in several stages. Liquid phase with chemical composition similar to gehlenite is formed initially. Subsequently, $CaMg_2Al_{16}O_{27}$ precipitation from mentioned liquid phase followed by $Ca_2Mg_2Al_{28}O_{46}$ formation takes place. The final stage is both CA_6 and $MgAl_2O_4$ generations. Mg^{2+} ions are characterized by faster diffusion at elevated temperatures than Al^{3+} ions, thus in situ spinel is formed in the matrix region and at the border of the alumina aggregates. This is also associated with even distribution of calcium hexaluminate crystals within microstructure. Nevertheless, the application of CAC favors the formation of low-melting phases during heating due to the presence of bauxite, mullite and microsilica in this type of castable [11,18,19]. Hence, the ultra-low cement castables (ULCCs) and cement-free/no-cement-content (NCCs) have developed rapidly in recent years and are widely used for e.g., steel ladles. These refractory castables exhibit valuable properties, including good thermal conductivity, low thermal expansion coefficient, good thermal shock resistance, good corrosion

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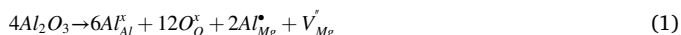
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resistance and high strength at both high and low temperatures [20–22].

The development of various new binders e.g. hydratable alumina [23–25], ultrafine- Al_2O_3 and MgO particles, colloidal silica [26–28], and mullite sol [29] has expanded the horizons for refractory technologists. The trend of recent years is the search for smart and modern supplementary binders, which constitute eco-friendly alternatives to CAC. Such an environmentally friendly alternative is the mixture of Al_2O_3 and MgO powders mixed with water. We have previously demonstrated [30–34] that by combining MgO powder with both powder or water-dispersed sol of fumed Al_2O_3 as a refractory castable matrix components, properly selecting the curing conditions, and then firing, Mg–Al hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) is first synthesized, followed by low-temperature in situ MgAl_2O_4 synthesis through the formation of $\text{MgO-Al}_2\text{O}_3$ mixed oxides. The synthesis of Mg–Al hydrotalcite takes place in few stages and forms through the disappearance of initially formed magnesium hydroxide. Firstly, $\text{Mg}(\text{OH})_2$ is precipitated as a layered structure on the surface of MgO and slightly dissolved. The release of $\text{Al}(\text{OH})_4^-$ ions occurs also. Secondly, the nucleation phase begins and precipitation of the $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ takes place. The thermal decomposition of samples containing pure Mg–Al hydrotalcite is associated with structural changes due to the removal of interlayer water and the dehydroxylation process, which ultimately result in the formation of Mg–Al spinel and MgO [30, 33].

The most commonly used method for obtaining Mg–Al spinel is the solid-state reaction of Al_2O_3 and MgO at 1600–1800 °C. During ceramic-powder processing formation of MgAl_2O_4 occurs by opposite directed diffusion of the aluminium (Al^{3+}) and magnesium (Mg^{2+}) ions through the rigid oxygen lattice of spinel [35]. The unit cell of spinel is characterized by general formula AB_2O_4 in which the cations A and B occupy tetrahedral and octahedral sites, respectively. According to the various literature sources two types of spinel can be distinguished: normal in which all sixteen Al^{3+} ions are in octahedral coordination and all of eight Mg^{2+} ions are in tetrahedral coordination and inverse in which the Mg^{2+} and Al^{3+} ions occupy the octahedral sites in equal proportions. Moreover, there exist intermediate phases with random cation distributions. This kind of partial inversion may be described as disorder parameter γ , which is the fraction of octahedral sites occupied by Mg^{2+} ions and ranges from 0 for the normal spinel to 0.5 for the inverse spinel [36]. Thus, the general formula may be written as $(\text{Mg}_{1-2\gamma}\text{Al}_{2\gamma})[\text{Mg}_{2\gamma}\text{Al}_{2-2\gamma}]\text{O}_4$, where () and [] denote tetrahedral and octahedral sites, respectively.

On the other hand, the general formula of spinel can be written as $\text{MgO}_x\text{Al}_2\text{O}_3$ also. In many cases x is greater than 1, which indicates nonstoichiometry where excess Al^{3+} ions occupying tetrahedral sites, substitute for Mg^{2+} ions. The Al^{3+} ions are characterised by smaller diameter than Mg^{2+} , thus proportional decrease of lattice parameter with the amount of excess Al^{3+} is observed. As some authors [37,38] have suggested, the excess Al^{3+} ions implemented a substitution defect on the tetrahedral magnesium site ($\text{Al}_{\text{Mg}}^{\bullet}$) or magnesium vacancy ($\text{V}_{\text{Mg}}^{\bullet}$) is formed to compensate for the excess positive charge as demonstrated in the following equations:



It is worth to notice that the quantity and type of defects both on the surface and in the bulk of the material changes as a function of spinel stoichiometry. According to various literature sources [39–41] defects in structure may lead to changes in the properties of material such as: surface and optical properties. Nevertheless, there are no published data concerning relationship between spinel stoichiometry and both thermomechanical and mechanical properties of spinel-containing refractory materials. Most of the scientific work [2, 42–45] focuses on the correlation between the amount and grain size of both pre-fabricated

and generated in situ magnesium aluminate spinel. It has been found that an optimal amount of pre-formed spinel ranges from 15 to 30 wt% while the most favourable content is between 20 and 25 wt% [2]. The thermomechanical properties like HMoR and RUL of low-cement content castables are improved by adding high purity magnesium aluminate spinel as shown by various authors [2,46,47]. The increase of these thermomechanical properties may be associated with the bridging between the spinel grains and the CAC crystals formed at high temperatures [48,49]. Moreover, the pre-formed spinel addition enhances the TSR of alumina-based castables which may be explained by the different thermal expansion coefficients between spinel ($\alpha = 7.6 \cdot 10^{-6} \text{ K}^{-1}$) and alumina ($\alpha_{\text{Al}_2\text{O}_3} = 8.5 \cdot 10^{-6} \text{ K}^{-1}$) [50–52]. The different expansion is associated with microcracks formation within the castable matrix that act as crack branchers and thus the TSR is improved [2]. On the other hand, according to the current state of knowledge, in situ spinel forming castables exhibit better properties e.g. slag resistance, both mechanical and thermomechanical properties, compared to pre-formed spinel containing castables. This is associated with more evenly distributed spinel grains within castable matrix [53]. However, the in situ spinel formation is associated with a relatively large volume expansion of about 8% and increase in porosity. This volumetric expansion may lead to spalling of castable linings due to the lack of the volume stability [2] while increase in apparent porosity deteriorate the mechanical strength (cold modulus of rupture MOR and cold crushing strength CCS). Braulio et al. [42] confirmed that the MgO grain size affects the expansion of spinel containing castables. The increase in the MgO grain size is associated with reduction in the magnesium aluminate spinel content and lead to a higher overall expansion. Additionally, the presence of coarse, unreacted magnesium oxide grains could be associated with the crack propagation during thermal cycling because of thermal expansion mismatch between alumina, spinel and magnesia [18, 50–52, 54]. Additionally, Shuhe Hu et al. [45] reported that the thermal shock resistance is improved while HMoR is decreased of spinel-forming castables with augmenting the MgCO_3 amount to 2.0 wt% which was used as spinel precursor. All mentioned above examples show how much important is properly designed castable composition and thus microstructure. The microstructure elements including apparent porosity, size, morphology and distribution of the crystalline phases and amount, composition and distribution of liquid phases determine the mechanical and thermomechanical properties significantly. RUL, CIC and HMoR properties are related to the formation of the liquid phases of different quantity and viscosity and thus strength of bonding between the fine-grained matrix and the aggregates. Solid-state compatibility and melting relationships in the Al_2O_3 –MgO–CaO–SiO₂, Al_2O_3 –CaO–SiO₂ and Al_2O_3 –MgO–CaO systems were studied by many authors [55–59]. The presence of microsilica significantly decreases the eutectic temperature. In the quaternary system Al_2O_3 –MgO–CaO–SiO₂ such phases may coexist together: CA_2 – CA – C_2AS , CM_2A_8 – C_2AS – CAS_2 , CAS_2 – CMS_2 – S , C_2MS_2 – CS – C_2AS , and CM_2A_8 – CAS_2 – A ($\text{A-Al}_2\text{O}_3$, M-MgO , C-CaO , S-SiO_2). For example CAS_2 causes the formation of liquid phase in the presence of C_2AS or MA at 1400 and 1425 °C, respectively, [56,59]. The high temperatures (1730 °C) of first liquid phase formation in the alumina rich part of Al_2O_3 –MgO–CaO system explains good thermomechanical properties of castables designed in this area of the ternary system, particularly if they are formulated within the Al_2O_3 – MgAl_2O_4 – $\text{CaAl}_{12}\text{O}_{19}$ subsystem. In that case the temperature of first liquid formation is about 1850 °C [55].

The objective of this study was to elucidate the role of the Mg–Al spinel content and synthesis method on structural, microstructural, and both mechanical and thermomechanical properties of cement-free (NCCs) and ultra-low cement castables (ULCCs). For this purpose cement-free and ultra-low cement containing castables with different type of spinel (in situ spinelization, mixed in situ spinelization and pre-formed) were prepared and subjected to RUL, CIC, HMoR and other measurements. The thermodynamic simulation via FactSage 8.2 allowed to determine the possible phases formed, the temperature of liquid

phase formation, the liquid content versus temperature and Mg-Al spinel composition changes versus temperature.

2. Experimental part

2.1. Materials preparation

In this work, three type of cement-free (NCCs, CAC-free spinel-forming castables) and two type of ultra-low cement containing (ULCCs, CAC-containing alumina-based spinel-forming/spinel-containing mixed castables) vibratable castables were designed considering the Dinger and Funk particle packing model and distribution coefficient (q) equal to 0.26. Tabular alumina (grain size: 0–6.0 mm, Almatiss) and Al-rich magnesium aluminate spinel (AR 90 grain size: 0–0.5 mm Almatiss) were used as aggregates. The matrix for no-cement content castables was obtained by mixing dead-burned magnesia, reactive alumina (CTC 40, Almatiss), microsilica (Elkem, 971) and some amount of Al₂O₃ sol. On the other hand the CAC- containing castables matrix comprised calcium aluminate cement (Górkal 70, 30% CaO) dead-burned magnesia, reactive alumina, microsilica and additives (water, Castament® FS 20 from BASF). Table 1 lists the nomenclature and compositions of the castables. Calculations of CAC-containing alumina-based spinel-forming/spinel-containing mixed castables composition included 3 wt% of MgO introduced as magnesia fume and pre-formed spinel. This calculation method of the initial composition of castables is unparalleled in the literature of refractory materials. In the laboratory-scale mixer, the mixtures were dry-mixed for 5 min and then wet-mixed for 5 additional minutes. Subsequently, vibration was used to cast the mixed castables into 40 × 40 × 160 mm and 230 × 110 × 60 mm moulds. The castable samples were then de-moulded after 24 h. CAC-containing alumina-based spinel-forming/spinel-containing mixed castables samples were immediately dried at 110 °C for 24 h, while CAC-free spinel-forming castables were firstly cured for at 50, 70 and 90 °C in a laboratory climatic chamber. Subsequently, samples were dried at 110 °C for 24 h also. After 24 h of drying at 110 °C, each sample was fired at 1500 °C with retention time 10 h.

The specimens of 40 × 40 × 160 mm were made for the measurement of the apparent porosity, bulk density and both mechanical (MOR and CCS) and thermomechanical (HMoR, TSR) tests. Additionally, both before and after first TSR test the cross-polish section was examined using a scanning electron microscope.

Samples of 230 × 110 × 60 mm were subjected to mechanical treatment in order to prepare them for further testing. A cylindrical test pieces (diameter and height 50.0 ± 0.5 mm with coaxial bore of 12–13.0 mm) for RUL and CIC tests have been cut. For X-ray diffraction (XRD) the castable pieces were ground using a ball mill to obtain fine powders with grains below 63 µm.

Table 1
Nomenclature and composition of cement- free and ultra-low cement containing castables.

Composition of samples [wt%]	Designation of samples				
	CAC-free spinel-forming castables			CAC-containing alumina-based spinel-forming/spinel-mixed castables	
	NCC_3M	NCC_5M	NCC_7M	ULCC_3M_2Mw	ULCC_3M_1Mw
Tabular alumina (1.0–6.0 mm)	38.42	38.42	38.42	40.14	39.64
Tabular alumina (0–1.0)	42.17	42.17	42.17	27.14	18.28
Spinel AR 90 (0–0.5 mm)	-	-	-	10.53	21.16
Reactive Al ₂ O ₃	15.41	13.41	11.41	15.90	15.70
Dead-burned MgO	3.00	5.00	7.00	2.01	0.99
SiO ₂ micro-powder	1.00	1.00	1.00	1.12	1.11
CAC	-	-	-	3.16	3.12
Al ₂ O ₃ sol	+	+	+	-	-
Dispersing additive	0.10	0.10	0.10	0.10	0.10
Water	3.50	3.50	3.50	4.50	4.50

2.2. FactSage 8.2 thermodynamic simulation

The chemical thermodynamic results, containing the details of the possible phases formed, the temperature of liquid phase formation, the liquid content versus temperature and Mg-Al spinel composition changes versus temperature were generated by entering the representative oxides of the chemical composition of the five castables (Table 2), in the “Equilib” module of the FactSage version 8.2 software, using the selection options “A-Slag-liq all oxides + S”, “A-Spinel” and “A-Monoxide” for CAC-free systems, and “A-Slag-liq all oxides + S”, “C-Spinel” and “A-Monoxide” for CAC-containing systems. For all phases, the selection option was used as “possible 2-phase immiscibility”. The databases “FactPS”, “FTmisc” and “FToxid” were used in all calculations. Calculation parameters were set at 1 atm pressure of air. All calculations were performed from 1000 °C to 1600 °C with an interval of 100 °C. Additionally, the changes in spinel composition within the MgO-Al₂O₃-CaO system with increasing temperature and CaO content (between 1 wt % and 5 wt%) has been simulated. Mentioned calculations were performed from 1300 °C to 2000 °C with an interval of 50 °C. Calculations were made for both modeled stoichiometric Mg-Al spinel and Al-rich Mg-Al spinel which chemical composition used as inputs for FactSage 8.2 thermodynamic simulations shows Table 2.

2.3. Detailed description of characterisation techniques

The XRD patterns were recorded on a X’Pert Pro PANalytical diffractometer within the range of 2θ values between 5° and 90° using Cu Kα radiation (λ = 1.54060 nm) at 45 kV (step size of 0.008°). The phases were identified using HighScore Plus software (Panalytical) used in conjunction with the ICDD-supported PDF-2 database and the JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997).

The bending strength of refractory castables was measured by a 3-point bending test using a specimen of 40×40×160 mm, a span of 100 mm and a test speed of 50 N/s. In order to determine the CCS, half of each sample after the 3-point bending test, was placed in the

Table 2
Chemical composition of castables used as inputs for FactSage 8.2 thermodynamic simulations.

Castable compositions	Oxides [wt%]			
	Al ₂ O ₃	MgO	SiO ₂	CaO
NCC_3M	95.98	2.96	1.06	-
NCC_5M	94.00	4.94	1.06	-
NCC_7M	92.02	6.91	1.07	-
ULCC_3M_2Mw	95.07	2.99	1.05	0.89
ULCC_3M_1Mw	95.03	3.02	1.05	0.90
Stoichiometric spinel MA	71.67	28.33	-	-
Al-rich spinel	90.00	10.00	-	-

compression testing equipment. The loading speed was 2.4 kN/s. Both MOR and CCS measurements were carried out according to EN 196-1:2005 and EN 993-5:1998 standards, respectively.

Bulk density and apparent porosity tests of refractory castables samples were carried out by standard methods, based on the Archimedes' principle, according to the PN-EN 993-1:2019-01 standard.

The Refractoriness Under Load (RUL, Netzsch, RUL 421) was determined according to the PN-EN ISO 1893:2008 standard. A cylindrical test piece was subjected to a constant compressive load (0.2 MPa) and heated at a 5 °C/min up to 1500 °C. The deformation of the test piece was recorded as the temperature increases, and the temperatures corresponding to specific deformation were determined.

The HMoR and CIC were determined according to PN-EN ISO 1927-6:2013-06 and PN-EN ISO 1927-6:2013-06 standards, respectively. To describe creep of each analysed samples the θ -projection concept [35, 60–63] was used. According to this model, the following constitutive relationship is proposed to evaluate the creep curve behavior of refractory castables:

$$\varepsilon = \theta_1 \bullet (1 - e^{-\theta_2 \bullet t}) + \theta_3 \bullet \theta_4 \bullet t \quad (3)$$

where ε is the creep strain [%], θ_1 , θ_2 , θ_3 and θ_4 are the fitting parameters, t - time [min]. Based on the experimental creep deformation–time curves the θ_i parameters were calculated by using the Origin software (OriginLab Corporation, USA, 2022) and the ExpLinear function. Mentioned mathematical fitting leads the following equation:

$$y = p_1 \bullet e^{-\frac{x}{p_2}} + p_3 + p_4 \bullet x \quad (4)$$

where p_1 , p_2 , p_3 and p_4 correspond to θ_1 , θ_2^{-1} , $-\theta_1$ and $\theta_3 \bullet \theta_4$, respectively.

The TSR of the corundum-spinel castables were carried out according to own laboratory procedure based on the ASTM C1171 – 05 standard. The samples with dimensions of 40×40×160 mm were put into furnace with a temperature of 950 °C for 45 min before they were shocked by quenched into water at 20 °C for 3 min. The percent sonic velocity along the longest direction of each specimen before and after each heating and cooling cycle was measured using the following equation:

$$\frac{V_0 - V_1}{V_0} \bullet 100[\%] \quad (5)$$

Where V_0 -original sonic velocity of each specimen [$m \bullet s^{-1}$].

V_1 - sonic velocity of each specimen after testing [$m \bullet s^{-1}$].

The TSR was additionally evaluated by comparing the MOR and CCS of three samples of each composition before first and after third and fifth thermal procedure.

A scanning electron microscope (SEM JEOL 6610) was used to investigate the changes in microstructure that occurred as a result of the castables TSR tests. Electron-probe microanalysis with an energy dispersive X-ray spectrometer (OXFORD X-Max) was used to determine the chemical compositions of the castables by EDS surface mapping. Castables samples both before and after first heating and cooling cycle was polished and using a pressing force of 40 [N], a rotational speed of 300 RPM, and a continuous water wetting of the diamond surface disc. After polishing, the specimen was placed in an ultrasonic cleaner with isopropyl alcohol in a baker for approximately an hour. The final stage was gold plating using sputter coater Cressington.

3. Results and discussion

3.1. Evaluation of thermodynamic simulation (FactSage 8.2) for the interpretation of the thermomechanical properties of castables

3.1.1. FactSage simulations of spinel composition

Mg-Al spinel composition changes versus temperature were simulated using FactSage 8.2. This was done to predict and compare the

products expected during the heat-treatment tests in RUL and CIC. The chemical compositions used for the preparation of each refractory castable (Table 2) were used as input in FactSage 8.2. Fig. 1 to Fig. 2 show the mass fraction of the products that were predicted by FactSage 8.2.

At temperatures higher than 1000 °C, FactSage 8.2 predicts the formation of spinel for the CAC-free spinel-forming castables. The Mg-Al spinel consists of Al_3O_4 [1 +], AlO_4 [5-], $MgAl_2O_4$, $AlMg_2O_4$ [1-], Mg_3O_4 [2-] and MgO_4 [6-] fractions, according to the FToxid-SPINA database (A-Spinel oxide Spinel (cubic) AB_2O_4 -type cubic spinel solution containing Al-Mg-O (2 + and 3 + oxidation states only)). These fractions vary with temperature, as shown in Fig. 1, for the NCC_3M, NCC_5M and NCC_7M castables. For the ULCC_3M_2Mw and ULCC_3M_1Mw castable compositions, the Mg-Al spinel consists of Al_3O_4 [1 +], AlO_4 [5-], $MgAl_2O_4$, $AlMg_2O_4$ [1-], Mg_3O_4 [2-], MgO_4 [6-], $CaAl_2O_4$ [1-] and $MgCa_2O_4$ [2-] fractions, according to the FToxid-SPINC database (A-Spinel oxide Spinel (cubic) AB_2O_4 -type cubic spinel solution containing Al-Mg-O (2 + and 3 + oxidation states only)).

