CONTROLLING THE SINTERING PROCESS OF MULLITE-ZIRCONIA BONDED REFRACTORIES MADE FROM ZIRCON AND ANDALUSITE

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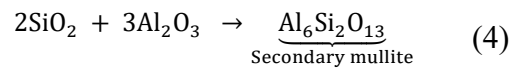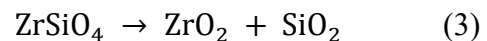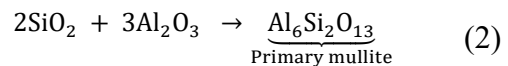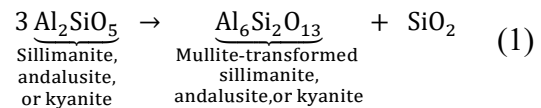[3] MINES Saint-Étienne, Fr. [4] SARPI-VEOLIA, Limay, Fr.

ABSTRACT

Although mullite–zirconia composites made from zircon, alumina, and andalusite meet the requirements for many high temperature applications, little effort has been made to transfer these composites to the bonding phase (the matrix) of refractory bricks. In this research, we investigate how this could be achieved through better control of secondary oxides: P_2O_5, Na_2O, and TiO_2 during the sintering. Thermodynamic calculations were performed to determine the phases at high temperatures. The calculations were compared to the microstructures, mineralogy, and properties of the composites. The results revealed that the system is very sensitive to Na_2O, which harmed the microstructure considerably. By contrast, TiO_2 and P_2O_5 additions proved beneficial, allowing complete zircon decomposition at 1550 °C while providing the required green strength. Decohesion between the matrix and aggregates due to high matrix shrinkage can be prevented by partially substituting andalusite with the volume-increasing mineral kyanite. Based on these findings, a novel refractory brick was developed and tested with success in hazardous waste incineration rotary kilns. The material resisted much longer than mullite–bonded refractories.

INTRODUCTION

Prior studies have showcased the benefits of mullite–zirconia refractories made from zircon, alumina, and andalusite including chemical stability in contact with slag [1], high strength [2,3], and thermal shock resistance [4]. These properties make mullite-zirconia system a promising candidate as bonding system of novel refractories. The sintering process of $ZrSiO_4$–Al_2O_3–Al_2SiO_5 mixtures can be divided into four steps:

$$3\underset{\substack{\text{Sillimanite,}\\\text{andalusite,}\\\text{or kyanite}}}{\underline{Al_2SiO_5}} \rightarrow \underset{\substack{\text{Mullite-transformed}\\\text{sillimanite,}\\\text{andalusite,or kyanite}}}{\underline{Al_6Si_2O_{13}}} + SiO_2 \quad (1)$$

$$2SiO_2 + 3Al_2O_3 \rightarrow \underset{\text{Primary mullite}}{\underline{Al_6Si_2O_{13}}} \quad (2)$$

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2 \quad (3)$$

$$2SiO_2 + 3Al_2O_3 \rightarrow \underset{\text{Secondary mullite}}{\underline{Al_6Si_2O_{13}}} \quad (4)$$

The first two mullitisation steps (Reactions (1) and (2)) begin at about 1300 °C upon heating and conclude at around 1400 °C [1,5]. From a technological point of view, the critical step is zircon decomposition (Reaction (3)), because it requires a high temperature. Pure zircon dissociates into zirconia and silica at 1673 °C [6]. In the presence of alumina, this temperature reduces to 1450–1600 °C, depending on the reactivity and purity of the starting powders [7]. The last step (Reaction (5)) is the reaction between the zircon-released silica and the remaining alumina to form secondary mullite [8].

In this research, we investigated the possibility of using mullite-zirconia

composite system as the bonding matrix phase of refractory bricks, with a focus on the impacts of secondary oxides Na_2O, TiO_2 and P_2O_5 on the high temperature sintering reactions, microstructures, and properties. The findings offer an understanding of how to successfully control the reaction-sintering process in refractory bricks. First, we focus on the matrix itself, regarding the phases that form at high temperature. Second, we shed light on the matrix–aggregate interdependence within a refractory brick. We also address the problem of matrix shrinkage and explain how kyanite can help to solve this problem.