As shown in Figs. 1 and 2, two of these curves, called the $MgAl_2O_4$ and Al_3O_4 , clearly confirm the existence of cluster structure in Mg-Al spinel phase. A three-sublattice model has been used with Mg^{2+} and Al^{3+} mixing on tetrahedral and octahedral sites while O^{2-} fills the third sublattice. When Al_3O_4 spinel is mixed with $MgAl_2O_4$ spinel to form spinel solid solution, Al^{3+} can enter in both tetragonal and octahedral sites of the spinel. Thus, this solution is the spinel solid oxide solution $MgAl_2O_4$ dissolving excess Al_2O_3 , called here Al-excess Mg-Al spinel. It can be commented here that the thermomechanical properties of all castable compositions were also affected by the microstructural changes induced by the structural changes of spinel phase connected with an increase in Al concentration. This structural changes as a result of introduction of aluminum ions into the Mg- Al spinel structure were also confirmed by XRD analysis (Fig. 3b) due to the shift in the characteristic diffraction peak belonging to the spinel to a higher 2 θ value.

Fig. 3a,b show changes in mole fraction of Al, Mg, O and Ca in the Mg-Al spinel phase obtained from FactSage 8.2 calculation during the heat treatment of mixtures containing stoichiometric or Al-rich Mg-Al spinel and CaO. Mixtures containing stoichiometric spinel or Al-rich spinel and CaO whose content varied from 1 to 5 wt% were considered. The chemical composition of stoichiometric and Al-rich spinel

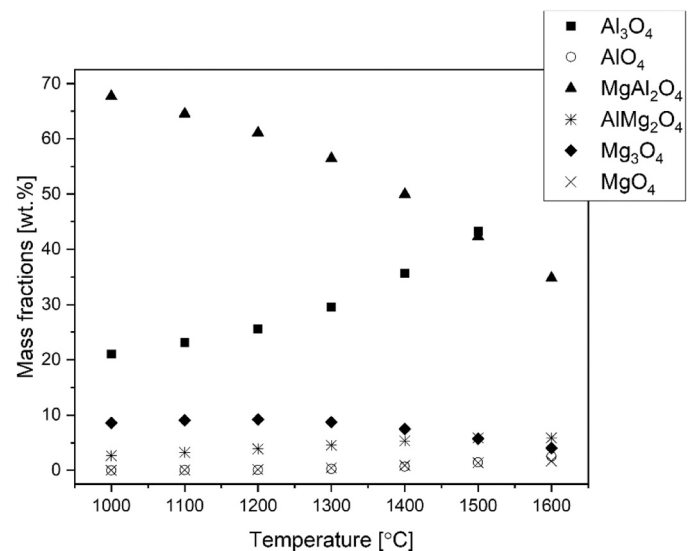


Fig. 1. Mass fraction of Al_3O_4 [1 +], AlO_4 [5-], $MgAl_2O_4$, $AlMg_2O_4$ [1-], Mg_3O_4 [2-] and MgO_4 [6-] in the Mg-Al spinel phase obtained from FactSage 8.2 calculation during the heat treatment of castable compositions, according to the FToxid-SPINA database. CAC-free castable compositions NCC_3M, NCC_5M and NCC_7M.

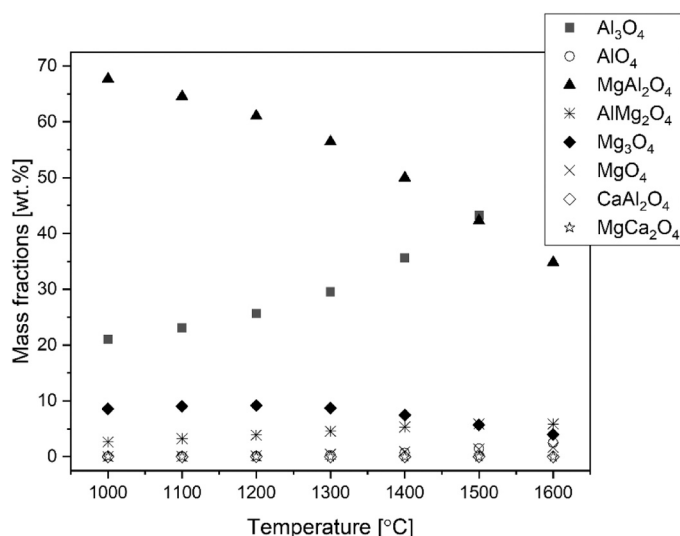


Fig. 2. Mass fraction of Al₂O₃ [1+], AlO [5-], MgAl₂O₄, AlMg₂O₄ [1-], Mg₃O₄ [2-], MgO [6-], CaAl₂O₄ [1-] and MgCa₂O₄ [2-] in the Mg-Al spinel phase obtained from FactSage 8.2 calculation during the heat treatment of castable compositions, according to the FToxid-SPINC database. CAC-containing castable compositions ULCC_3M_2Mw and ULCC_3M_1Mw.

used as inputs for FactSage 8.2 thermodynamic simulations have been presented in Table 2. According to obtained results it is clearly seen that both the stoichiometry of spinel phase and initial amount of CaO in the mixture significantly determines the Ca mole fraction. The Ca mole fraction increase to the temperature of 1850 °C for mixtures containing stoichiometric spinel, while for mixtures which contain Al-rich spinel, the concentration of Ca increase to 1750 °C. Mentioned increase is associated with the incorporation of Ca into spinel structure. Changes in spinel composition are directly associated with the liquid phase composition which amount increase with increasing temperature.

3.1.2. FactSage simulations of liquid phase

The RUL represents the resistance of refractory material to deformation when heated at high temperature and load of 0.2 MPa for dense refractory castables. CIC refers to the percent of shrinkage of a refractory test piece under a constant load and exposed to a constant high temperature over a long period of time. Whereas HMoR concerns the maximum load at high temperature and is defined as the maximum stress of a test piece which can withstand maximum load until it breaks. Both RUL, CIC and HMoR are of more practical significance than refractoriness of refractory material. As it is possible to see in Fig. 6, Fig. 7, Fig. 8, Table 3 and Table 4, the RUL/CIC and HMoR results (Fig. 6, Fig. 7, Fig. 8) are very dependent on liquid content (Table 3, Table 4) as calculated from equilibrium FactSage 8.2 considerations. Analyzing the FactSage 8.2 results, it can be seen that all castable compositions showed liquid phase formation. Table 3 presents the results of calculations for the finding the temperature at which the targeted liquid phase begin to form (temperature of first liquid phase formation). The results presented in Table 4 showed that the formation of liquid phase was mainly affected by an increasing temperature. For NCC_3M, NCC_5M and NCC_7M compositions, the liquid phase formation occurred at 1471 °C, whereas for ULCC_3M_2Mw and ULCC_3M_1Mw samples it happened close to 1432 °C. It is well established that there is a strong correlation between mass fraction of liquid obtained from FactSage 8.2 calculation versus temperature (Table 4) and RUL-CIC results for all castable compositions (Fig. 6 Fig. 7). Additionally, it is clearly seen that amount of liquid phase content strongly depends on the spinel content.

Fig. 6, Fig. 7 presents the RUL and CIC curves of the five castables after firing at 1500 °C. CAC addition had significant effect on the

percent of shrinkage of castables test pieces under a constant load of 0.2 MPa and exposed to a constant high temperature (1500 °C) over a long period of time (25 h). This deformation is mainly related to the presence of large amounts of liquid phase (Table 4) and spinel distribution/the amount, particle size and distribution of spinel in these two alumina-based spinel-forming/spinel-containing mixed castables with an initial MgO content of 3 wt% (ULCC_3M_2Mw, ULCC_3M_1Mw). It is worth noting that the ULCC_3M_2Mw sample showed higher amount of in situ spinel formation from dead-burned magnesia and alumina within the fine-grained refractory matrix. On the other hand, CIC tests revealed an reduction in the creep behavior of three CAC-free spinel-forming castables treated at 1500 °C in comparison to the CAC-bonded alumina-spinel castables, since to three CIC curves derived from NCC_3M, NCC_5M and NCC_7M samples lie above the curves belonging to both ULCC_3M_2Mw and ULCC_3M_1Mw samples. Moreover, the findings from both RUL-CIC and XRD results, and FactSage simulations presented here demonstrate that the deformation resistance determined in the RUL-CIC and HMoR tests (Figs. 6, 7, 8) of the 3 M, 5 M and 7 M spinel-forming refractory castables depends mainly on the spinel content (Table 5), since the chemical composition of liquid phase versus temperature predicted based on the FactSage 8.2 are the same for these three NCC_3M, NCC_5M and NCC_7M samples. In this regards, the softening behavior is similar for NCC_3M and NCC_5M samples up to 1500 °C, and these composition were better correlated with NCC_7M. Furthermore, the CAC-free compositions were more resistant to creep at 1500 °C (Fig. 7) in comparison with the CAC-containing castables both ULCC_3M_2Mw and ULCC_3M_1Mw samples. The RUL-CIC properties of these two samples are not consistent with the NCC_3M sample, where an initial MgO content was kept constant at 3 wt% in these three castable compositions. It can be hence concluded that the RUL-CIC properties of the ULCC_3M_1Mw and ULCC_3M_2Mw castable compositions were affected mainly by the amount of spinel phase and particle size distribution of all crystalline phases.

Based on the FactSage 8.2, according to the FToxid-Slag database for both CAC-free spinel-forming castables and CAC-bonded alumina-spinel castables compositions chemical composition predictions of liquid phase versus temperature were performed. As mentioned above, predicted chemical composition of liquid phase versus temperature there is no change in composition within the compositions of CAC-containing and CAC-free corundum castables. The liquid at 1500°C predicted by FactSage consists mainly of Al₂O₃ (39.95%), MgO (16.43%) and SiO₂ (43.62%) for NCC_3M, NCC_5M, NCC_7M castable compositions, whereas it consists mainly of Al₂O₃ (38.66%), MgO (8.66%), SiO₂ (38.01%) and CaO (14.67%) for ULCC_3M_2Mw and ULCC_3M_1Mw castable compositions. It is worth to notice that with increasing temperature the liquid phase is enriched with aluminum ions. The liquid at 1600°C predicted by FactSage consists of Al₂O₃ (48.16%), MgO (15.90%) and SiO₂ (35.94%) for NCCs, whereas it consists of Al₂O₃ (48.03%), MgO (7.56%), SiO₂ (29.20%) and CaO (15.22%) for ULCCs. Moreover, with increasing temperature, both liquid phase content and oxide content in liquid phase increase. It is worth noting that the appearance of the liquid phase is a consequence of the appearance of eutectics in a system equivalent to the given chemical composition. The equilibrium liquid phase composition for CAC-free spinel-forming castables (NCC_3M, NCC_5M, NCC_7M) which chemical composition used as inputs for FactSage thermodynamic simulations have been presented in Table 2 is 37.619 wt% Al₂O₃, 46.015 wt% SiO₂ and 16.366 wt% MgO. For both CAC-containing alumina-based spinel-forming/spinel-containing castables ULCC_3M_2Mw and ULCC_3M_1Mw the equilibrium liquid phase composition is 33.893 wt% Al₂O₃, 43.169 wt% SiO₂, 14.324 wt% CaO and 8.6141 wt% MgO.

The findings presented here demonstrate that the key factors affecting the thermomechanical properties of the castable compositions investigated here can be summarized as follows: (i) the degree of direct bonding among different particles; (ii) the amount, composition and distribution of liquid phases; (iii) the amount, particle size and

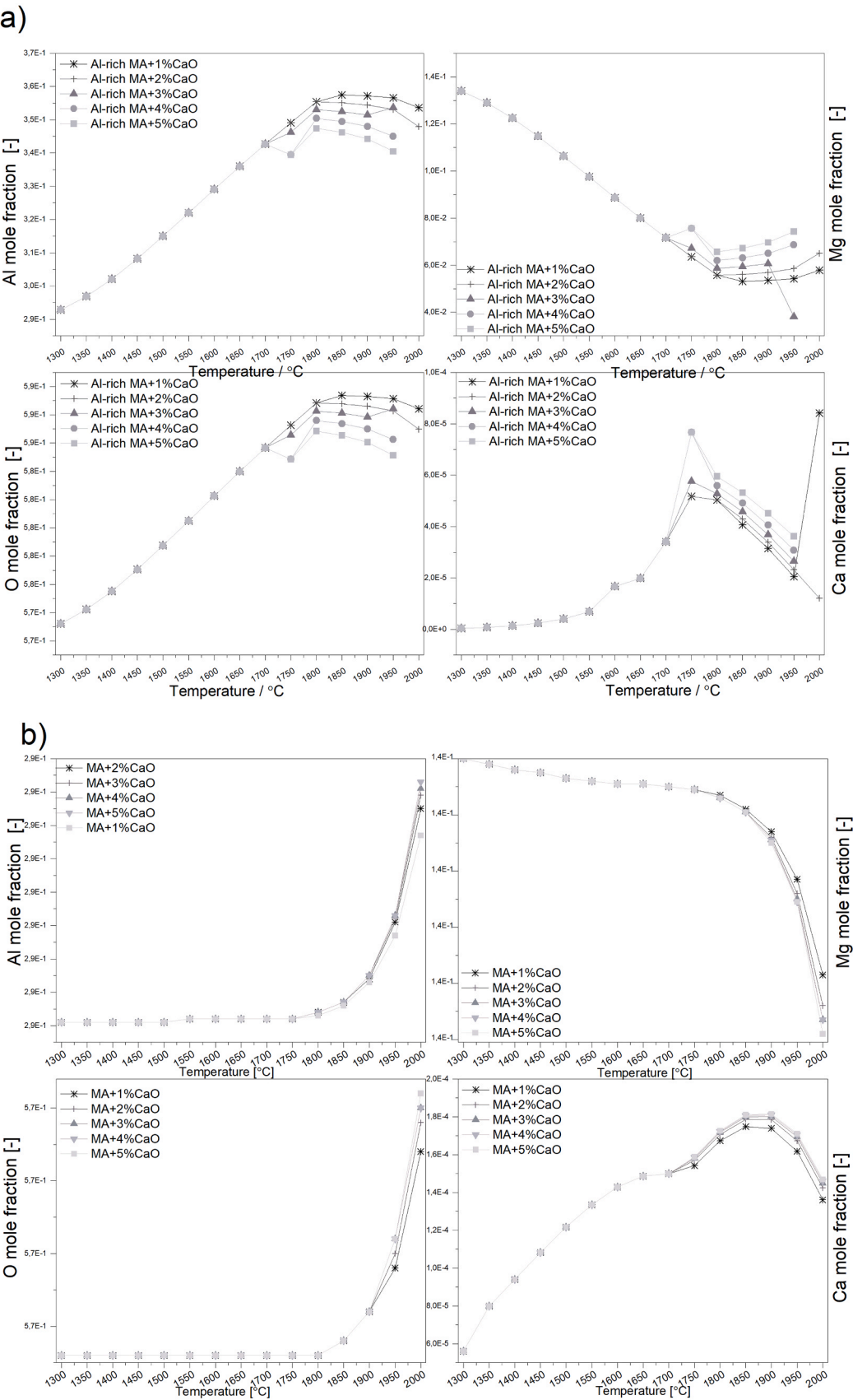


Fig. 3. Mole fraction of Al, Mg, O and Ca in the Mg-Al spinel phase obtained from FactSage 8.2 calculation during the heat treatment of mixtures containing Al-rich spinel and CaO (a) and stoichiometric spinel and CaO (b).

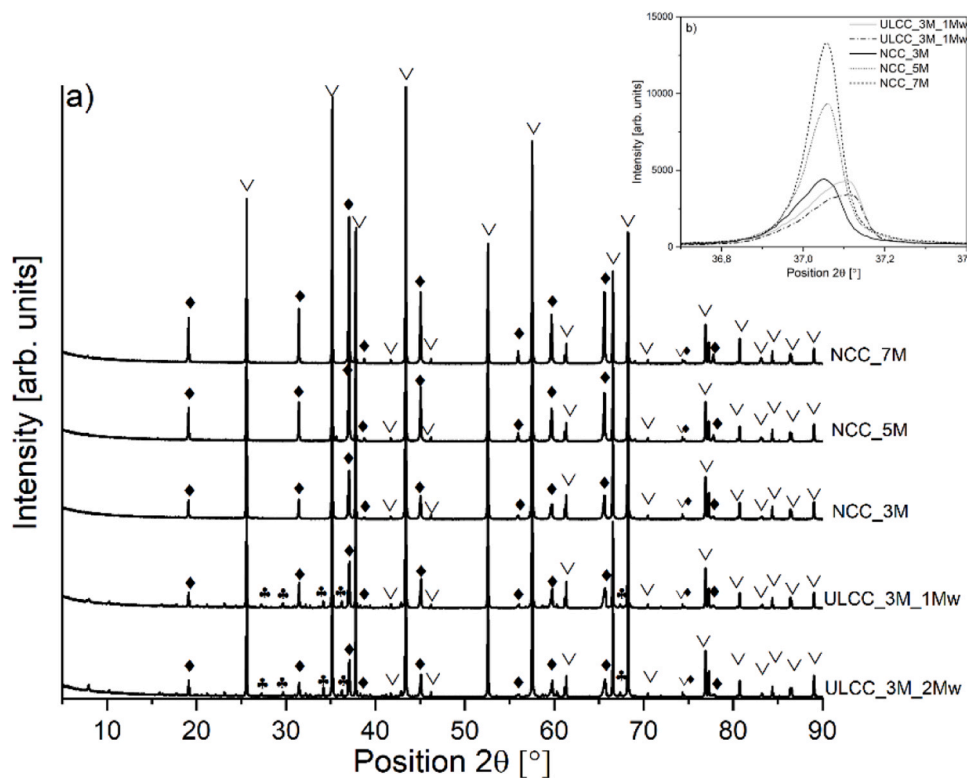


Fig. 4. Low-temperature XRD patterns of ULCCs and NCCs in the range of 5–90° (a) and 36.7–37.4° (b). Down arrowheads: α - Al_2O_3 (JCPDS Card No. 96–900–9674), black diamond: Al-excess Mg-Al spinel ss (ICSD Card No. 98–005–6355) and Mg-Al spinel ss (ICSD Card No. 98–009–6833), clover: CA_6 , (ICDD Card 01–084–1613).

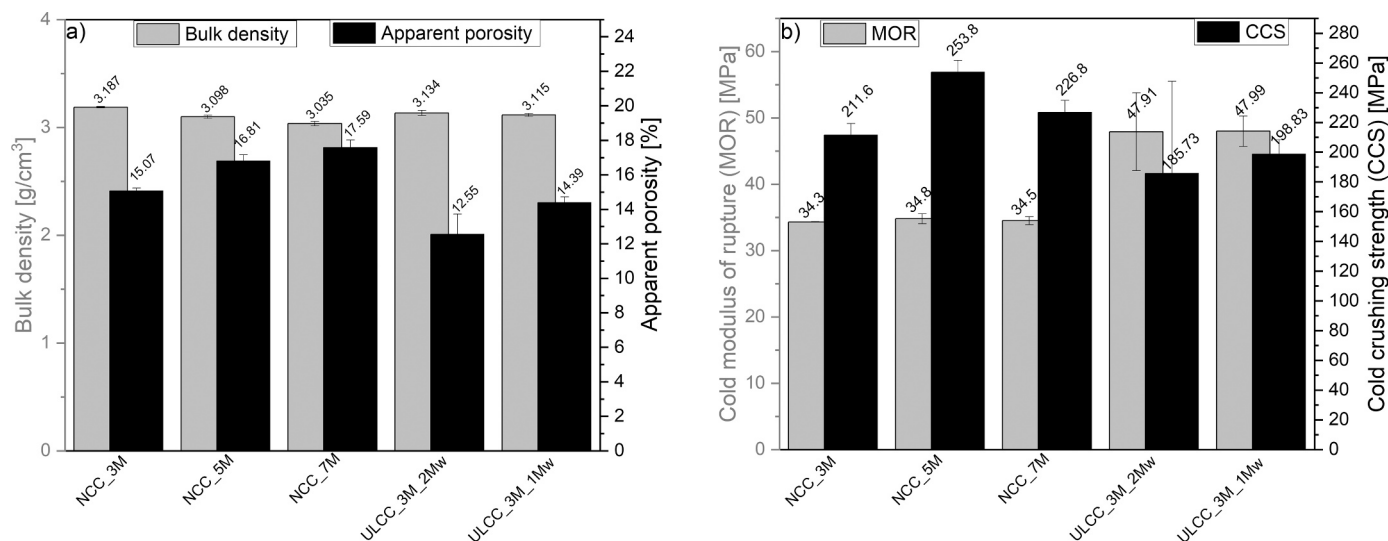


Fig. 5. Summary of the apparent porosity, bulk density (a) and mechanical properties (b) of NCCs and ULCCs after firing at 1500°C.

distribution of spinel phase, and (iv) the porosity of the castables.