RESULTS AND DISCUSSION

PART 1- THE BONDING PHASE

> ### Effect of secondary oxides on mineralogy and microstructure of the matrix

All four reactions (1)-(4) are diffusion dependent, making them sensitive to the presence of a liquid phase. This explains why impurities are so critical to this system [7].On one hand, they accelerate the reaction sintering processes, but on the other, they can harm the microstructure and deteriorate the final properties.

Zircon dissociation takes place between 1450 and 1570 °C in zircon–alumina–andalusite mixtures (without additives).

The effects of secondary oxides are illustrated in the diffractograms in Fig.1. Adding 1 mol% (0.34 wt%) Na_2O lowers the zircon transformation start and finish temperatures by approximately 50 °C. By 1500 °C, almost all the zircon has already dissociated.

TiO_2 is the most effective at promoting zircon dissociation. The zircon peaks have mostly disappeared in the diffractogram of the sample fired at 1500 °C, whereas the zircon peaks are still well pronounced in the Na_2O-doped sample sintered at the same temperature.

For the P_2O_5-doped samples, after sintering at 1550°C, the zircon peaks are yet well visible. Crystalline $AlPO_4$ was not detected by X-ray diffraction. $AlPO_4$ might have been incorporated into the silica-rich amorphous phase.
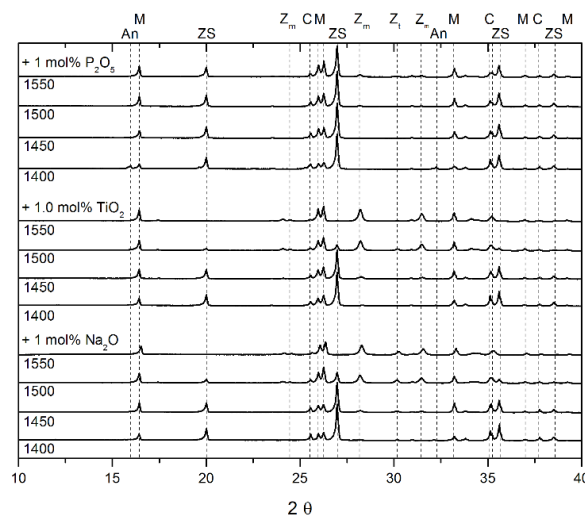

Fig.1 X-ray diffraction patterns of zircon–alumina–andalusite–additive mixtures sintered at different temperatures. C:corundum(Al_2O_3),M:mullite ($Al_6Si_2O_{13}$), An: andalusite (Al_2SiO_5), ZS: zircon ($ZrSiO_4$), Z_m :monoclinic zirconia (m-ZrO_2), and Z_t :tetragonal zirconia (t-ZrO_2).

The effects of the three additives on the microstructures can be compared in Fig.2.

- When Na_2O is added (Fig 2 (b)), the resulting ZrO_2 particles are 0.5–3 μm in size, which is noticeably smaller than those in the other samples. However, there are notable amounts of amorphous phase. The liquid phase causes densification of the matrix sample, leading to reduced porosity.

- With the addition of TiO_2 (Fig 2 (c)), zircon is completely transformed after sintering at 1550 °C. Nevertheless, the microstructure does not vitrify, contrary to the case for Na_2O, although the porosity is still reduced somewhat compared to that in the additive-free matrix. The final zirconia grains are about 5 μm in size, similarly to the

zirconia grains in the additive-free matrix with fully dissociated zircon, sintered at 1570 °C.

- The impact of P_2O_5 on the zircon decomposition is marginal (Fig.2 (d)).

Further experiments revealed that a combination of 2 mol% P_2O_5 and 3 mol% TiO_2 provided optimal green properties and complete zircon dissociation at 1550 °C. Therefore, these combined additives were chosen for the brick samples.
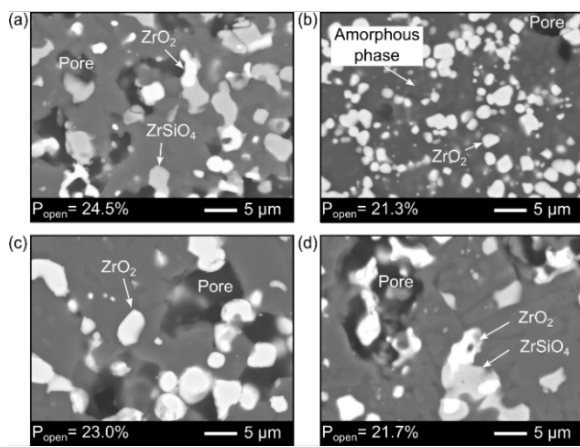