3.2. Characteristic of phase composition and physical properties of NCCs and ULCCs

The castables samples were analysed using XRD to determine the phase composition of mentioned samples and to monitor changes in magnesium aluminate spinel stoichiometry. XRD measurement was performed on samples obtained by crushing and grinding a piece of castables. Fig. 4a presents the low-temperature XRD patterns of both CAC-free spinel-forming castables and CAC-containing alumina-based

spinel-forming/spinel-containing mixed castables samples after firing at 1500 °C. Fig. 4b presents the same diffractogram of the examined castables within the narrower range 2 theta of 36.7–37.4°. Additionally, the separation of main diffraction peak associated with magnesium aluminate spinel was carried out using Gaussian deconvolution. The summary of Gaussian deconvolution is presented in Table 5. Table 6 shows the quantitative phase composition of the both ULCCs and NCCs by the Rietveld method. Table 7 summarizes both lattice and oxygen parameters of the Mg-Al stoichiometric spinel ss and Al-excess Mg-Al spinel ss.

The XRD analysis revealed the presence of α - Al_2O_3 (JCPDS Card No. 96–900–9674), Al-excess Mg-Al spinel ss (ICSD Card No. 98–005–6355)

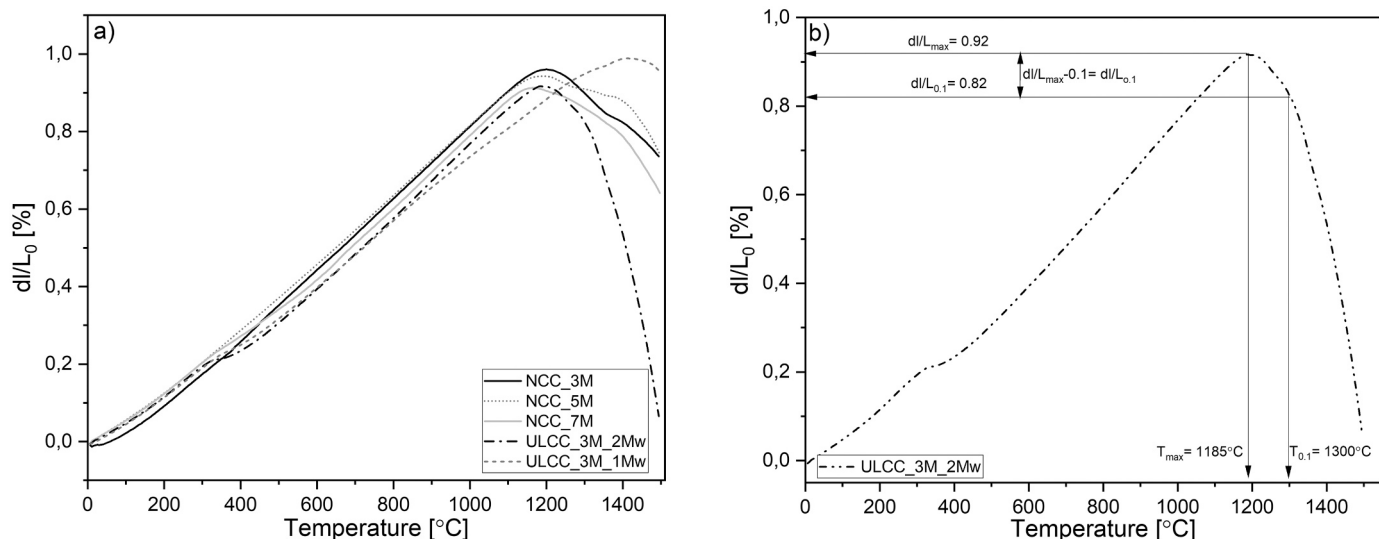


Fig. 6. RUL data for both NCCs and ULCCs prefired at 1500°C for 10 h (a) and RUL data for ULCC_3M_2Mw sample (b) with the methodology of characteristic temperature determining.

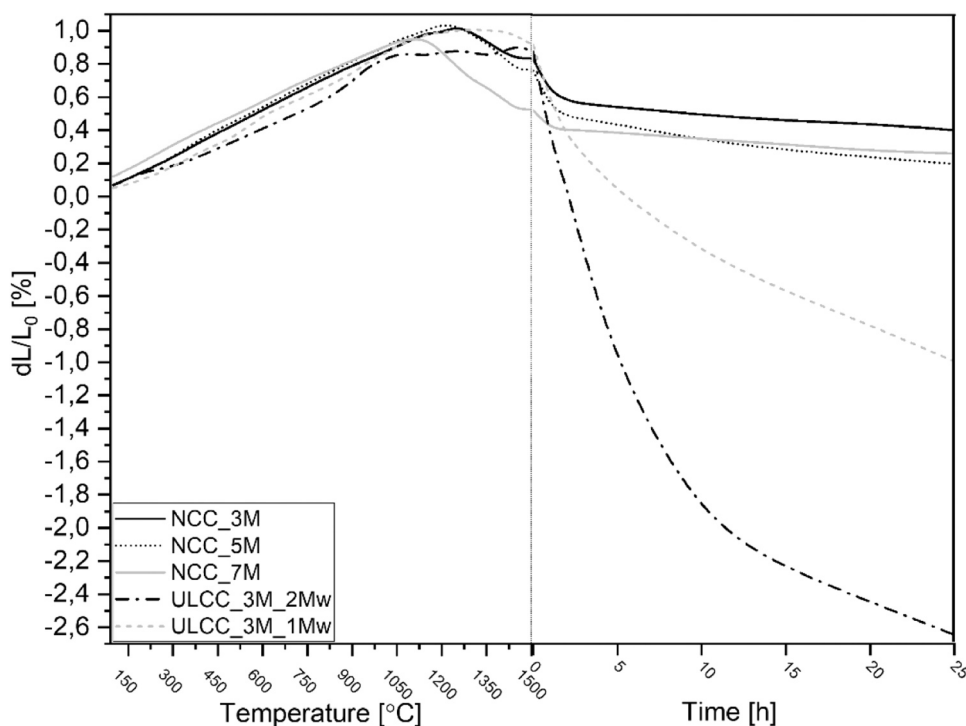


Fig. 7. Creep resistance (24 h at 1500 °C) of both ULCCs and NCCs prefired at 1500°C for 10 h.

and Mg-Al spinel ss (ICSD Card No. 98–009–6833) as the major phases in each samples and CA_6 (ICDD Card No. 98–020–2616) as minor phase in CAC-containing alumina-based spinel-forming/spinel-containing mixed castables. The amount of magnesium aluminate spinel phase in NCCs results from the spinel formation as a consequence of reactive sintering of MgO and Al_2O_3 while in ULCCs is a sum of both the addition of prefabricated spinel as aggregates and generated in situ. We have previously demonstrated [31] that by combining dead-burned MgO with a water-dispersed sol of fumed Al_2O_3 as a refractory castable matrix and properly selecting the curing conditions leads to $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ synthesis. The thermal decomposition of samples containing primarily Mg-Al hydrotalcite ultimately results in the formation of Mg-Al spinel and magnesium oxide [33]. The obtained results

did not show the presence of MgO in the both CAC-free and CAC-containing castables matrix. Magnesium oxide both added and formed as a result of thermal decomposition and calcination of Mg-Al hydrotalcite, finally reacted with the alumina oxide to generate spinel. Additionally, these results confirm also that fully reacted samples were obtained.

According to obtained results (Fig. 4a,b), it can be seen, that the main diffraction peak associated with magnesium aluminate spinel shifts towards a higher 2θ value. This indicates that Al-excess Mg-Al spinel was obtained in the examined samples due to the excess of alumina oxide in relation to magnesium oxide. It is worth noting that the position of characteristic diffraction peak belonging to spinel for both ULCC_3M_1Mw and ULCC_3M_2Mw samples was more shifted towards a

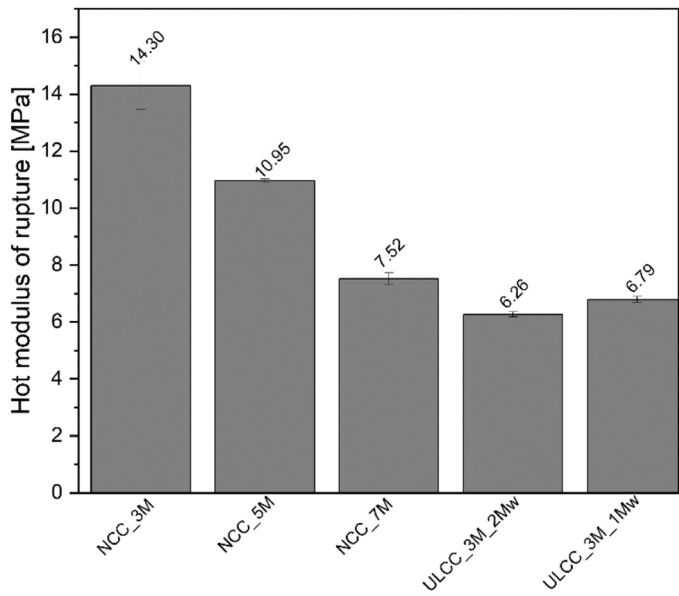


Fig. 8. HMoR (at 1450 °C) of both NCCs and ULCCs prefired at 1500°C for 10 h.

Table 3
Temperatures of first liquid phase formation for all castable compositions.

CAC-free spinel-forming castables			CAC-containing alumina-based spinel-forming/ spinel-containing castables		
NCC_3M	NCC_5M	NCC_7M	ULCC_3M_2Mw	ULCC_3M_1Mw	
1471 °C	1471 °C	1471 °C	1432 °C	1432 °C	

higher 2θ value than for CAC-free spinel-forming castables samples. This indicates that Al-rich magnesium aluminate spinel aggregates were also enriched in aluminium ions during firing process. Table 5 presents the summary (full width at half maximum (FWHM), fitted 2θ position, area intg.) of the separation of main diffraction peak associated with magnesium aluminate spinel. The obtained results for CAC-free samples confirms the presence of both Al-excess Mg-Al spinel ss and Mg-Al spinel ss in a 2θ position approximately 36.97° and 37.06°, respectively. Interestingly, obtained results for CAC-containing samples indicates the presence of not only Mg-Al spinel ss but also Al-excess Mg-Al spinel ss with two maxima in a 2θ position approximately 37.07° and 37.12°. The

Table 4
Mass fraction of liquid obtained from FactSage 8.2 calculation versus temperature for NCC_3M, NCC_5M, NCC_7M, ULCC_3M_2Mw and ULCC_3M_1Mw castable compositions.

Castable compositions	Temperature / °C									
	1500	1550	1600	1650	1700	1750	1800	1850	1900	2000
NCC_3M	2.43	2.67	2.95	3.28	3.71	4.29	5.16	6.64	9.68	67.03
NCC_5M	2.43	2.67	2.95	3.28	3.71	4.29	5.16	6.64	9.68	100
NCC_7M	2.45	2.70	2.98	3.31	3.74	4.33	5.21	6.70	9.77	100
ULCC_3M_2Mw	2.76	3.09	3.60	4.57	6.27	7.61	9.61	12.88	19.18	84.01
ULCC_3M_1Mw	2.76	3.09	3.60	4.57	6.32	7.67	9.68	12.98	19.31	84.81

Table 5
Results of fitting of XRD fitted to the Gaussian function of spinel phase.

Sample	Mg-Al spinel ss			Al-excess Mg-Al spinel ss		
	FWHM [°]	Fitted position 2θ [°]	Area Intg [%]	FWHM [°]	Fitted position 2θ [°]	Area Intg [%]
NCC_7M	0.10439	36.999	30.29	0.07844	37.063	69.71
NCC_5M	0.12913	36.982	27.71	0.09091	37.060	72.29
NCC_3M	0.11696	36.958	24.92	0.10795	37.052	75.08
ULCC_3M_1Mw	0.11545	36.928	11.86	0.136740.06364	37.06037.121	69.5518.59
ULCC_3M_2Mw	0.14308	36.965	22.71	0.132150.04474	37.08337.129	69.248.05

2θ position and thus the difference in magnesium alumina stoichiometry result from the initial castable composition. Moreover quantities of both Al-excess Mg-Al spinel ss and Mg-Al spinel ss evaluated by the Rietveld method were consistent with surface area of Gaussian deconvoluted diffraction peaks.

According to the Rietveld quantitative analysis method (Table 6), the highest content of Al-excess Mg-Al spinel ss was obtained in NCC_7M sample which results directly from the highest magnesium oxide content in castable composition. The ULCC_3M_1Mw, ULCC_3M_2Mw and NCC_3M castables should have comparable amount of Mg-Al spinel. Nevertheless, according to obtained results and Rietveld quantity analysis, ULCC_3M_1Mw sample contain higher total amount of magnesium-aluminate spinel (16.9 wt%) than castables with equal content of MgO. The total amount of magnesium- aluminate spinel is the sum of both Mg-Al spinel ss and Al- excess Mg-Al spinel ss. The Al-excess Mg-Al spinel ss content in ULCC_3M_1Mw is highest which is associated with the highest Al³⁺ ion enrichment which is confirmed by both integrate area under the peak and fitted position 2θ (Table 5). Additionally, Al-rich Mg-Al spinel ss in ULCC_3M_1Mw may be characterized by higher degree of

Table 6
The quantitative phase composition of both ULCCs and NCCs samples by the Rietveld method.

Phase	Sample				
	NCC_7M	NCC_5M	NCC_3M	ULCC_3M_1Mw	ULCC_3M_2Mw
	wt% according to Rietveld method				
Al-excess Mg-Al spinel ss	21.3	19.1	10.9	14.2	10.3
Mg-Al spinel ss	9.8	6.7	3.5	2.7	3.9
α-Al ₂ O ₃	68.9	74.2	85.6	78.7	81.2
CA ₆	-	-	-	4.4	4.6

Table 7
Lattice and oxygen parameters of the Mg-Al spinel phases.

Phase	Lattice parameter a ₀ [Å]	Oxygen parameter
Stoichiometric Mg-Al spinel ss	8.0670	0.23739
Al-excess Mg-Al spinel ss	8.0410	0.23970

crystallinity. Lattice parameter decreases with the amount of excess Al^{3+} ions (Table 7). The decrease in lattice parameter is due to the smaller ionic radius of Al in comparison to Mg [37,38].

It is worth to notice that the differences between Mg-Al spinel both stoichiometry and quantity may affect the microstructure and thermo-mechanical properties of castables.

Fig. 5a-b illustrate the results of bulk density, apparent porosity, CCS and MOR of CAC-containing and CAC-free corundum castables after heat treatment at 1500 °C. Mentioned measurements were performed to determine the relationship between castables composition and physical properties. According to obtained results, bulk density slightly decreased whereas apparent porosity increased with increase of Al-excess Mg-Al spinel content for both CAC-free and CAC-containing castables. The in-situ spinel formation via sintering of magnesium and alumina oxides is associated with a volume increase, which result in an increase in the apparent porosity, as well as induce the formation of several microcracks in the microstructure [64]. This is why in CAC-free spinel-forming castables the apparent porosity increase with the increased MgO content in initial castables composition. An inverse relationship was observed in case of CAC-containing alumina-based spinel-forming/spinel-containing mixed castables. It is clearly seen that amount of magnesium oxide did not significantly affect the bulk density.

MOR (Fig. 5b) of CAC-free samples suggests that the amount of the magnesium-aluminate spinel phase no influence the cold modulus of rupture. In case of application of CAC than mixed oxide binder, a significant improvement in bending strength is observed (about 38%). The significant improvement in MOR of CAC-containing castables results from CA_6 enhances direct bonding between alumina and spinel grains. Obtained results suggest that the application of prefabricated magnesium-aluminate spinel was more beneficial than presence of generated in situ in terms of MOR.

It is worth noting that CAC-free castables are characterized by higher CCS than CAC-containing castables, despite higher apparent porosity. Moreover, NCC_3M sample is characterized by much better compressive strength than both ULCC_3M_2Mw and ULCC_3M_1Mw castables which contain similar MgO amount. This suggest, that the use of magnesium and alumina oxides as in situ spinel precursors was more advantageous than prefabricated spinel as castable matrix component in view of CCS. This was probably related to both particle size and more even distribution of spinel within the castable matrix and alumina-spinel grains direct bonding. Nevertheless, comparing the bulk density, apparent porosity and mechanical test results obtained only for ULCCs it can be concluded that the application of prefabricated spinel was more advantageous than generated in situ.

3.3. Composition effects on the thermo-mechanical behavior of smart ULCCs and NCCs refractory

3.3.1. Refractoriness Under Load (RUL) test

Fig. 6 shows thermomechanical behavior in term of RUL of CAC-free

and CAC-containing castables. The characteristic temperatures including peak temperature (T_{max} , the temperature corresponding to the maximum linear expansion point) and temperatures of deformation $T_{0.05}$, $T_{0.10}$, $T_{0.15}$, $T_{0.20}$, $T_{0.25}$, $T_{0.30}$, $T_{0.35}$, $T_{0.40}$, $T_{0.45}$ and $T_{0.5}$ (the temperatures corresponding to the deformation of 0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% and 0.50% of initial height, respectively) are the most important determinant of RUL. According to various sources of literature, $T_{0.5}$ is considered as the recommended maximum working temperature of the examined refractory castables [65]. For samples for which it was impossible to determine $T_{0.5}$ based on the RUL test results, the theoretical temperature $T_{0.5}$ was determined. The summary of characteristic temperatures for each castables is presented in Table 8. Generally, RUL of the refractory castables depends on three microstructural features termed; (1) apparent porosity, (2) amount, composition and distribution of glassy phases, and (3)-size, morphology and distribution of the crystalline phases.

All refractory castables samples revealed similar expansion behavior in the temperature range from 20 °C to 1175 °C. In the given temperature range, the thermal expansion coefficient varied from $7.66 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$ to $8.82 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$ for ULCC_3M_1Mw and NCC_3M, respectively. According, to the obtained results and corresponding literature sources [18], it can be noticed that the determined thermal expansion coefficient is similar to thermal expansion coefficient of corundum $8.5 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$. Comparing the results obtained for CAC-free spinel-forming castables it can be noticed that with the increasing magnesium aluminate spinel content, thermal expansion coefficient decreased which is associated with a lower thermal expansion coefficient for spinel than corundum ($\alpha_{\text{Al}_2\text{O}_3} = 8.5 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$, $\alpha_{\text{spinel}} = 7.6 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$). Further temperature increase above 1175 °C lead to continuous subsidence of all samples which was associated with the softening of the refractory structures. Nevertheless, the subsidence rate of the samples was different and dependent on the castables matrix composition and, consequently, the amount, particle size and distribution of spinel, apparent porosity and amount of liquid phase. The softening of structure and liquid phase formation was explained through thermodynamic simulation via FactSage 8.2.

The maximum expansion of ULCC_3M_2Mw castable made using high purity CAC was 0.92% at 1185 °C and $T_{0.50}$ was 1427 °C. Above 1185 °C mentioned sample started to rapidly deform under combined effects of mechanical load and increasing temperature. This was associated with the softening and melting of low melting point phases in the matrix. According to other literature sources [22–24] and obtained results it can be suspected that due to the presence of SiO_2 in castable composition, both CAS_2 and C_2AS were formed locally in micro-areas, which could have been associated with the formation of liquid phase at mentioned temperature. Moreover, it can be suggested that application of prefabricated spinel was more favorable in CAC-containing alumina-based spinel-forming/spinel-containing mixed castables than generated in situ from the perspective of RUL. Quite different behavior is presented by each CAC-free spinel-forming castables, dl/L_0 -temperature

Table 8

Characteristic temperatures of the corundum- spinel refractory castables based on the RUL tests.

Samples	NCC_3M	NCC_5M	NCC_7M	ULCC_3M_2Mw	ULCC_3M_1Mw
T_{max} [°C]	1200	1191	1159	1185	1410
dl/L_{max} [%]	0.96	0.94	0.91	0.92	0.99
$T_{0.05}$ [°C]	1285	1341	1298	1260	1500
$T_{0.10}$ [°C]	1340	1435	1373	1300	-
$T_{0.15}$ [°C]	1415	1470	1422	1324	-
$T_{0.20}$ [°C]	1469	1495	1457	1344	-
$T_{0.25}$ [°C]	-	-	1467	1357	-
$T_{0.30}$ [°C]	-	-	-	1377	-
$T_{0.35}$ [°C]	-	-	-	1390	-
$T_{0.40}$ [°C]	-	-	-	1406	-
$T_{0.45}$ [°C]	-	-	-	1414	-
$T_{0.50}$ [°C]	1658(Theoretical)	1604 (Theoretical)	1596(Theoretical)	1427	1549(Theoretical)
α [K^{-1}]	$8.82 \cdot 10^{-6}$	$8.49 \cdot 10^{-6}$	$8.17 \cdot 10^{-6}$	$8.03 \cdot 10^{-6}$	$7.66 \cdot 10^{-6}$

curves were almost horizontal which is probably associated with both better distribution of ultra-fine grained spinel and structural stability as a result of alumina-spinel grains direct bonding due to both matrix composition and application of sol.

Based on the obtained results, RUL curves for CAC-free spinel-forming and ULCC_3M_1Mw castables were extrapolated in order to determine the theoretical characteristic temperature $T_{0.50}$. Characteristic temperature $T_{0.5}$ was determined with a very good correlation, with regression coefficient (r^2) values higher than 0.99. According to the obtained results it can be seen that all analyzed CAC-free spinel-forming castables are characterized by a high theoretical $T_{0.5}$ (Table 8) while both ULCCs castables has significantly lower recommended working temperature. This may suggest higher amount of liquid phase at mentioned temperatures in ULCCs than NCCs. Additionally, the obtained results should be compared with the results of the CIC and TSR in order to evaluate the structural stability of materials and assess the applicability of the designed castables.

3.3.2. Creep in Compression (CIC) test

Creep resistance similarly to RUL depends on microstructural features such as liquid phase, apparent porosity and size and location of crystalline phases. To investigate the structural stability of the CAC-containing and CAC-free refractory castables during long-term exposure at elevated temperatures and under compressive stress, the creep strain-time curves at 1500 °C were analysed, as depicted in Fig. 7. It is worth noting that CAC-free spinel-forming castables were creep resistant and presented quite similar results despite significantly different magnesium aluminate spinel content. Higher in situ spinel content should influence the greater amount of both cracks and pores in the microstructure which deteriorate the creep resistance. Comparing the results obtained for CAC-free castables it is clearly seen that NCC_3M castable is characterized by the highest creep resistance that can be directly related to the apparent porosity and thus with microstructure. Moreover, considering the apparent porosity higher creep for the NCC_7M castables should be expected because it exhibits the highest values after sintering at 1500°C for 10 h (Fig. 5a). Nevertheless, the highest creep was observed for both CAC-bonded alumina-spinel castables which were characterized by low apparent porosity. Obtained results suggests that application of both pre-formed spinel and CAC as binder were unfavorable.

According to the θ -projection model [60,66], two parts can be distinguished in a typical creep curve, i.e. the primary stage showing a declined creep rate and the stationary stage with a constant creep rate, which can be expressed by the Eq. 3. The θ_i parameters, i.e. θ_1 and θ_2 refer to the total strain and curvature in the primary stage, respectively while $\theta_3 \bullet \theta_4$ parameter is analogue to the creep rate in the second stage [60–63, 66]. For all analyzed castables, the fitting of the θ_i parameters resulted in a very good correlation, with regression coefficient (r^2) values higher than 0.96. Based on Eqs. 3 and 4 and employing the mathematical fitting by using the Origin software, the creep rate of samples in the second stage were calculated and the results are shown in Table 9. The calculated creep rate in second stage of CAC-free spinel-forming castables was order of magnitude lower than creep rate of CAC-bonded alumina-spinel castables. This clearly indicates that, CAC-free spinel-forming castables are a better alternative to CAC-containing alumina-based spinel-forming/spinel-containing mixed castables in terms of view of technological properties.

All these results imply that the presence of liquid phase played the most important role in the creep behavior of the analyzed refractory castables. Probably the liquid phase formation occurred at lower temperature for the CAC-bonded alumina-spinel castables than CAC-free spinel-forming castables as confirmed by the thermodynamic simulation via FactSage 8.2. Moreover, higher liquid phase content for CAC-containing alumina-based spinel-forming/spinel-containing mixed castables should be expected. Temperatures of first liquid phase formation and amount of the liquid phase results directly from castable matrix composition and thus with type of used binder. Additionally, CIC of the refractory castables depends on microstructural features such as the amount of spinel phase and particle size distribution of all crystalline phases.

3.3.3. Hot Modulus of Rupture (HMoR)

The HMoR is mainly influenced by both microstructure and liquid phase contents in the castables. Fig. 8 illustrates the effect of composition on HMoR of CAC-bonded alumina-spinel castables and CAC-free spinel-forming castables. As indicated in Fig. 8 the HMoR of CAC-bonded castables are lower than that of castables without calcium alumina cement. Moreover, comparing the MOR (Fig. 5b) and HMoR (Fig. 8) measurements results it can be seen that HMoR as opposed to MOR significantly depends on the spinel content (Table 6). According to the obtained results it is clearly seen that, with the increasing in situ spinel content the HMoR decreased. This is probably associated with microstructural features like apparent porosity (Fig. 5b), amount and distribution of magnesium aluminate spinel phase and amount, composition and distribution of glassy phases. Additionally, loosening of structure found in some regions of spinel grains. Despite equal content of MgO at 3 wt% for NCC_3M and both ULCC_3M_1Mw and ULCC_3M_2Mw castables, the HMoR properties of mentioned castables are not comparable. The CAC-containing alumina-based spinel-forming/spinel-containing mixed castables presented more than twice lower hot strength than NCC_3M sample. It may therefore be concluded that the HMoR properties of both ULCC_3M_1Mw and ULCC_3M_2Mw castables mainly depended on presence of greater amounts of liquid phase which was confirmed by FactSage 8.2 simulations. Additionally, ULCC_3M_1Mw sample presented slightly higher hot elastic modulus what suggest that for ULCCs the use of pre-formed spinel was more advantageous than generated in situ.

3.3.4. Thermal Shock Resistance (TSR)

Among the diverse phenomena causing the wear of refractory linings, the harsh alteration of temperature at the surface (thermal shock) is the most likely to lead to premature and uncontrolled wear. Proper evaluation of resistance to thermal shock is a key issue for both producers and users of refractory materials. This is why refractory technologists are forced to develop smart and modern materials with outstanding the TSR. An equally important is to develop a method that allows evaluate and compare the TSR of refractory materials.

The results of the percent sonic velocity vs. heating and cooling cycle number, as well as the results CCS and MOR are summarised in Fig. 9 and Fig. 10a, b, respectively. According to the obtained results it can be seen that with each successive heating and cooling cycle the sonic velocity decreased. It is clearly seen that, for CAC-free spinel-forming castables changes in sonic velocity and mechanical properties are directly associated with magnesium aluminate spinel content.

Table 9

Summary of θ_i parameters calculation for corundum- spinel refractory castables based on the CIC tests.

Samples	NCC_3M	NCC_5M	NCC_7M	ULCC_3M_2Mw	ULCC_3M_1Mw
T_{max} [°C]	1250	1200	1100	1450	1300
dI/L [%]	1.03	1.04	0.95	0.91	1.01
$\theta_3 \bullet \theta_4$ [%/min]	$-5.37 \bullet 10^{-5}$	$-4.20 \bullet 10^{-5}$	$-7.01 \bullet 10^{-5}$	$-2.98 \bullet 10^{-4}$	$-4.02 \bullet 10^{-4}$
r^2	0.996	0.995	0.960	0.999	0.999

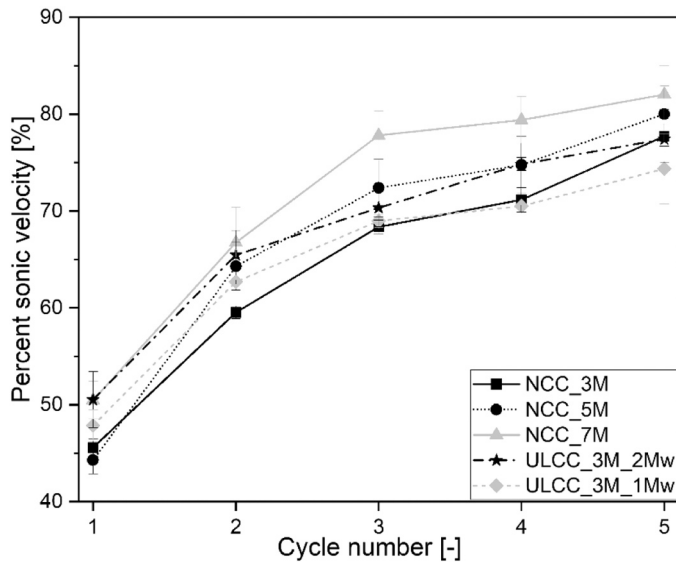


Fig. 9. Percent sonic velocity after each heating and cooling cycle.

According to scientific knowledge and obtained results, the process of in-situ spinel formation is related to an increase in volume and thereby in an increase in apparent porosity (Fig. 5a). As the apparent porosity increase, the amount of stress concentrators increase also. This leads to the formation of greater number of microcracks in the microstructure which was confirmed by faster decrease in both sonic velocity and mechanical strength for NCC_7M and NCC_5M than NCC_3M castables. Additionally, a network of microcracks which were formed within the fine-grained NCC_3M castable matrix absorbed the energy of another crack's propagation probably. Thus the TSR for NCCs which had the content of MgO as 3 wt% was improved. It can be suspected that the character of the microcracks in NCC_3M castable was different than in other NCCs, which was confirmed by microstructural examination.

The results obtained for ULCCs show that ULCC_3M_1Mw presents higher TSR than ULCC_3M_2Mw sample. The significant difference in the results is probably associated with the CA_6 distribution within the microstructure. The location of calcium hexaluminate crystals depends on the type of spinel (generated in situ and pre-formed) [12]. This suggests that in ULCCs application of pre-formed spinel was more

favourable than generated in situ. Summing up the results of castables with 3 wt% MgO it can be concluded that despite similar results of percent sonic velocity after each heating and cooling cycle, technologically most appropriate variant of analysed castables was NCC_3M due to the lowest percentage decrease in mechanical strength.

3.4. Microstructural examination

The microstructure of the studied castables was examined by means of SEM analyses on polished samples before and after first thermal shock. Fig. 11 a-e shows the microstructure of the castables after heat treatment at 1500 °C; NCC_3M (a), NCC_5M (b), NCC_7M (c), ULCC_3M_2Mw (d) and ULCC_3M_1Mw (e). Figs. 12 and 13 show the microstructure of the same castables after the first thermal shock. The low-magnification SEM images of the NCCs samples can be seen in Fig. 12a-c together with the element distribution maps for two selected elements Mg and Al. The low-magnification SEM images of the ULCCs samples can be seen in Fig. 13a-b together with the element distribution maps for two selected elements Mg, Al and Ca. However, Si and O were omitted from the presentation in these figures. Characteristic X-ray energy maps of Mg and Al or Mg, Al and Ca are very effective in revealing the location and distribution the alumina and spinel phase or alumina, spinel phase and calcium hexaluminate (CA_6) within the microstructure of both NCCs (Fig. 12a-c) and ULCCs (Fig. 13a-b), respectively.

It can be seen from Figs. 11a-e, 12a-c and 13a-b that both NCCs and ULCCs are composed of fractions of fine to fairly coarse particles. The NCCs microstructure after heat treatment at 1500 °C consists of corundum aggregates, held together by a bond of fine alumina and Al-rich spinel phase which is different stoichiometry. The ULCCs microstructure after heat treatment at 1500 °C consists of corundum aggregates, held together by a bond of fine alumina, Al-rich spinel phase with different stoichiometry and calcium hexaluminate or CA_6 (Fig. 11d-e). In addition, in order to better differentiate the microstructure elements, the corundum aggregates has been marked in white. The corundum aggregates are marked as A, fine-grained matrix is designated as B. Elemental distribution maps of main regions in the NCCs after one thermal shock cycle in water at 950 °C show homogeneous distribution of Al and Mg in the two phases present. The Mg sites are concentrated within the Al-rich spinel phase located within the fine-grained castable matrix (Fig. 12a-c). Generally, Fig. 12a-c confirms the homogeneous distribution of spinel grains in the matrix of NCCs. Samples ULCCs are typical of a microstructure showing additional CA_6 bonding between

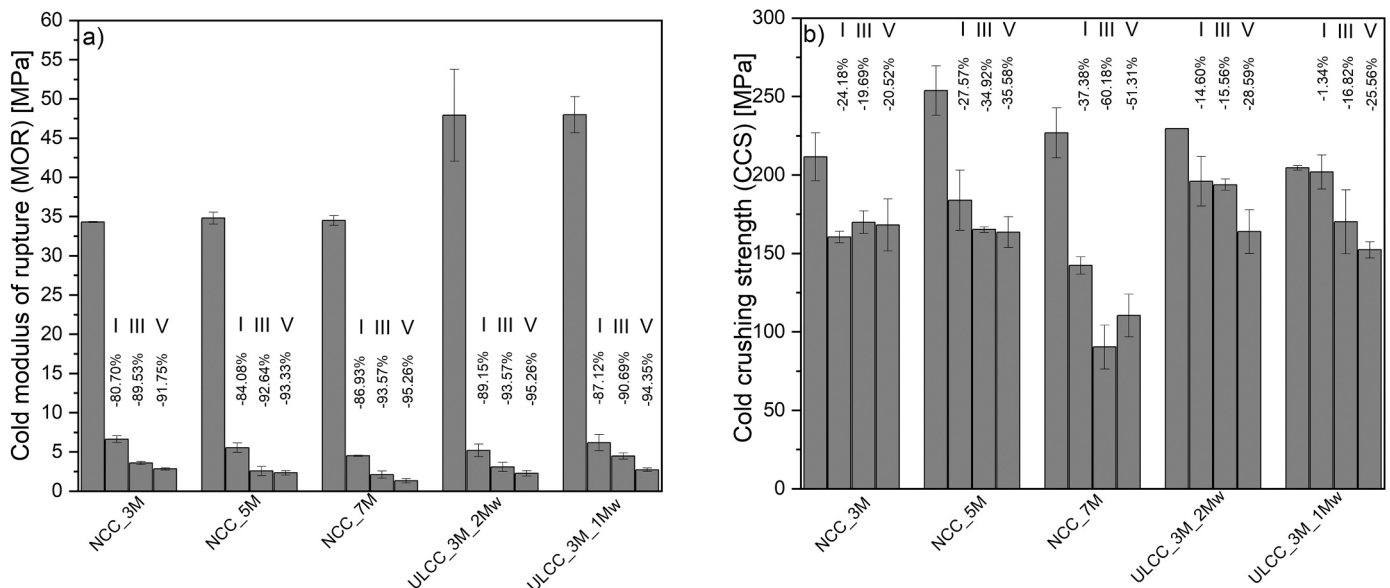


Fig. 10. Mechanical properties of NCCs and ULCCs before and after 1., 3., 5. heating and cooling cycle.

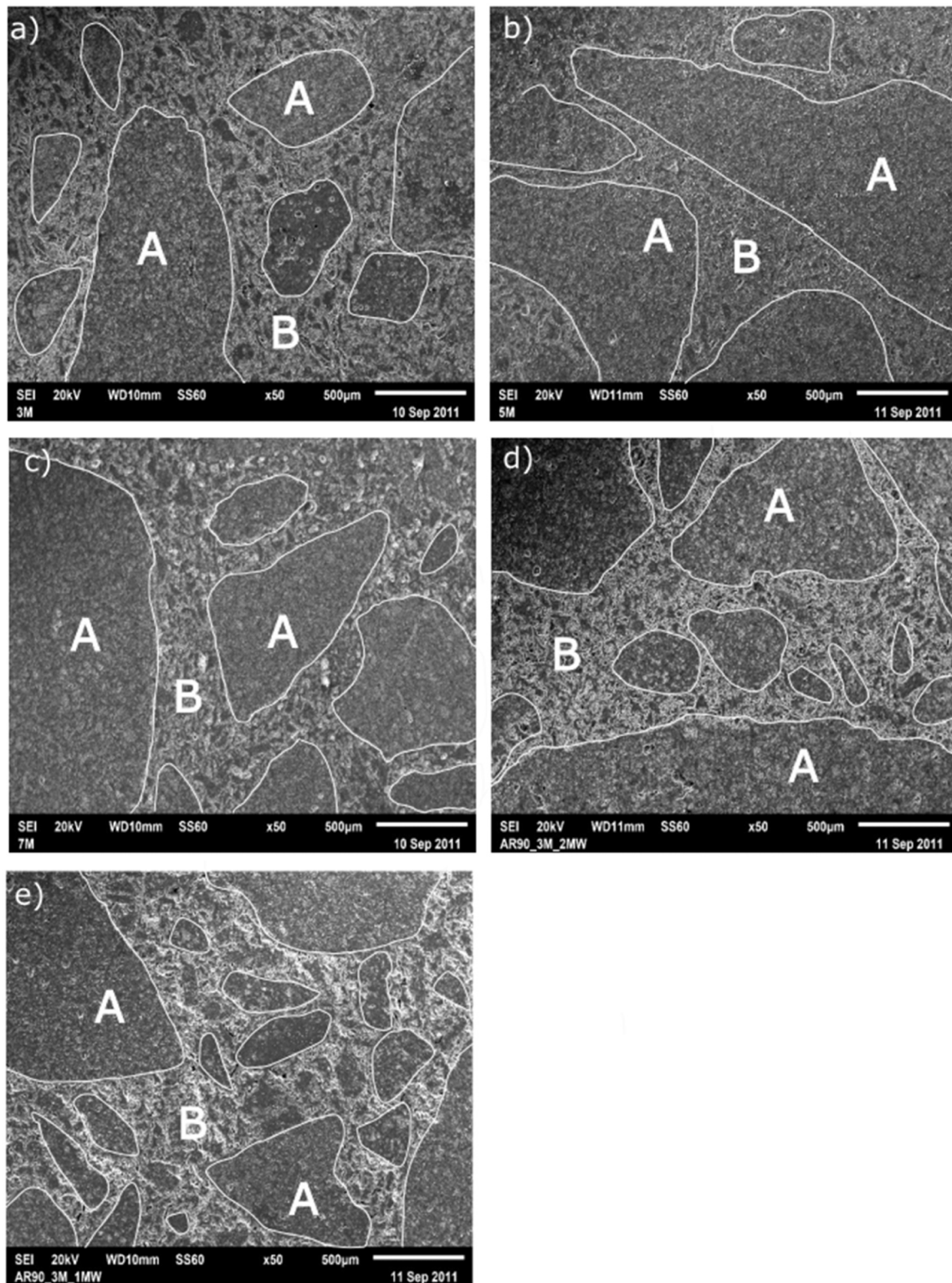


Fig. 11. Microstructural overview of the castables after heat treatment at 1500 °C and before the first thermal shock cycle; NCC_3M (a), NCC_5M (b), NCC_7M (c), ULCC_3M_2Mw (d) and ULCC_3M_1Mw (e). A- corundum aggregates, B- fine-grained matrix.

alumina and Al-rich spinel phases (Fig. 13a-b). Because of the thermal expansion mismatch between the alumina and Al-rich spinel in the NCCs ($\alpha_{\text{Al}_2\text{O}_3} = 8.5 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_{\text{spinel}} = 7.6 \cdot 10^{-6} \text{ K}^{-1}$) [50–52], and alumina, Al-rich spinel and CA_6 in the ULCCs, cracks nucleate at the level of the fine grained matrix boundaries after the sintering and the first thermal shock cycle in water at 950 °C, as can be seen in Figs. 12–13. Moreover, CA_6 exhibits significant thermal expansion

coefficient anisotropy, $\alpha_p = 11.8 \cdot 10^{-6} \text{ K}^{-1}$ and $\alpha_b = 7.5 \cdot 10^{-6} \text{ K}^{-1}$ within the temperature range between 20 and 800 °C, where b and p indicate basal planes and perpendicular to the basal planes, respectively [52].