Fig.2 Impact of additives (1 mol%) on the final microstructure and open porosity of zircon–alumina–andalusite mixtures sintered at 1550 °C:(a) without additives, (b) 0.34 wt% Na_2O, (c) 0.88 wt% TiO_2, and (d) 1.55 wt% P_2O_5.

The effects of secondary oxide additions (Na_2O, TiO_2, and P_2O_5) are exhibited in the equilibrium phase diagrams in Fig.3.

- The Na_2O addition had a strong but negative impact. According to the thermodynamic calculations depicted in Fig. 3 (a), an addition of 0.3 wt% Na_2O would increase the liquid portion at 1200 °C (from 1.3 to 3.8 wt%) and more than double it at 1550 °C (from 3.0 to 6.6 wt%). Consequently, Na_2O shifted the first two mullitisation steps to lower temperatures. This might explain the smaller zirconia grain sizes obtained when Na_2O was added: the low

temperature liquid could have promoted primary mullite growth (Reaction (3)), and the zirconia grains from zircon decomposition could have been trapped within the primary mullite network, hindering the zirconia grains from growing together. Unfortunately, while the small grain size is desirable, the final matrix exhibited very high amounts of a glassy phase. Thus, Na_2O is highly undesirable for refractory purposes.
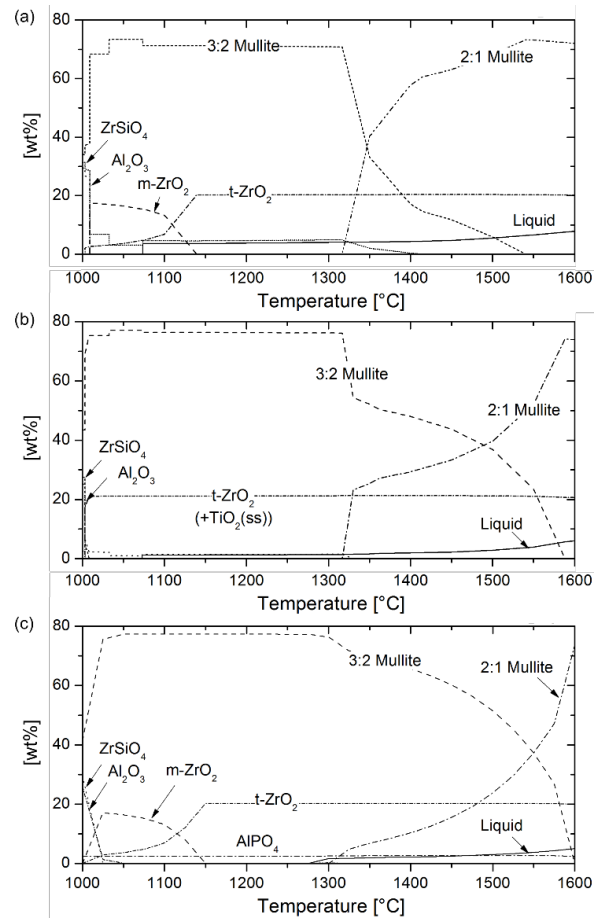

Fig.3 Impacts of 1 mol% oxide additions on the thermodynamic equilibrium of a 30% $ZrSiO_4$–36% Al_2O_3–34% Al_2SiO_5 (wt%) mixture (including impurities): (a) +0.34 wt% Na_2O, (b) +0.88 wt% TiO_2, and (c) +1.55 wt% P_2O_5. m- and t-ZrO_2 are monoclinic and tetragonal zirconia, respectively. ss: solid solution.