It was found that the MgO or spinel content was able to alter the thermal shock characteristics of the NCCs, as presented in Fig. 12a-c. The NCCs which had the content of MgO as 3 wt% was able to develop a

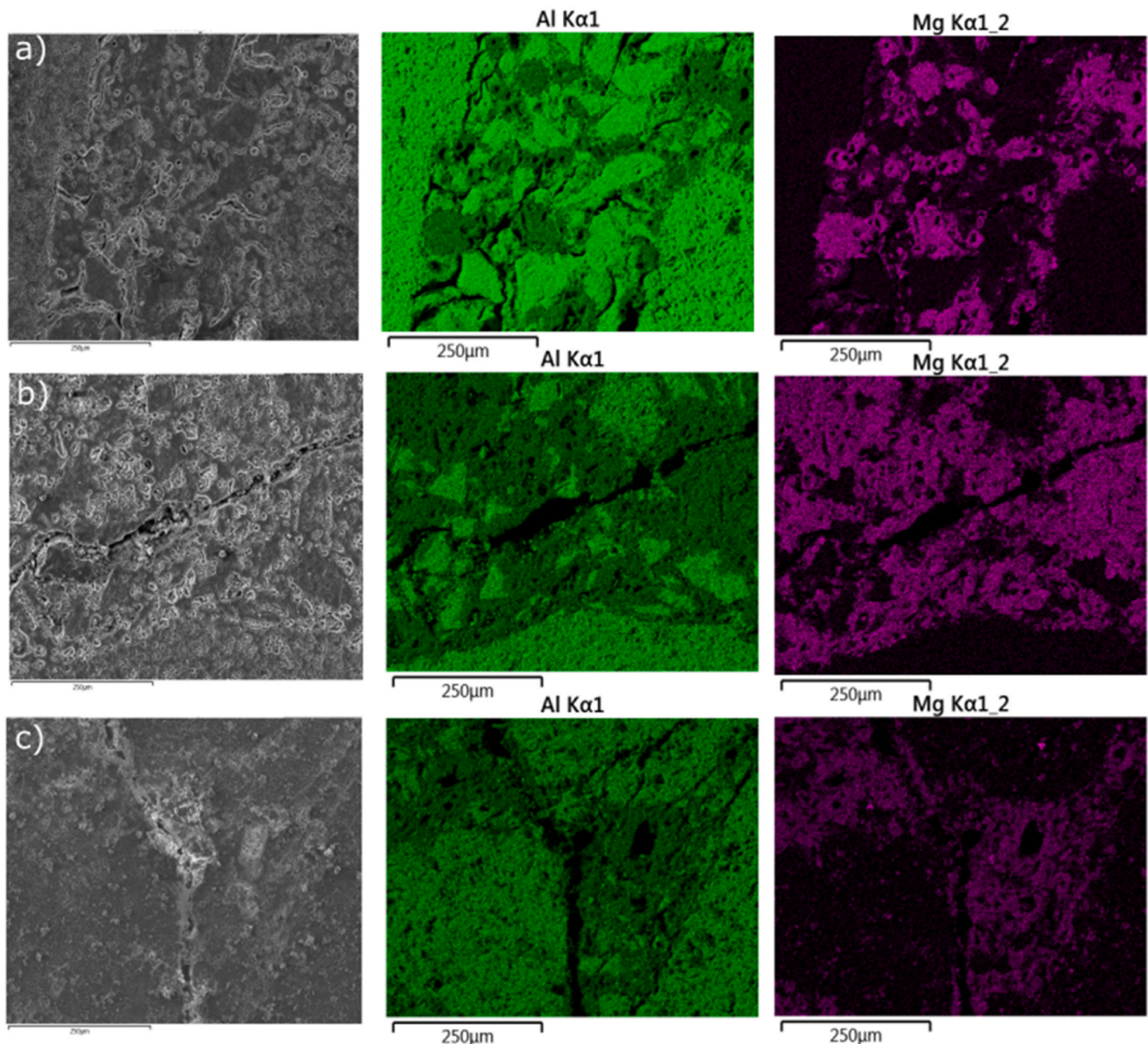


Fig. 12. Microstructure and EDS element distribution maps (Mg, Al) of the NCCs after heat treatment at 1500 °C and after one thermal shock cycle in water at 950 °C; NCC_3M (a), NCC_5M (b), NCC_7M (c).

network of small microcracks within the fine-grained castable matrix. Those microcracks can later absorb the energy of another crack's propagation, and are particularly important in imparting TSR on castables. The NCCs containing the 5 and 7 wt% of MgO showed more significant evidence of thermal shock while undergoing a similar heating cycle. Here, the stresses induced by the temperature difference of the thermal shock causes nucleation of deep and wide cracks within the matrix because of obvious high degree of connections between the alumina and spinel grains. These cracks are also able to propagate within the matrix and along the alumina aggregate grains, where the individual grains of alumina were very effectively separated from the binder matrix (Fig. 12c). Elemental X-ray distribution image of NCCs showing crystal boundaries and Mg distribution demonstrates that the sample with 3 wt% MgO shows a spinel phase separation (Fig. 12a). The samples with 5 and 7 wt% begin to exhibit spinel phase connection and the amount of this phase increases with the increase of MgO content within the NCCs matrix. Based on the microstructural examination and other results, the TSR of the NCCs can be ordered according to the MgO

content as the NCCs with 3 wt% with the best TSR, and the NCCs with 7 wt% with the worst TSR.

From the Fig. 13a-b, it is observed that a calcium-enriched phase is distinguishable from the X-ray mapping of the ULCCs. Its concentration was extremely high in the region of plate-like shape of CA_6 crystals. An important aspect related to CA_6 distribution is its location within the microstructure of ULCCs, where CA_6 crystals have occurred in the fine-grained matrix region (comprised by alumina and spinel), at the border of the tabular alumina coarse aggregates and inside the aggregates. The obtained results can be clearly confirmed by other authors [12–17, 67, 68] according to which CA_6 location depends on the spinel source (in situ generated or pre-formed) and the microsilica content. Here, the location and morphology influence various castables' properties, such as thermomechanical properties and TSR. Based on the microstructural examination and other results, the best TSR of the ULCC's exhibits the sample ULCC_3M_1Mw with two spinel sources i.e. in situ generated and pre-formed (mixing thereof), where pre-formed spinel was dominated. The TSR of ULCC's with the mixed spinel sources is closely related to the

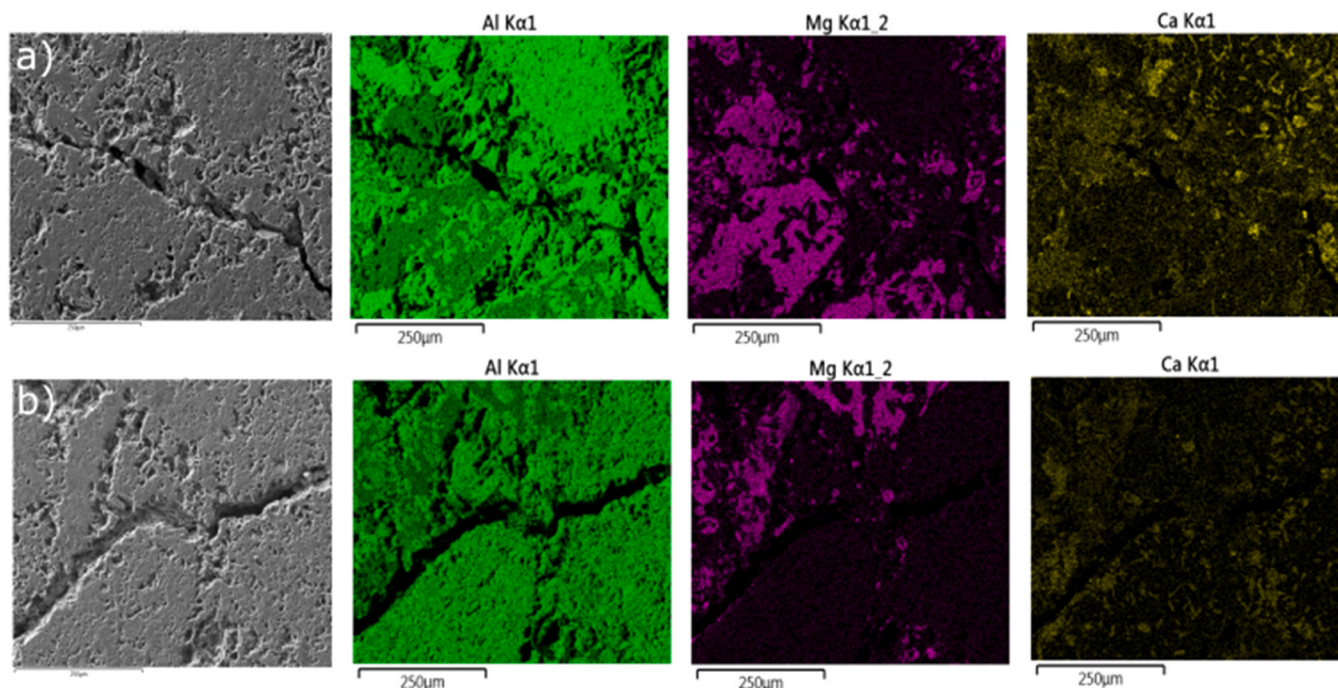


Fig. 13. Microstructure and EDS element distribution maps (Mg, Al and Ca) of the ULCCs after heat treatment at 1500 °C and after one thermal shock cycle in water at 950 °C; ULCC_3M_2Mw (a), ULCC_3M_1Mw (b).

initial open microstructure, where a volumetric expansion during synthesis both spinel and CA_6 phases occurs. An open microstructure was created by synthesis of phases with very different thermal expansions which on cooling cause characteristic microcracks and the distribution of reinforcing agent CA_6 between in situ generated and pre-formed spinel. Hence, technologically most appropriate variant of the ULCCs is the ULCC_3M_1Mw sample. Nevertheless, the NCCs counterpart with 3 wt% MgO was better, considering the results of percent sonic velocity after each heating and cooling cycle.

4. Summary and conclusions

The main purpose of this study was to determine the role of the magnesium aluminate spinel content and synthesis method on structural, microstructural, and both mechanical and thermomechanical properties of CAC-free spinel-forming castables and CAC-containing alumina-based spinel-forming/spinel-containing mixed castables. First, the structural (XRD) characterisation and mechanical measurements of designed ULCCs and NCCs were performed as part of basic research. This approach was used to monitoring of the both amount and stoichiometry of magnesium aluminate spinel and evaluate the influence of matrix composition on physical properties of refractory castables. The XRD analysis revealed the presence of $\alpha-Al_2O_3$, Al-excess Mg-Al spinel ss and Mg-Al spinel ss as the major phases in each samples and CA_6 as minor phase in CAC-containing castables. From these findings it is clear that firing of analyzed castables led to in situ $MgAl_2O_4$ synthesis, followed by Al^{3+} enrichment of spinel.

Second, the thermomechanical measurements such as RUL, CIC, HMoR were performed to evaluate their structural stability and the application capabilities of the designed castables. All these results imply that thermomechanical properties of the analyzed refractory castables have been greatly improved by removing calcium alumina cement or decreasing spinel content to 3 wt%. Additionally, the use of CAC as binder was associated with liquid phase formation at lower temperature than application of environmentally friendly mixture of Al_2O_3 and MgO powders mixed with water as a binder. According to FactSage 8.2 calculations approximate temperature of liquid phase formation was 1432

and 1471 °C for ULCCs and NCCs, respectively. Hence NCCs presented significantly better thermomechanical properties than ULCCs. The thermomechanical tests results (RUL, CIC, HMoR) clearly revealed that the key factors which affect the thermomechanical properties were: the degree of direct bonding among different particles; the amount, composition and distribution of liquid phases; the amount, particle size and distribution of spinel phase, and the porosity of the castables.

Finally, the thermodynamic simulation via FactSage 8.2 confirmed that the formation of liquid phase was mainly affected by an increasing temperature and its amount depended on the spinel content. Additionally, Mg-Al spinel composition changes versus temperature and the existence of cluster structure in Mg-Al spinel phase were confirmed. The amount of magnesium aluminate spinel increasingly stronger impacted on amount of liquid phase with increasing temperature. Thus, several conclusions can be drawn from the obtained data:

1. XRD data for CAC-containing and CAC-free castables revealed that the main diffraction peak associated with magnesium aluminate spinel shifts towards a higher 2θ value which indicate that Al-excess Mg-Al spinel was obtained in the examined samples. Additionally, obtained results for CAC-containing samples indicates the presence of Al-rich spinel phase with different stoichiometry.
2. Comparing the results obtained for ULCCs it can be concluded that the use of pre-formed spinel was more advantageous than generated in situ in this kind of castable. This results directly from the distribution of reinforcing agent CA_6 between in situ generated and pre-formed spinel and thus open microstructure formation.
3. It has been demonstrated that more effective in terms of the bonding strength of a coarse grained castable microstructure at temperature of 20–25°C is a ceramic castable truss which contain after firing magnesium aluminate spinel and CA_6 (CAC-containing castables), while at temperature of 1450 °C a matrix without CA_6 (CAC-free) turned out to be more effective, as confirmed MOR and HMoR tests results, respectively.
4. It was also shown that the increase in the magnesium oxide content in castable composition, led to the loosening of the texture of NCCs during firing, which was confirmed by an increase in apparent

porosity. The consequence of increase in apparent porosity and loosening of texture was evident deterioration of the thermo-mechanical properties.

5. The results of thermomechanical (RUL, CIC, HMoR), TSR, mechanical and microstructural measurements clearly showed that technologically most appropriate variant of analysed refractory materials was cement free castable which contain 3 wt% magnesium oxide.

Author Contributions

Karina Warmuz:, methodology, writing - original draft, visualization, data curation, investigation, software, project administration, funding acquisition; Dominika Madej: conceptualization, methodology, validation, formal analysis, software, writing - original draft, resources, writing - review & editing, supervision, project administration, funding acquisition; Krzysztof Ziewiec: SEM measurement. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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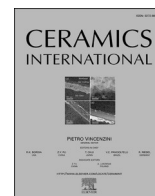
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Comprehensive experimental verification and theoretical modeling of cement-free alumina-based castables forming in-situ spinel (MgAl_2O_4) with enhanced thermal shock resistance

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ABSTRACT

No-cement spinel-forming castable refractories exhibit significantly improved resistance to mechanical and corrosive environments at high temperatures compared to calcium aluminate cement-bonded, spinel-containing monolithic refractories. In the present study, the effects of microsilica, nano-colloidal alumina, and MgO content on thermal shock resistance were investigated.

This study involved experimental analysis of modified spinel-forming, alumina-based castable refractories, combined with a theoretical evaluation based on Thermal Shock Resistance (TSR) theory. The analysis was supported by FactSage software, XRD, SEM-EDS, thermal property tests, mechanical tests, and compactness measurements. TSR was evaluated experimentally and expressed using parameters (R , R'' , R''' , R_{st}) based on the theories developed by Kingery and Hasselman.

Both spinel and silica additions influence thermal shock resistance, as reflected in the theoretical TSR parameters and supported by experimental data on Young's modulus after each thermal shock cycle. Analysis of the TSR parameters shows that increasing the amount of in situ spinel formed improves resistance to crack initiation (R parameter) during thermal shock but deteriorates resistance to crack propagation (R'' and R''' parameters). There is no evidence suggesting that the precursor (nano-colloidal alumina or alumina powder) of the spinel affects the TSR parameters. While silica enhances resistance to crack initiation (R parameter) during thermal shock, it negatively impacts crack propagation resistance (R'' and R''' parameters). This is connected to the glassy phase in which silica is present.

1. Introduction

One of the most important factors determining the wear resistance of refractory materials under operating conditions is their resistance to thermal shock (TSR). Thermal shocks are always associated with mechanical stresses, which affect the microstructural properties and, consequently reduce the corrosion resistance of refractory materials.

Numerous studies have been conducted on the thermal shock resistance of refractory materials [1–8], aiming to understand their behavior under rapid temperature changes. These studies explore various aspects regarding the thermal stress resistance of ceramics, including the general theory of spalling, methods for evaluating thermal shock resistance in refractory materials using ultrasonic pulse velocity, investigations into the thermal shock behavior of porous refractories through the strain-life fatigue method, influence of temperature of heat treatment of

the materials, technological strategies to enhance thermal shock resistance, and theoretical analyses of refractory performance under thermal shock conditions [1–8]. Many of them address the issue of thermal stresses from both theoretical and experimental perspectives.

Similarly, extensive research efforts have been directed toward improving the thermal shock resistance of refractory materials, reflecting the critical role this property plays in high-temperature applications [9–20]. One effective method for improving the thermal shock resistance of refractories involves introducing foreign phases into the host material [9–11]. Many research efforts have been directed specifically toward corundum-spinel refractories [18–24].

The study [14] concentrated on the interface between aggregates and the matrix in corundum-spinel castables. The authors reported that modifying the surface of corundum aggregates with a lanthanum hexaaluminate layer significantly enhanced the material's resistance to

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thermal shock. A comparable effect was observed in another study [15], where the addition of CaCl_2 led to a more homogeneous distribution of calcium hexaaluminate, thereby improving thermal shock resistance. In a separate investigation [16], the influence of fused zirconia-alumina (FZA) on the fracture behavior and thermal shock resistance (TSR) of alumina-spinel castables was examined. The authors showed that the introduction of micrometric FZA induced non-linear fracture behavior of the material, which was associated with a reduction in stored elastic energy, an increase in specific fracture energy, and a notable improvement in TSR. Similarly, Liu et al. [17] demonstrated that by controlling the hydration of calcium aluminate cement (CAC), it is possible to influence pore structure and fracture characteristics. The improved toughness was attributed to the complex pore network, which facilitated the dissipation of elastic energy at crack tips and resulted in more stable fracture propagation. Further research [18] confirmed that incorporating a submicrometric spinel component into the bonding system also enhances the thermal shock resistance of alumina-spinel castables. Additionally, Chen et al. [19,20] showed that the inclusion of hydratable magnesium carboxylate (HMC), either alone or in combination with submicron alumina, creates more homogeneously distributed, fine-grained spinel and significantly improves the TSR of alumina-spinel castables.

Spinel (MgAl_2O_4) is a well-studied phase that enhances the thermal shock resistance of alumina-based materials [20,21]. From this perspective, spinel can improve the performance of ordinary corundum castables [20], but its effect varies depending on the method used to introduce the spinel phase into the material. In this work, alumina-spinel castables with in situ synthesized spinel were tested for their thermal shock resistance. The results of this investigation were compared with theoretical predictions based on TSR theory.

Several theories have been developed to describe the phenomena that occur during thermal shocks. Kingery's theory, known as the thermoelastic theory, was the first comprehensive attempt to describe ceramic materials in terms of thermal shock resistance [1]. This theory focused on the crack initiation process and introduced the R and R' parameters, which characterize crack initiation in materials under different heat transfer rates. A different approach was presented by Hasselman, who focused on crack propagation and introduced the R'' parameter [22]. Based on these two theories, a unified theory of thermal shock resistance was proposed, incorporating parameters that describe both crack initiation and crack propagation. This theory introduces two new parameters, R''' and R_{st} , which represent materials with smaller and larger initial crack sizes, respectively [23–26].

Despite the development of a unified theory, thermal shock resistance remains a challenge in refractory materials technology, particularly in reconciling theoretical predictions with experimental results and ensuring consistency across different testing methods.

Many tests evaluating the thermal shock resistance of refractories have been presented in the literature [27–29]. In reference [27], Schmitt presents the application of numerical tools to predict the macroscopic thermal shock resistance of heterogeneous refractory materials. Bourdel et al. [28] studies the thermo-mechanical behaviour of magnesia-spinel refractories in relation to their microstructures, using the non-linear mechanical properties of these materials. Due to the thermal expansion mismatch between magnesia and spinel, radial matrix micro-cracking occurs around the spinel grains. According to this study, increasing the spinel content increases thermal damage and decreases tensile strength, but simultaneously improves fracture energy. Fracture energy is associated with strain to rupture, and an increase in this parameter enhances thermal shock resistance. Andreev et al. [29] present alternative methods for assessing thermal shock in silica refractories. The authors compare the thermal shock test with cyclic three-point bending, monotonic wedge splitting, and standard three-point bending tests. They state that mechanical strain-controlled fatigue tests correlate with thermal shock tests for silica refractories. Once similar correlations are established for other refractory materials,

these methods could serve as effective tools for comparing thermal shock resistance. Despite the development of new techniques for evaluating thermal shock resistance, most of the methods currently in use rely on heating and cooling cycles, with results assessed by measuring the residual Young's modulus, residual flexural strength, or the number of cycles to failure [30]. Although the results of these analyses are often difficult to compare, it should be noted that these tests are relatively easy to perform under industrial conditions. In such methods, the heating and cooling cycles, as well as the shape and size of the test samples can vary significantly. Cooling is typically performed using water or air, which poses challenges for certain materials. For example, evaluating the thermal shock resistance of magnesia-carbon refractories is difficult due to the reactivity of magnesia with water and the oxidation sensitivity of carbon. All these factors make it very difficult to compare results across different types of tests and to establish a universal testing method for all types of refractory materials [26–28]. Similarly, comparing experimental methods with theoretical predictions also remains a challenge.

In this study, no-cement alumina-based castables with in situ spinel forming were investigated with respect to their thermal shock resistance, both theoretically and experimentally. The first section of the paper focuses on quantifying properties relevant to the unified theory of thermal shock resistance. The second section presents the results of thermal shock resistance testing. The primary objective was to establish a correlation between theoretical predictions derived from the unified theory and the experimental results, aiming to support the effective design and application of spinel-containing castables.

2. Experimental part

2.1. Materials preparation

In this work, vibratable no-cement in situ spinel-forming alumina based castables were designed according to the Dinger and Funk particle packing model with distribution coefficient of $q = 0.26$. The tabular alumina (grain size 0–6.0 mm, Almatiss) was used as aggregate (80.59–81.59 wt%) with other fine-grained components. General information on the chemical compositions of the selected raw materials is presented in Table 1. Considering the castable matrix, three kind of castables can be distinguished. First type of no-cement castables contained dead-burned magnesia, reactive alumina (CTC 40, Almatiss), microsilica (Elkem, 971) and some 2 % of water-dispersed sol of fumed Al_2O_3 . The second type of considered castables contained dead-burned magnesia and reactive alumina as a binder only, while the third kind included dead-burned magnesia, reactive alumina and microsilica as a binder. Table 2 presents the detailed compositions of castables and nomenclature.

Corundum ($\alpha\text{-Al}_2\text{O}_3$) is the dominant phase in both reactive alumina (CTC 40) and tabular alumina. According to our previous work [35] nanometric Al_2O_3 sol is composed of both transition aluminas, $\gamma\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$. Taking into account high BET specific surface area and great susceptibility to hydration of nanometric Al_2O_3 sol, the presence of transition aluminas leads to greater reactivity than that seen for $\alpha\text{-Al}_2\text{O}_3$.

Table 1
Typical chemical compositions of raw materials [31–34].

Chemical composition [wt. %]	Tabular alumina (Almatiss)	Dead-burned MgO	Microsilica (971) (Elkem)	Al_2O_3 (CTC 40, Almatiss)	Nanometric Al_2O_3 sol (Elkem)
Al_2O_3	>99.50	<1.80	0.07	>99.80	>99.80
SiO_2	<0.09	<5.00	>97.00	0.03–0.07	–
MgO	–	>90.00	0.18	–	–
CaO	–	<2.50	0.29	0.03–0.07	–
Na_2O	<0.40	–	0.25	0.08–0.12	–
K_2O	–	–	0.22	–	–
Fe_2O_3	<0.02	<1.30	0.07	0.03	–

Table 2

Nomenclature and detailed composition of no-cement in situ spinel forming alumina based castables.

Composition of samples [wt. %]	Designation of samples				
	7M_SA	5M_SA	3M_SA	5M_S	5M
Tabular alumina (1.0–6.0 mm)	38.42	38.42	38.42	38.42	38.42
Tabular alumina (0–1.0)	42.17	42.17	42.17	42.17	43.17
Reactive Al ₂ O ₃	11.41	13.41	15.41	13.41	13.41
Dead-burned MgO	7.00	5.00	3.00	5.00	5.00
SiO ₂ micro-powder	1.00	1.00	1.00	1.00	0.00
Total	100	100	100	100	100
Al ₂ O ₃ sol	2.00	2.00	2.00	–	–
Dispersing additive	0.10	0.10	0.10	0.10	0.15
Water	3.50	3.50	3.50	4.50	4.5

Additionally, nanometric alumina oxide sol contain 49–51 % wt. of Al₂O₃ and is characterised by negative surface charge as a result of stabilization based on citric acid. The stabilization based on citric acid is favorable due to potential retarding of MgO hydration. The average grain sizes in the dead-burned ranged between 2.507 and 64.694 μm ($d_{0.5} = 17.353 \mu\text{m}$), BET surface area 0.9077 m²/g which indicated that dead-burned MgO has a good ability to form hydrated counterparts. Each different type of no-cement in situ spinel-forming alumina based castables contained water and Castament FS 20 or FW 10 from BASF as additives. Water, dispersing additives, and Al₂O₃ sol were all added in amounts exceeding 100 wt% of each castable's composition.

In the laboratory-scale mixer, the mixtures were dry-mixed for 5 min and then wet-mixed for 5 additional minutes. For castables which contained Al₂O₃ sol, the final stage of sample preparation was the addition of MgO and quick mixing. Subsequently, vibration (5 min, amplitude 50 Hz) was used to cast the mixed castables into 40 × 40 × 160 mm molds. Firstly, castables containing Al₂O₃ sol (3M_SA, 5M_SA, 7M_SA) were cured at room temperature (22 °C) for next 24 h, then were de-moulded and cured at 50, 70 and 90 °C for 24 h at each temperature in a laboratory climatic chamber. The castables labeled 5M_S and 5M were conventionally cured at 22 °C for 24 h before being removed from their molds. Then, castables were dried at 110 °C for 24 h. The final stage was two-stage firing at 830 °C and 1500 °C with retention time 10 h.

2.2. Thermochemical simulations

Results of thermodynamic calculations performed using FactSAGE™ 8.3 containing the temperature of first liquid phase formation, the liquid content versus temperature and the effect of temperature on viscosity changes were generated by entering the representative oxides of the chemical composition of NCCs (Table 3), in the “Equilib” module of the FactSAGE™ version 8.3 software, using the selection options “A-Slag-liq all oxides + S”, “A-Spinel” and “A-Monoxide”. For all phases, the selection option was used as “possible 2-phase immiscibility”. The databases “FactPS”, “FTmisc” and “FToxid” were successfully used in all calculations. Calculation parameters were set at 1 atm pressure of air.

Table 3

Chemical composition of castables used as inputs for FactSAGE™ 8.3 thermodynamic simulations.

Castable compositions	Oxides/wt.%		
	Al ₂ O ₃	MgO	SiO ₂
7M_SA	92.02	6.91	1.07
5M_SA	94.00	4.94	1.06
3M_SA	95.98	2.96	1.06
5M_S	94.00	4.94	1.06
5M	95.06	4.94	–

2.3. Detailed description of characterization techniques

2.3.1. Physical and mechanical properties

The XRD patterns were recorded on a samples milled under 63 μm on a X'Pert Pro PANalytical diffractometer within the range of 2 θ values between 10° and 90° using Cu K α radiation ($\lambda = 1.54060 \text{ nm}$) at 45 kV (step size of 0.008°). The phases were identified using HighScore Plus software (Panalytical) used in conjunction with the both ICDD-supported PDF-2 database and the JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997), additionally the Rietveld quantitative analysis were performed.

A scanning electron microscope (SEM, FEI Nova Nano SEM 200) was used to investigate the microstructure of the castables. Electron-probe microanalysis with an energy-dispersive X-ray spectrometer (EDAX, Sapphire Si(Li) EDS detector) was used to determine the chemical compositions of the samples. The representative sample of each castables was both polished and then mechano-chemically etched to reveal microstructure details. Each sample was polished using a pressing force of 40 N, a rotational speed of 300 RPM, and a continuous water wetting of the diamond surface disc. After polishing, castable samples were placed in an ultrasonic cleaner with isopropyl alcohol in a beaker for approximately an hour, and before examination sputtered with carbon conductive layer.

Apparent porosity and bulk density tests of refractory in situ spinel-forming alumina based castables samples after firing at 1500 °C, were carried out by standard methods, based on the Archimedes' method, according to the EN 993-1:2019-01 [36] standard.

The bending strength (CMOR) of refractory in situ spinel-forming alumina based castables was determined by a 3-point bending test using a specimen measuring 40 × 40 × 160 mm, with a span dimension of 100 mm, and a test speed of 50 N/s. To determine the cold crushing strength CCS, half of each sample after the 3-point bending test, was placed in the compression testing equipment. The loading speed was 2.4 kN/s [37].

2.3.2. Thermal properties

The thermal expansion coefficient (α) was determined from dependance (1) [38]. The factor dL/L_0 as a function of temperature was measured by a Netzsch DIL 402C dilatometer in the range 20–1500 °C with heating rate of 5 °C/min.

$$\alpha = \frac{\Delta L}{L_0 \Delta T} [1/K] \quad (1)$$

where:

L_0 - initial length of the sample [m]

ΔL - linear expansion of the sample after change of temperature [m]

ΔT - change of temperature [K]

The specific heat ($C_p(T)$) was measured by Netzsch STA 449 F3 by Differential Scanning Calorimetry (DSC) method in Pt crucibles in Ar atmosphere in the range of 20–1250 °C with heating rate 5 °C/min.

The thermal diffusivity ($a(T)$) was measured by Netzsch LFA 427 equipment by Laser Flash Analysis (LFA) method. The measurement were conducted under Ar atmosphere with Radiation + pulse correction calculation model on six different temperature levels. The laser voltage was 550 V with thermal pulse duration of 0.8 ms.

The thermal conductivity ($\lambda(T)$) was calculated on the base of the above measured thermal properties according to following equation (2) [39]:

$$\lambda(T) = a(T) \cdot C_p(T) \cdot \rho(T) \quad (2)$$

where:

$a(T)$ - thermal diffusivity [mm^2s^{-1}],
 $C_p(T)$ - specific heat [$\text{Jg}^{-1}\text{K}^{-1}$],
 $\rho(T)$ - bulk density [gcm^{-3}].

2.3.3. Properties connected with TSR

The velocity of the ultrasonic waves was measured using the pass-through method, by Material Tester CT 3 apparatus with transducer for longitudinal waves 1 MHz and UZP-1 apparatus with transducer for longitudinal waves 2 MHz. Based on measuring the velocity of longitudinal and transverse ultrasonic waves the dynamic Poisson's ratio has been calculated according to following equation (3) [40]:

$$\mu = \frac{(V_L^2 - 2V_T^2)}{(2V_L - 2V_T^2)} \quad (3)$$

where:

V_L - longitudinal wave,
 V_T - transverse wave.

The Thermal Shock Resistance (TSR) of the corundum-spinel castables were carried out according to own laboratory procedure based on the ASTM C1171 - 05 standard [41]. The samples with dimensions of $40 \times 40 \times 160$ mm were put into furnace with a temperature of 950°C for 45 min before they were shocked by quenched into water at 20°C for 3 min. The specimens after each heating and cooling cycle was dried in 110°C for 24 h to remove any physically adsorbed water. The percent sonic velocity loss (longitudinal waves) along the longest direction of each specimen before and after each heating and cooling cycle was measured using the following equation (4):

$$\text{Percent sonic velocity loss} = \frac{V_0 - V_1}{V_0} \cdot 100 [\%] \quad (4)$$

where:

V_0 - original sonic velocity of each specimen [$\text{m}\cdot\text{s}^{-1}$],
 V_1 - sonic velocity of each specimen after testing [$\text{m}\cdot\text{s}^{-1}$].

Additionally, Young's modulus was calculated according to Panakkal and Ghosh [42,43] using equation (5):

$$E = \frac{V_i^2 \cdot \rho(1 + \mu) \cdot (1 - 2\mu)}{(1 - \mu)} \quad (5)$$

where:

V_i - sonic velocity before or after testing [$\text{km}\cdot\text{s}^{-1}$],
 μ - dynamic Poisson's ratio,
 ρ - bulk density of specimen after testing.

The fracture toughness K_{IC} was estimated by equation (6) [44-46].

$$K_{IC} = \frac{1.5FLY_c^{0.5}}{bh^2} \left[\text{MPa}\cdot\text{m}^{\frac{1}{2}} \right] \quad (6)$$

where:

Y is defined according to equation (7) [45,46]:

$$Y = 1.93 - 3.07 \frac{c}{h} + 13.66 \left(\frac{c}{h} \right)^2 - 23.98 \left(\frac{c}{h} \right)^3 + 25.22 \left(\frac{c}{h} \right)^4 \quad (7)$$

where:

F - load applied [N],
L - support span length [mm],
b - width of the bar [mm],
h - height of the bar [mm],

c - depth of the notch [mm].

The energy needed to create a new surface area during crack initiation γ_{NBT} was estimated by fracture toughness K_{IC} and Young modulus according to equation (8) [45-47].

$$\gamma_{NBT} = \frac{(K_{IC})^2}{2E} [J] \quad (8)$$

Respectively, the work of fracture γ_{WOF} was calculated according to the area under the curve of the strain-stress relationship from equation (9) [46,47].

$$\gamma_{WOF} = \int \frac{\sigma d\varepsilon}{2A} [J/m] \quad (9)$$

where:

ε - displacement [m],
 σ - load [N],
A - new created surface area [m^2].

Based on obtained results and calculation series of parameter characterizing Thermal Shock Resistance (TSR) were evaluated according to Unified Theory (UT) of thermal shock fracture initiation and crack propagation in brittle materials [23,40].

In the case of this theory, the R parameter describes the resistance to sudden changes of the temperature under conditions of rapid heat flow from the material to the environment and applies to surface phenomena. R parameter is often related with ΔT_c or the critical temperature difference that lead to the formation of unstable crack. It means that fracture of the material appears when the thermal stress equals or exceeds fracture strength of the material. The R parameter is given by equation (10) [1,27,47]:

$$R = \frac{\sigma_f(1 - \nu)}{E\alpha} \quad (10)$$

where:

σ_f - load [N],
 α - thermal expansion coefficient [1/K].

Different approach is presented by Energy Balance Approximation (EBA) developed by Hasselman. In this case fracture of the samples occurs when thermoelastic energy exceed energy needed for the creation of the new crack surfaces. In this approach two new parameters are defined R'' given by equation (11) and R''' given by equation (12). The later one is also linked with critical crack length L_c equation (12) [27,47,48].

$$R'' = \frac{E}{\sigma_f^2(1 - \nu)} \quad (11)$$

$$R''' = R'' \gamma_{WOF} = \frac{E \gamma_{WOF}}{\sigma_f^2(1 - \nu)} = L_c \quad (12)$$

Another parameter defined by the Unified Theory (UT) is the thermal stress crack stability (R_{st}). This parameter is given by equation (13) and define how crack after initiation will behave, under the thermal stress [27,47,48].

$$R_{st} = \left[\frac{\gamma_{WOF}}{\alpha^2 E} \right]^{\frac{1}{2}} \quad (13)$$

It can be state that in Unified Theory (UT), the first parameter R is connected with crack initiation during sever thermal shock while parameters R'' , R''' and R_{st} are rather connected with situation when crack already propagate. The R' parameter in this case is omitted because its define situation with slow heat flow while during thermal shock the heat

flow is very fast (high Biot number) [27,47].

3. Results and discussion

3.1. Thermochemical calculations

The behaviour of materials during thermal shocks can be differentiated by both thermal shock resistance parameters (discussed in the 3.3 part), the content of liquid phase (Fig. 1), both chemical composition (Fig. 2) and viscosity (Fig. 3) [49]. To calculate content and parameters of the liquid phase the EQUILIB module of FactSAGE™ 8.3 was used. Analysing these thermodynamic calculation results, it can be seen that the 3M_SA, 5M_SA, 7M_SA and 5M_S NCCs showed liquid phase formation during firing at 1500 °C. No liquid formation was identified both at 1450 °C, and for the 5M composition. Based on the calculation results for determining the temperature at which the targeted liquid phase starts to form (temperature of initial liquid phase formation), it can be stated that this liquid phase appears at 1471 °C in the 3M_SA, 5M_SA, 7M_SA and 5M_S NCCs, whereas it happens close to 2005 °C in the 5M NCC. In the latter scenario, this is true at temperature above the heat treatment temperature.

The results of FactSAGE™ 8.3 thermodynamic calculations also indicated that the formation of the liquid phase was primarily influenced by increasing temperature, as shown in Fig. 1. Based on the results of this study, it can be concluded that the addition of microsilica (Table 2) enhances the liquid phase formation, whereas no liquid formation was predicted in silica fume-free composition. This is related to the ability of SiO₂ to form a liquid phase at elevated temperatures, which in turn initiates the dissolution of other components of the material. This is why samples with silica addition are enriched in the liquid phase, while those without it do not exhibit liquid phase formation, even at high temperatures. The chemical composition of the liquid phase for the microsilica-containing NCCs stays unchanged, regardless of the MgO content in the samples. However, it varies with temperature (Fig. 2).

The liquid phase composition at 1500 °C (Al₂O₃ 39.95 mas.%, MgO 16.43 mas.% and SiO₂ 43.62 mas.%) was chosen to further determine the viscosity of the liquid phase. Fig. 3 shows the effect of temperature on viscosity changes in 3M_SA, 5M_SA, 7M_SA and 5M_S NCCs, predicted by FactSAGE™ thermodynamic calculations. It can be said that the temperature has a large influence on the viscosity of liquid phase, especially up to around 850 °C.

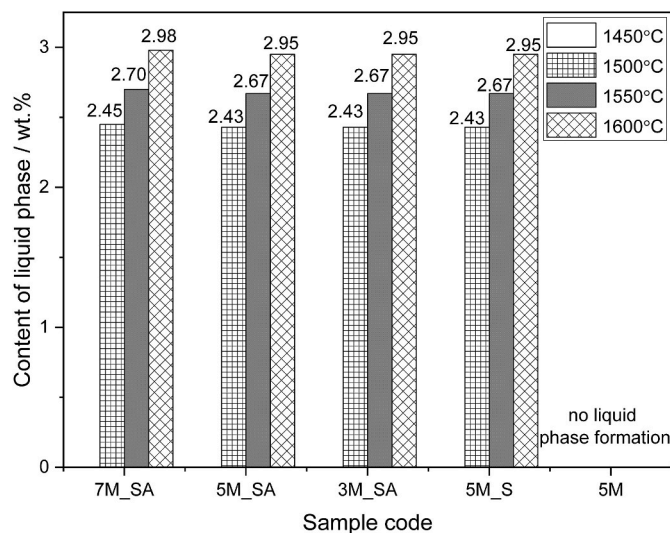


Fig. 1. The effect of temperature and castable composition on total liquid phase content in all NCCs, predicted by FactSage thermodynamic calculations. No liquid formation was identified at 1450 °C, and for the 5M composition.

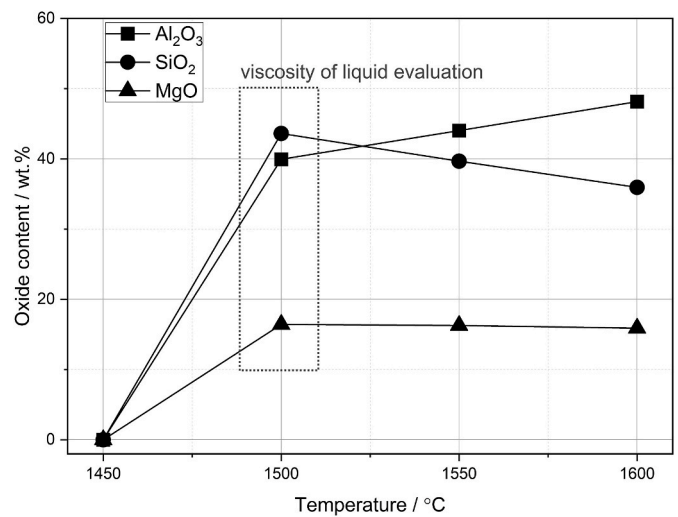


Fig. 2. The effect of temperature on the Al₂O₃, SiO₂ and MgO oxides contents in 3M_SA, 5M_SA, 7M_SA and 5M_S castables, predicted by FactSage thermodynamic calculations.

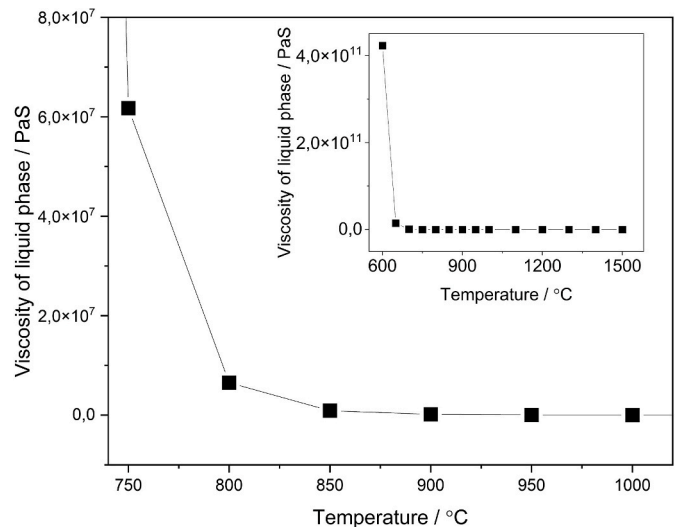


Fig. 3. The effect of temperature on viscosity changes in 3M_SA, 5M_SA, 7M_SA and 5M_S castables, predicted by FactSage thermodynamic calculations.

3.2. Phase composition of in situ spinel-forming alumina-based castables

The XRD phase analysis with the Rietveld refinement allows define type and content of the phases in analysed materials. The type and quantity of the phases present in refractory materials can have crucial impact on their behavior during thermal shocks.

Analyses of the diffractograms of the studied castables after heat treatment at 1500 °C are shown in Fig. 4a. The results indicate on the absence of periclase in the samples, in which place can be observe the spinel phase. This means that the synthesis of the spinel has occurred, however, due to the excess of aluminum oxide, spinel show some non-stoichiometry. This is visible on diffractograms in slightly shifts of the peaks assigned to the spinel phase to the higher values of 2θ angle with increase of the MgO content in the sample. Mentioned shift to the higher values of 2θ angle has been revealed at Fig. 4b on the example of the main diffraction line characteristic for spinel. This indicate on presence of magnesium aluminate spinel as well as Al-excess magnesium aluminate spinel. In addition to spinel, an α-alumina phase can be also observed. Based on the presented diffractograms, it can be concluded

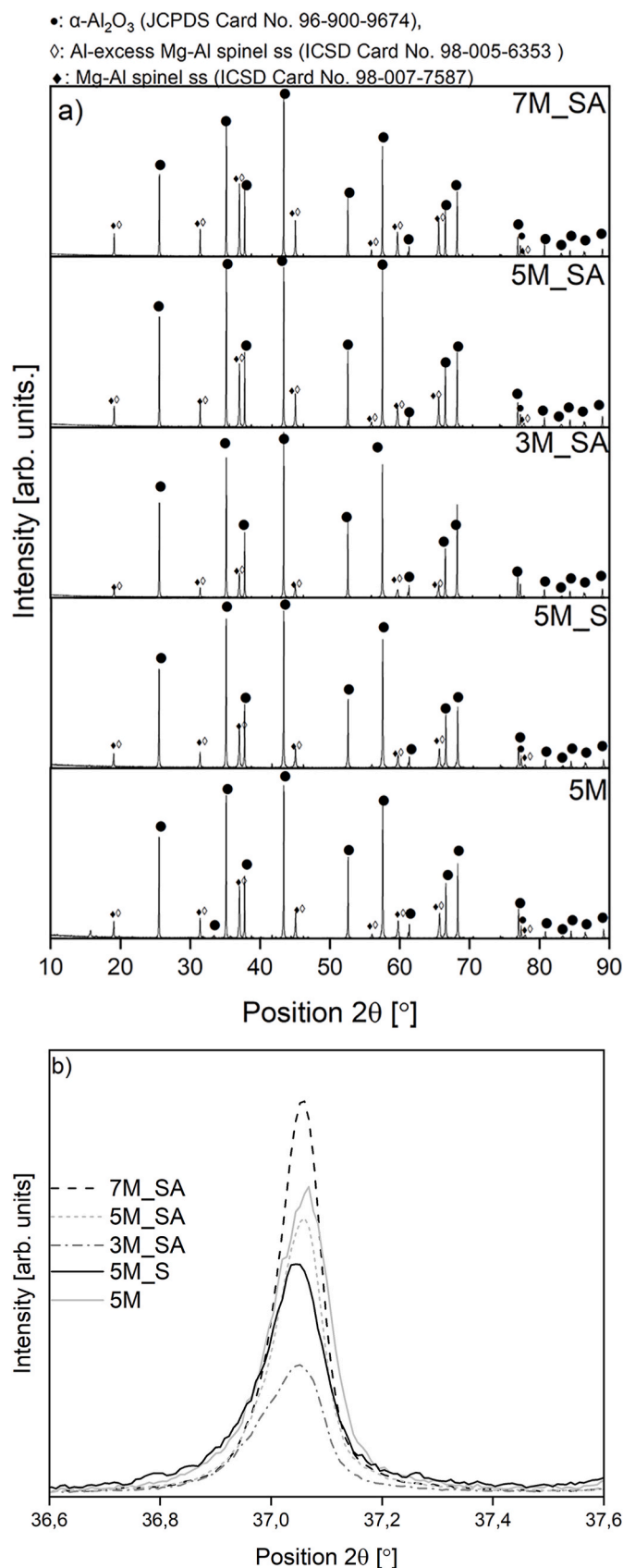


Fig. 4. Diffractograms of the in situ spinel-forming alumina-based castables after heat treatment at 1500 °C in the range of 10–90° (a) and 36.6–37.6° (b) (JCPDS Card: α - Al_2O_3 No. 96-900-9674; ICSD Cards: Al-excess Mg-Al spinel ss No. 98-005-6353, Mg-Al spinel ss No. 98-007-7587).

that at 1500 °C, the periclase phase has completely reacted to form spinel, while the addition of SiO_2 at this temperature can form a glassy phase similar in its composition to mullite phase. This may be the reason for the absence of mullite in the SiO_2 -added castables samples confirmed by by FactSAGE™ thermodynamic calculations and the SEM analysis (presented in 3.3 section).

According to Rietveld analysis Fig. 5 the quantitative content of the phases in analysed samples varied depending on the silica and fumed alumina presence. In case samples with fumed alumina, amount of α -alumina decrease with increase of magnesium oxide, from 85.7 % for 3M_SA sample to 68.9 for 7M_SA sample. Simultaneously overall amount of spinel's phases increase. But amount of the Al-excess magnesium aluminate spinel is much higher than for stoichiometric spinel around twice times (in case of sample 5M_SA over 2.5 times). Getting in to account Wagner mechanism of the synthesis of the spinel, the reactivity of the alumina plays crucial role in both spinel formation as well as saturation of the spinel by excess of alumina ions [50,51]. Opposite situation is observed for samples without fumed alumina where main substrate in synthesis of the spinel is less reactive α -alumina. In samples 5M and 5M_SA content of the stoichiometric spinel in relation to Al-excess spinel is higher and vary from around 4 times higher for sample 5M to 5.5 higher for sample 5M_S. Base on this findings it could be state that mobility of the Al ions is important factor in saturation of the spinel by the excess of the Al ions. Also silica addition to the samples effect on overall spinel content (stoichiometric spinel and Al-excess spinel).

The effect of the silica addition is visible when results for samples 5M and 5M_S are compare. The results shows that sample without silica has higher amount of spinel than sample with silica addition, around 26 % versus 21 %. This suggest that silica addition inhibit spinel synthesis. This can be connected with creation of the silica liquid phase, which have high content of the magnesium oxide in its composition (around 16.5 %) and trap some Mg ions. Moreover this phase can also create some insulating layer on the surface of the alumina grains, which decrease contact of the MgO with Al_2O_3 grains. Low viscosity of the liquid phase in temperature of the spinel synthesis can also support this claim.

3.3. Mechanical characterization, thermal and physical properties of in situ spinel-forming alumina-based castables

Evaluation of the physicommechanical properties allows to determine basic properties of the studied castables as well as theoretical thermal

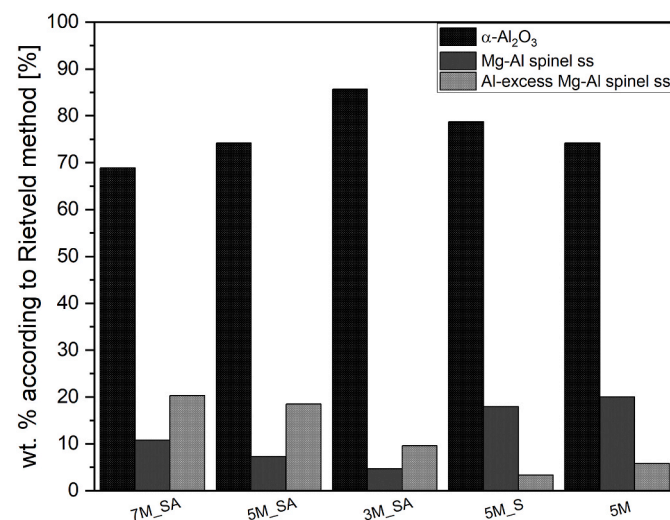


Fig. 5. Rietveld analysis of the in situ spinel-forming alumina-based castables after heat treatment at 1500 °C.

shock resistance parameters. The physicomaterial studied castables were measured with respect to procedures presented in experimental part of the work. Tables 4–6 present the summary of sample dimensions, bulk density, apparent porosity and mechanical, thermal and fracture properties of the studied materials, respectively.

The tests results of the density (Table 5) indicated that with increasing in situ magnesium-aluminate spinel content the apparent porosity increases while bulk density decreases. Overall, it can be concluded that the increase in the MgO content in initial castable composition, led to the texture weakening during firing process. This was confirmed by both our previous work [52,53], other literature sources and results. From the volume increase between 5 % and 7 % during spinel formation [54]. According to obtained results (Table 6), it is clearly seen that samples which contain microsilica 3M_SA, 5M_SA, 7M_SA, 5M_S in initial castables composition were characterized by significantly better both CMOR and CCS than samples without microsilica 5M. Moreover, CMOR and CCS of analysed castables suggest that there is no correlation between the amount of spinel phase generated in situ and mechanical properties (sample 7M_SA versus 5M_SA and 3M_SA). But, CMOR and CCS of analysed castables suggest that there is optimal content of spinel (sample 5M_SA) that improve/do not decrease mechanical properties of the castables. Nevertheless, based on the CMOR test results (Table 6), it can be observed that the presence of water-dispersed sol of fumed alumina in initial castable matrix composition results in improvement in bending strength of analysed castables despite higher apparent porosity (Table 5). This indicate that the application of nanoparticles from sol can result probably in microstructure compacting at lower temperatures, intensifying the sintering process and thus enhances direct bonding between alumina and spinel grains and/or create beneficial microstructure which relaxed stresses or deflect crack propagation.

Obtained results for Young Modulus (E) and Poisson's ratio (ν) for each analysed castables are comparable (Table 6). Moreover, E and ν decrease with increasing spinel content while the presence of water-dispersed sol of fumed alumina in initial castable matrix composition led to their increase, sample 5M_S versus 5M. The work of fracture of castables which contain microsilica in initial composition is high. For all analysed refractory castable samples, γ_{NBT} is significantly lower than γ_{WOF} (17–25 times for 5M_S and 3M_SA, respectively (Table 6)). This indicate that studied castables are more resistant to propagation than to crack initiation which is common for refractories and in accordance with other literature sources [55,56].

Thermal expansion coefficients at 950 °C (Table 4) varied from $5.68 \cdot 10^{-6} \text{ K}^{-1}$ to $7.86 \cdot 10^{-6} \text{ K}^{-1}$ for 5M_S and 5M_SA, respectively. Taking into account that composition of mentioned castables (5M_S and 5M_SA) differs only in the introduction into the castable matrix as a water-dispersed sol of fumed alumina (Table 2), it is clearly seen that the thermal expansion coefficient α slightly increases as the grain size within the matrix composition decreases. This is probably due to the better contact between neighboring microvolumes of the material.

Based on the obtained results (Table 5) and corresponding literature sources [57], it is clearly seen that, the determined thermal expansion coefficient is lower than thermal expansion coefficient of corundum $8.5 \cdot 10^{-6} \text{ K}^{-1}$ which is related to the presence of the spinel phase (thermal expansion coefficient: $7.6 \cdot 10^{-6} \text{ K}^{-1}$) and also probably amorphous

aluminosilicate phase.

According to current state of knowledge, heat may be transferred through convection, radiation and conduction. The dominant type of heat transfer in refractory materials is conduction. Moreover, for the heterogeneous materials just like refractories, the thermal conductivity depends especially on physical structure and microstructure [58]. The thermal conductivity of gas through the pores of the refractory castables is much lower than that of through solid substance, this is why the material microstructure is extremely important. Based on the obtained results and other literature sources [59], the key factors affecting the thermal conductivity of analysed castables can be summarized as follows: both magnesium aluminate spinel and also amorphous aluminosilicate phase (similar in its composition to mullite) content, porosity, density and presence of microcracks.

The determined values of work of fracture, thermal expansion coefficients, thermal conductivity as well as Young's modulus, Poisson's ratio and fracture toughness (Tables 5 and 6) allowed to determine the correlation among TSR, R, R'' , R''' and R_{st} what is presented below (3.5 section).

3.4. Microstructural examination of in situ spinel-forming alumina-based castables

SEM analysis was performed to compare the microstructure of in situ spinel-forming alumina-based castables and was carried out on polished samples. Fig. 6a–e illustrate the microstructure and 7 a–e chemical composition analysis in the micro areas obtained by the SEM-EDS measurements of the castables after heat treatment at 1500 °C. The microstructure of all castables after heat treatment at 1500 °C (7M_SA (Fig. 6 a), 5M_SA (Fig. 6 b) and 3M_SA (Figs. 6 c), 5M_S (Figs. 6 d), 5M (Fig. 6 e)) consists of corundum aggregates, held together by a bond of fine alumina and magnesium-alumina spinel phase. In fact, this is the typical distribution of coarse tabular alumina grains within a fine-grained matrix. Corundum aggregates are labeled as A, the fine-grained matrix as B, and microcracks as C. Pores are additionally highlighted with circles. It is worth noting, that the obtained castables are characterised by significantly denser microstructure than conventional castables. The significantly denser microstructure may results from the well-selected grain composition of castables, small amount of water in initial composition and presence of nanoparticles which were introduced previously via water-dispersed sol of the fumed Al_2O_3 (7M_SA, 5M_SA, and 3M_SA samples (Fig. 6a–c)). The small amount of amorphous phase could also be distinguished in the matrix due to the presence of SiO_2 (Table 2) in initial castable composition.

According to current state of knowledge, the in situ spinel synthesis via sintering of MgO and Al_2O_3 is associated with a volume increase between 5 % and 7 %, which may led to both increase in the apparent porosity and formation of microcracks in the microstructure [54]. Nevertheless, despite the lowest content of the MgO in initial castables composition and therefore spinel phase in castables after heat treatment, the microstructure of 3M_SA sample (Fig. 6 c) contains a network of small microcracks within the fine-grained castable matrix which separated alumina aggregate grains. Taking into consideration the apparent porosity and bulk density of analysed castables it is worth to notice that 3M_SA sample was characterised by the highest compactness. This suggest that dense microstructure in combination with intensification of the sintering process at a lower temperature due to the presence of nanoparticles may led to difficult in both dehydration and dehydroxylation, therefore propagation of microcracks within the matrix. Mentioned network of microcracks maybe contribute to the absorb the energy of another crack's propagation, therefore may improve the TSR and on the other hand, reduced mechanical properties (CMOR and CCS) of castables. The SEM images of the 5M_SA, 7M_SA, 5M_S and 5M (Fig. 6a–e) also confirmed the presence of few microcracks within the matrix. It is clearly seen that microstructure of 5M_S, 5M and 5M_SA (Fig. 6b, d, e) castables contain definitely lower amount of microcracks

Table 4

The summary of sample dimensions, bulk density and apparent porosity of studied castables.

Sample	Width of the bar [mm]	Height of the bar [mm]	Depth of the notch [m]
7M_SA	40.72	39.94	0.1002
5M_SA	40.68	39.87	0.0999
3M_SA	41.06	39.85	0.1006
5M_S	40.50	40.51	0.1040
5M	41.18	41.19	0.1096

Table 5

Density and thermal properties of the studied castables.

Sample	Bulk density [g/cm ³]	Apparent porosity [%]	Thermal diffusivity [mm/s]	Specific heat [Jg ⁻¹ K ⁻¹]	Thermal conductivity coefficient λ [W/mK]	Thermal expansion coefficient α [1/K]
7M_SA	3.035	17.59	1.054394	1.34461	4.86	5.73E-06
5M_SA	3.088	16.81	1.160641	1.43553	5.66	6.99E-06
3M_SA	3.187	15.07	0.940737	1.35448	4.38	6.69E-06
5M_S	3.110	16.12	0.922834	1.46668	4.48	6.93E-06
5M	3.090	16.42	0.884757	1.38816	3.75	6.55E-06

Table 6

Mechanical and fracture properties of the studied castables.

Sample	Load applied [N]	Cold modulus of rupture (CMOR) [MPa]	Cold crushing strength (CCS) [MPa]	Young Modulus E [Pa]	Poisson's ratio [–]	Work of fracture γ_{WOF} [N/m]	Kic [MPa/m ^{1/2}]	Crack initiation energy γ_{NBT} [J]
7M_SA	5915.0	3.4500E+07	226.8	1.410E+11	0.194	291.8	2.397	20.372
5M_SA	5913.3	3.4810E+07	253.8	1.580E+11	0.202	321.3	2.403	18.273
3M_SA	6280.0	3.4320E+07	211.6	1.610E+11	0.203	341.7	2.543	20.080
5M_S	6095.0	3.4200E+07	249.0	1.550E+11	0.162	341.5	2.467	19.639
5M	4153.3	1.4500E+07	89.9	1.510E+11	0.217	177.9	1.652	9.033

than 7M_SA (Fig. 6 a) castable due to the lower content of magnesium oxide in initial castable composition. In this case the presence of microcracks probably results more from the in situ magnesium-aluminate spinel synthesis during heat treatment than difficult water evacuation.

Fig. 7a–e presents the detailed microstructure analysis with EDS analysis results of analysed castables. The EDS analysis of 5M_S, 3M_SA, 5M_SA and 7M_SA (Fig. 7a–d) castables fine-grained matrix confirm the presence of magnesium aluminate spinel, α -Al₂O₃. The SEM did not show presence of mullite phase which is also in agree with XRD analysis. But according to results of these analysis, it could be confirmed presence in the samples of β -Al₂O₃ and some amorphous silicate phase. The silicate phase is absent in case of sample 5M (Fig. 7 e), but in this sample there can be identified spinel, corundum (α -Al₂O₃) and β -Al₂O₃.

3.5. Thermal shock resistance of in situ spinel-forming alumina-based castables

The TSR is one of the most important properties of refractory materials because sudden temperature changes at the surface (thermal shock) may lead to uncontrolled and premature damage of refractory linings. There is not just one universal test which allow to evaluate the TSR of refractories and also take into account the thermal cycles, sample geometry and working conditions. Nevertheless, experimental methods based on sudden heating and cooling allows compare the TSR of similar ceramic materials.

The results of the percent sonic velocity loss vs. heating and cooling cycle number, same as the results of Young Modulus are summarized in Fig. 8a and b, respectively. Obtained results show that course of changes, for each sample is similar. Taking into account castables with different amount of the MgO in initial, it is clearly seen that the percent sonic velocity reduction is higher for sample with higher spinel content. Sample 5M without microsilica shows initial strong decrease percent sonic velocity and after second thermal cycle moderate decrease reaching similar value as sample with highest spinel content 81.6 % and 82.02 % respectively. The lowest percent sonic velocity decrease shows samples 3M_AS and 5M_S after fifth thermal cycle reach 77.74 % and 78.20 % respectively. An increased number of heating and cooling cycles may lead to sample failure due to the formation of a critical-length crack. According to above, sample 7M_AS will be destroyed first, which is in good agreement with theoretical predictions. According to theoretical calculations of R''' parameter, 7M_AS is characterized by the shortest critical crack length (R'''). This result highlights the importance of optimizing phase composition and microstructure in refractory materials to enhance their thermal shock resistance. Similar course of

changes as for percent sonic velocity loss shows Young modulus, but it should be notice that this results are dependent on Poisson ratio measurements. Therefore, they are subject to additional uncertainty of the determination of the Poisson modulus.

3.6. Thermal shock-both fracture initiation and damage resistance parameters evaluation/calculations

The sample dimensions concerns the single edge notched beams which were used to determine both work of fracture γ_{WOF} and K_{IC}. According to other literature sources, the γ_{WOF} is considered as the work done in propagating a crack to break a sample with a notch, divided by twice the fracture surface areas (since two new faces are created). Besides the work of fracture, the second important parameter related to the resistance to crack propagation initiation is γ_{NBT} . Based on the γ_{WOF} vs γ_{NBT} relationship (presented in Table 6), it can be determined whether the material will be more resistant to propagation than to crack initiation ($\gamma_{NBT} < \gamma_{WOF}$). Additionally, $\gamma_{WOF}/\gamma_{NBT}$ ratio is a reliable indicator theoretical thermal shock resistance and is beneficial that it be large. Taking in to account results $\gamma_{WOF}/\gamma_{NBT}$ ratio for considered samples with the highest value shows sample 5M around 19.698 while for samples containing silica around 17.583–17.017 to 14.324. Although such value should be beneficial for sample 5M, it should be notice that high value of the $\gamma_{WOF}/\gamma_{NBT}$ ratio is connected with low values of crack initiation energy γ_{NBT} as well as work of fracture γ_{WOF} , in comparison with others samples. Its indicate that this sample is less resistant to propagation as well as initiation process than it would be indicated by $\gamma_{WOF}/\gamma_{NBT}$ ratio.

Table 7 presents the summary of theoretical thermal shock resistance parameters (R, R'', R''' and R_{st}) for each analysed in situ spinel-forming alumina-based castables which were calculated according to equations (10)–(13). Mentioned calculations were performed based on determined mechanical and thermal properties which were given in Tables 4 and 6. Thermal shock parameters may be divided at these which concern the resistance to fracture caused by thermal stresses (R) or ability of the material to resist crack propagation and further damage (R'', R'''). The R_{st} parameter which relates to the thermal stress crack stability has been also defined by other authors. According to obtained results it is clearly seen that parameter R which consider crack initiation is very different and ranges from 11.48 °C to 34.39 °C for sample respectively 5M and 7M_SA, respectively. The low value of this parameter for sample 5M confirm low resistant to crack initiation under thermal shock condition. But at the same time due to low mechanical strength of sample 5M indicate on lower risk of catastrophic cracking occurring and strong decline in mechanical properties of the material [60]. Among samples with fumed nano Al₂O₃ addition we can see that R parameter value for

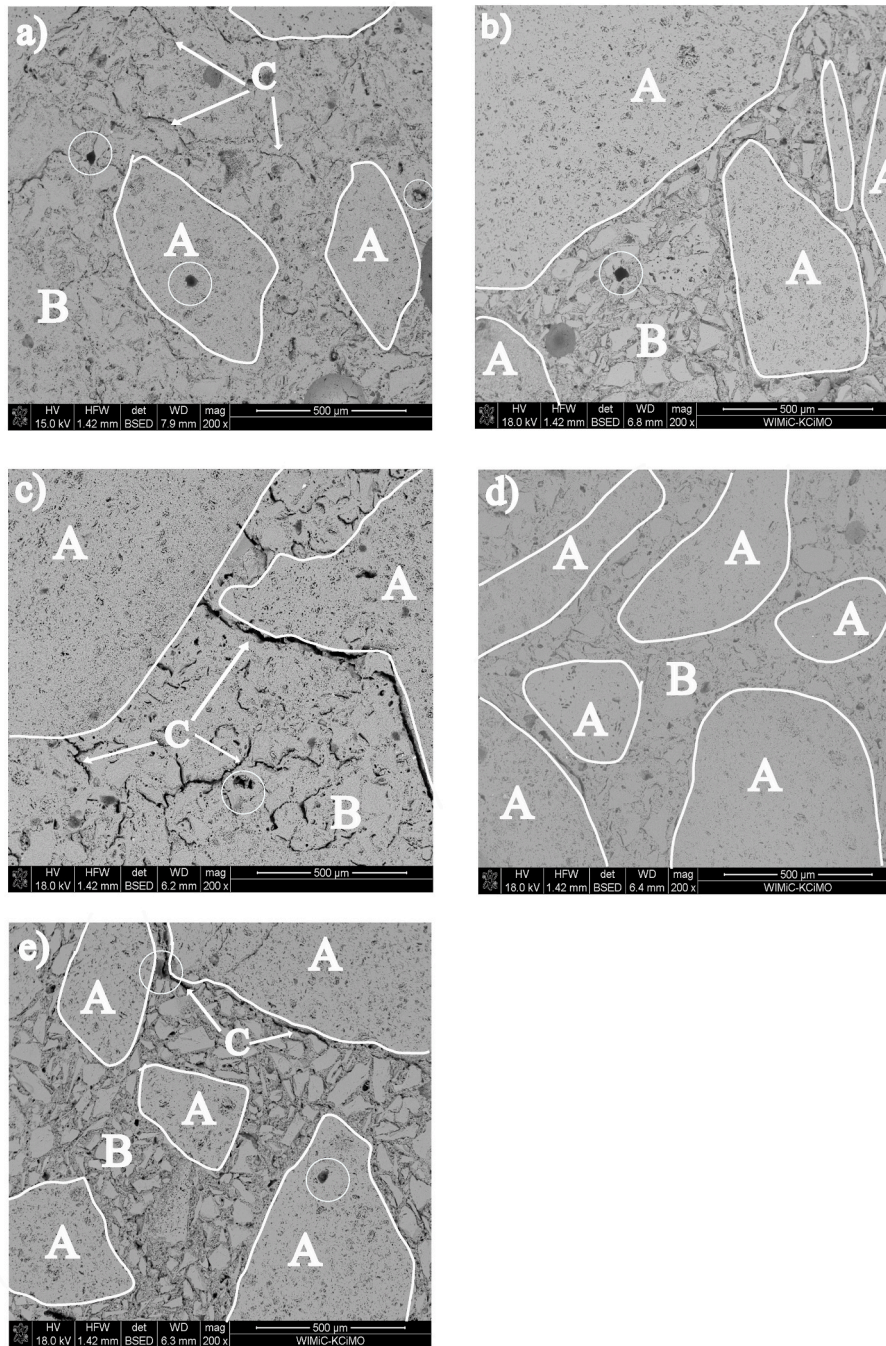


Fig. 6. Microstructural overview of the in situ spinel-forming alumina-based castables after heat treatment at 1500 °C; 7M_SA (a), 5M_SA (b), 3M_SA (c), 5M_S (d), 5M (e). A-corundum aggregates, B- fine-grained matrix, C- microcracks, circle-pores.

samples 3M_SA and 5M_SA and 5_S reach respectively 25.40 °C and 25.16 °C and 26.68 °C while for sample 7M_SA 34.39. It's meant that samples 7M_SA has higher critical temperature difference that lead to the formation of unstable crack in comparison to samples with lower MgO content in initial composition.

Both R'' and R''' values for 5M_S, 3M_SA, 5M_SA and 7M_SA are at similar level while 5M sample is characterized significantly higher values of the mentioned parameters. R'' values for first group of samples is in range $1.47 \cdot 10^{-4}$ – $1.72 \cdot 10^{-4}$ [Pa⁻¹] while for sample 5M around $9.17 \cdot 10^{-4}$ [Pa⁻¹]. Similarly in case of the R''' parameter different between 5M sample and the samples containing silica is about threefold. This suggest that 5M sample should have the highest resistance to crack propagation, unstable cracking and further damage. This can find

confirmation in results of percent sonic velocity after each heating and cooling cycle. Although sample 5M has initial strong decrease of sonic velocity which can be connected with crack initiation further decline is small and almost constant which mean that propagation of the crack occurs uniformly without drastic changes. While for others samples percent of sonic velocity change much stronger and do not stabilized but change after each thermal cycle. Thermal crack stability parameter R_{st} shows different results, with sample 5M showing the lowest value of this parameter while sample 7M_SA has the highest value of the R_{st} 5.243 and 7.933 [mK^{1/2}] respectively.

Obtained results of both R'' and R''' indicate that with increasing spinel content mentioned parameters decreases. Surprising there is no evidence for effect of the fumed alumina on TSR parameters (results

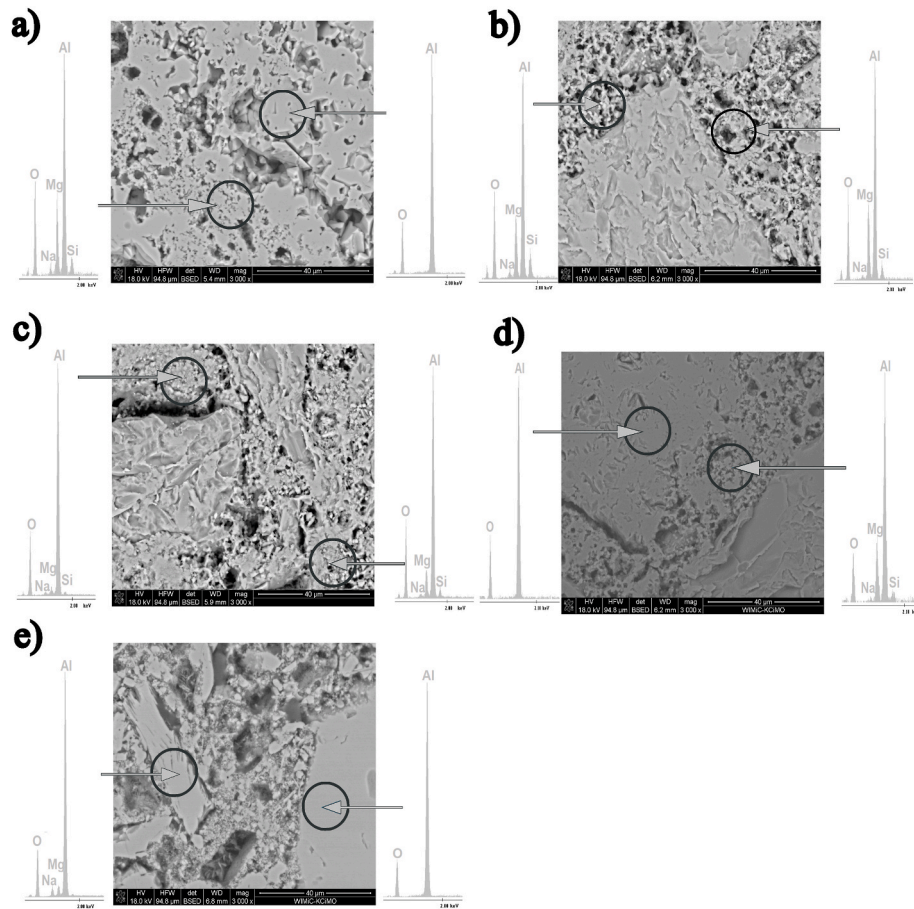


Fig. 7. Detailed microstructure analysis (SEM images with magnification of 3 000x) of the in situ spinel-forming alumina-based castables after heat treatment at 1500 °C and EDS analysis results; 7M_SA (a), 5M_SA (b), 3M_SA (c), 5M_S (d), 5M (e)

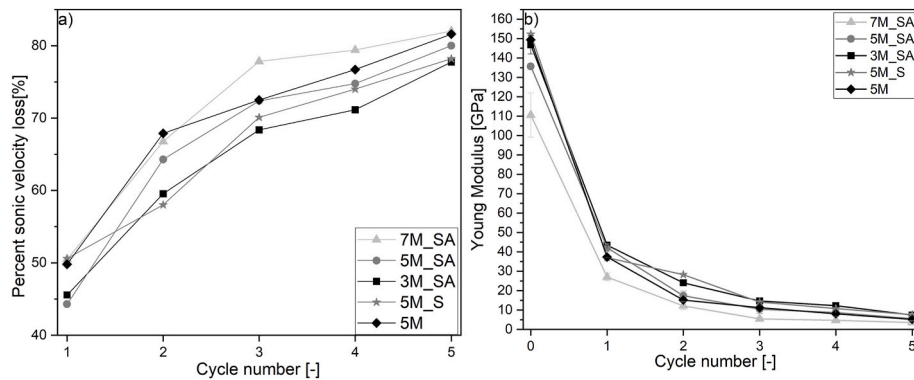


Fig. 8. Percent sonic velocity loss (a) and calculated Young Modulus (b) after each heating and cooling cycle.

Table 7

Thermal shock resistance parameters.

Sample	R (ΔT_c) [°C]	R'' [Pa^{-1}]	R''' [m]	R_{st} [$\text{mK}^{1/2}$]	$\gamma_{WOF}/\gamma_{NBT}$ [-]
7M_SA	34.39	1.47E-04	0.043	7.933	14.324
5M_SA	25.16	1.63E-04	0.052	6.453	17.583
3M_SA	25.40	1.72E-04	0.059	6.886	17.017
5M_S	26.68	1.58E-04	0.054	6.773	17.389
5M	11.48	9.17E-04	0.163	5.243	19.698

sample 5M_S versus 5M_SA).

4. Summary

Thermal shock resistant of in situ spinel-forming alumina-based castables is shaping up similarly for all castables with silica content. In this case decrease the MgO content in initial composition (decrease in spinel content) has beneficial effect on thermal shock resistance. The results of both theoretical calculations of the unified theory (UT) of thermal shocks fracture initiation and crack propagation (R'' , R''') as well as experimental data are consistent. Although sample 3M_SA has lower R parameter and its less resistant to crack initiation than sample

7M_SA it has more stable cracks for further propagation (higher R'' and R''' parameters as well as $\gamma_{WOF}/\gamma_{NBT}$ ratio). This is supported by the lowest decrease of percent sonic velocity after 5 cycles of heating and cooling during determination of the thermal shock resistant. This could be connected with the microcracks network present in the microstructure especially the 3M_SA sample. Newly formed crack's, propagating owing thermal stresses during temperature changing can be deflect and its energy can be adsorb on microcracks in microstructure of the material. Contribution of this mechanism in improvement of thermal shock resistant can be confirm by results of work of fracture and also K_{Ic} factor.

Another factor that should be taken into account is addition of fumed alumina in composition of the castables. In direct comparison samples 5M_S versus 5M_SA (samples without and with fumed alumina respectively) it can be notice that addition of nanometric alumina increase compactness and mechanical properties of the studied castables. It need to be notice that this differences has almost no effect on theoretical thermal shock resistance parameters. But in experimental results differences are apparent and the sample 5M_S shows better results than sample with nano-addition.

The castables without silica addition distinct from samples with silica in initial composition. Theoretical thermal shock resistant parameters indicate that sample 5M has small resistant against crack initiation R (ΔT_c) 11.48 [°C] this is reflected in experimental results where sample 5M has high decline of percent sonic velocity after first and second heating and cooling cycle 49.8 % and 67.9 %. In the next thermal heating and cooling cycles changes of percent sonic velocity are almost at constant level. This results can be connected with specific crack propagation where crack are stable and increase in each cycle in the same way without catastrophically cracks propagation. This find its reflection in theoretical thermal shocks parameters where R''' shows threefold higher than for samples with silica addition. It mean that this sample has higher resistant for unstable crack propagation but simultaneously is less resistant for stable crack propagation connected with R_{st} parameter [48]. For the samples containing silica changes of the percent sonic velocity indicate on more unstable character of crack propagation. This character can be connected with a glassy phase created from silica in samples in high temperature.

The present study introduces a novel approach to enhancing the thermal shock resistance (TSR) of aluminum-based castables by combining in-situ spinel formation, both nano-scale alumina water dispersant and microsilica addition. Additionally, the experimental results were compared with both theoretical calculations and FactSage thermodynamic simulations.

According to current literature sources [20,61,62] the presence of spinel is desirable from the point of view of TSR. In accordance with obtained results, with increasing MgO content in initial castable composition, the TSR decreased which is associated directly with microstructure of the castables (Fig. 6). Moreover, according to theoretical considerations with increasing spinel content, increase resistant for crack initiation but at the same time has negative effect for crack propagation processes. This dual effect is consistent with the observed experimental trend. Comparing TSR results of samples 5M and 5M_S it is clearly seen that microsilica addition strongly affect the TSR. Sample 5M_S was characterized by higher TSR which was confirmed by lower percent sonic velocity loss. Taking into account the theoretical R parameter, sample with silica addition has better resistance to crack initiation and stable crack propagation connected with R_{st} parameter. On the other hand, samples without silica addition has higher resistance for unstable crack propagation and also has higher $\gamma_{WOF}/\gamma_{NBT}$ ratio. The experimental investigation indicated that the presence of nano- Al_2O_3 water dispersant in the initial composition of castables doesn't affect the TSR. In light of FactSage thermodynamic simulations, this lack of influence of the presence of alumina sol on the TSR results can be explained by the absence of meaningful differences in the theoretical amount and chemical composition of the liquid phase formed during the firing process. These findings demonstrate the complex interplay

between phase composition, microstructure, and thermal shock resistance, and highlight the need for a balanced design strategy that optimizes both crack initiation and crack propagation.

5. Conclusion

It has been proven that silica content in in situ spinel-forming alumina-based castables has strong influence on thermal shock resistance. This phenomenon is primarily attributed to the phase and pores distribution within the microstructure and the content of the glassy phase, which significantly affect the mechanisms of crack initiation and propagation under thermal shock conditions. Sample with microsilica addition has better resistance for crack initiation (R parameter) and stable crack propagation connected with R_{st} parameter. Samples without microsilica addition exhibit enhanced resistance to unstable crack propagation, as evidenced by a higher $\gamma_{WOF}/\gamma_{NBT}$ ratio.

Based on Thermal Shock Resistance (TSR) theory, materials can be differentiated in terms of their susceptibility to degradation, either due to crack initiation or due to crack propagation sensitivity. As a result, this approach enables a more accurate prediction of material behavior under thermal shock conditions, specifically in determining whether strength degradation is more pronounced during the initial stages due to crack initiation, or in the later stages during next thermal shocks, where the propagation of pre-existing cracks becomes the dominant factor.

Spinel content increase resistant for crack initiation but at the same time has negative effect for crack propagation processes. Addition of nano-metric alumina, although change compactness and mechanical properties of in situ spinel-forming alumina-based castables do not change notably thermal shock resistance.

Research on thermal shock resistance remains critically important for the future, as it directly contributes to extending the service life of refractory materials.

CRedit authorship contribution statement

Ryszard Prorok: Writing – review & editing, Writing – original draft, Validation, Software, Resources, Methodology, Formal analysis, Conceptualization. **Karina Warmuz:** Writing – original draft, Investigation, Data curation. **Dominika Madej:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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We confirm that we are the Authors of this publication and that there are no other persons who satisfied the criteria for authorship but are not listed.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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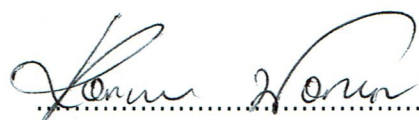
Oświadczam, że w publikacji:

„Effect of the particle size on the reactivity of $MgO-Al_2O_3$ hydrating mixtures: A long-term kinetic investigation of hydrotalcite synthesis”, Karina Warmuz, Dominika Madej, Applied Clay Science, 211, 2021, s. 1-14, doi: 10.1016/j.clay.2021.106196

powstałej w ramach projektu badawczego pt. *„Innowacyjne bezzementowe ogniotrwałe betony korundowo-spinelowe o zmodyfikowanej osnowie”* finansowanego przez NCBiR w ramach programu LIDER VIII - nr umowy LIDER/5/0034/L-8/16/NCBR/2017 (Kierownik: Dominika Madej),

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1. **Karina Warmuz (50%)**: przygotowanie próbek do badań, przeprowadzenie badań laboratoryjnych, zebranie materiału badawczego, analiza wyników badań XRD, FT-IR, potencjału dzeta, pH, wizualizacja wyników badań, analiza merytoryczna wyników, udział w przygotowaniu treści manuskryptu, korespondencja z redakcją czasopisma i recenzentami.
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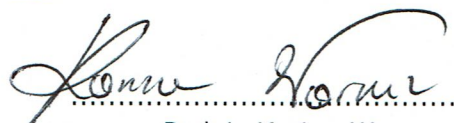
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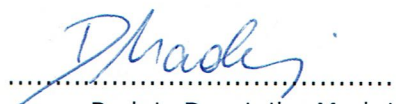
„Comparison of the CAC-containing and CAC-free hydraulic binders in term of the hydrated matrix formation within refractory castables designed for the fast drying procedure”, Karina Warmuz, Dominika Madej, Journal of Thermal Analysis and Calorimetry, 147, 18, 2022, s. 9975-9986, doi: 10.1007/s10973-022-11351-2

powstałej w ramach projektu badawczego pt. „*Innowacyjne bezcementowe ogniotrwałe betony korundowo-spinelowe o zmodyfikowanej osnowie*” finansowanego przez NCBiR w ramach programu LIDER VIII - nr umowy LIDER/5/0034/L-8/16/NCBR/2017 (Kierownik: Dominika Madej),

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Oświadczam, że w publikacji:

„Synthesis and evaluation of Mg-Al hydrotalcite formation and its influence on the microstructural evolution of spinel-forming refractory castables under intermediate temperatures”, Karina Warmuz, Dominika Madej, Journal of the European Ceramics Society, vol. 42, 5, 2022, s. 2545-2555, doi: 10.1016/j.jeurceramsoc.2022.01.009

powstałej w ramach projektu badawczego pt. *„Innowacyjne bezcementowe ogniotrwałe betony korundowo-spinelowe o zmodyfikowanej osnowie”* finansowanego przez NCBiR w ramach programu LIDER VIII - nr umowy LIDER/5/0034/L-8/16/NCBR/2017 (Kierownik: Dominika Madej),

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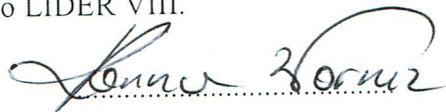
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„Thermomechanical evaluation and thermodynamic simulations of MgO-based ULC castables with different Al_2O_3 content” Karina Warmuz, Krzysztof Ziewiec, Dominika Madej
Journal of the European Ceramic Society, Volume 44, Issue 2, February 2024, Pages 1239–1255
DOI: <https://doi.org/10.1016/j.jeurceramsoc.2023.09.036>,

powstałej w ramach projektu badawczego pt. „Innowacyjne bezcementowe ogniotrwałe betony korundowo-spinelowe o zmodyfikowanej osnowie” finansowanego w ramach programu LIDER VIII - nr umowy LIDER/5/0034/1-8/16/NCBR/2017 (kierownik: dr hab. inż. Dominika Madej), wkład merytoryczny był następujący:

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Podpis: Karina Warmuz

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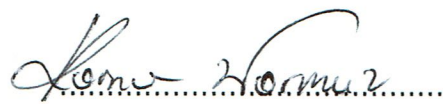
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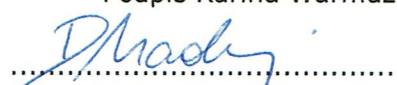
„Comprehensive experimental verification and theoretical modeling of cement-free alumina-based castables forming in-situ spinel ($MgAl_2O_4$) with enhanced thermal shock resistance”, Prorok Ryszard, Karina Warmuz, Dominika Madej, Ceramics International, 2025, doi:10.1016/j.ceramint.2025.07.325,

powstałej w ramach projektu badawczego pt. „Innowacyjne bezcementowe ogniotrwałe betony korundowo-spinelowe o zmodyfikowanej osnowie” finansowanego przez NCBiR w ramach programu LIDER VIII - nr umowy LIDER/5/0034/L-8/16/NCBR/2017 (Kierownik: Dominika Madej),

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- 3. Dominika Madej (20%)**: przeprowadzenie analizy termodynamicznej przebiegu reakcji chemicznych wraz z opracowaniem, analizą i opisem wyników, analiza i opis wyników badań, nadzór merytoryczny, udział w przygotowaniu treści manuskryptu, korekta merytoryczna i edytorska publikacji, zapewnienie finansowania badań z projektu badawczego LIDER VIII.


.....
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.....
Podpis Dominika Madej


.....
Podpis Ryszard Prorok