- The TiO_2 addition promoted zircon dissociation while generating minor amounts of amorphous phase (Fig.3

(b)). The addition of 1 mol% (0.88 wt%) TiO_2 generates 1.3 and 3.9 wt% liquid at 1200 and 1550 °C, respectively, which is slightly greater than that in the additive-free matrix. Moreover, TiO_2 forms a solid solution with ZrO_2, which stabilises the tetragonal zirconia (t-ZrO_2) modification below 1170 °C. Nevertheless, the stabilising effect of TiO_2 on the t-ZrO_2 phase suggested in the literature and our thermodynamic calculations was not observed experimentally in our TiO_2-doped samples. It could be that TiO_2 merely did not have enough time to diffuse from the transitory liquid phase into the zirconia grains. Furthermore, the rather high zirconia grain size (5 μm) and the high porosity both work against the tetragonal zirconia stabilisation. Overall, TiO_2 is a suitable sintering aid for mullite–zirconia bonded refractory materials.

- In the P_2O_5 doped mixture, the thermodynamic calculations predict the formation of a liquid phase at approximately 1300 °C, i.e. 200 °C higher than that for the additive-free matrix (Fig.3 c). Consequently, the primary mullitisation step and the zircon decomposition were delayed. To enable full zircon dissociation at 1550 °C, the phosphate needed to be added in conjunction with TiO_2. The matrix with 2 mol% P_2O_5 and 3 mol% TiO_2 yielded the most promising results.

> ### *Solution for matrix shrinkage*

Matrix shrinkage should be avoided because it leads to decohesion at the matrix/aggregate interface and a noticeable drop in mechanical strength. SEM observations (Fig. 4) revealed that a decohesion between the aggregates and matrix when a certain sintering temperature was surpassed.

It is possible to counter high matrix shrinkage by employing Kyanite (Al_2SiO_5), a polymorph of andalusite, that increase in volume during sintering.
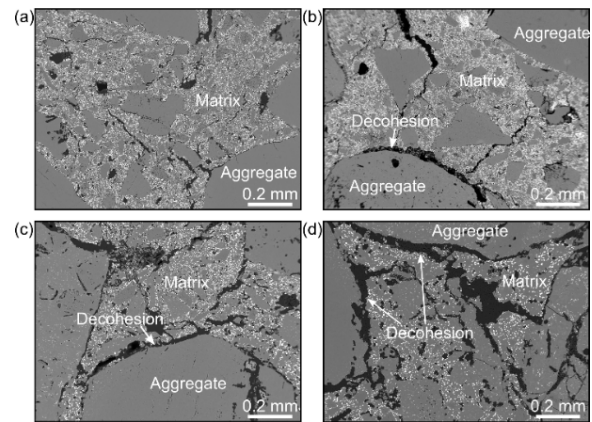

Fig.4. SEM images of a mullite–zirconia-bonded brick sintered at (a) 1450 °C, (b) 1500 °C, (c) 1550 °C, and (d) 1600 °C, revealing decohesion between the matrix and aggregates (Mulcoa 60) caused by matrix shrinkage.

Figure 5 shows that, in the additive-free matrix, approximately one third of the andalusite needs to be replaced by kyanite to obtain a matrix that neither shrinks nor expands at 1550 °C.
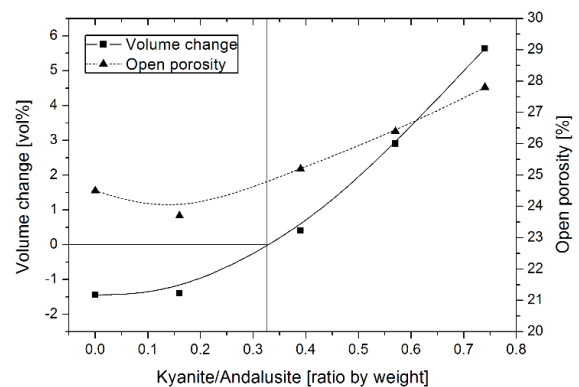

Fig.5. Impact of kyanite on the volume expansion and porosity of a sintered (1550 °C) mullite–zirconia (20 wt% ZrO_2) matrix made from andalusite/kyanite, alumina, and zircon.

Accordingly, the kyanite and andalusite contents of the matrix were adjusted to

attain zero shrinkage when sintering at 1550 °C.

PART 2 - FABRICATION AND PROPERTIES OF NOVEL BRICKS

The brick formulations contained a matrix composed of 31.3 wt% zircon, 37.8 wt% alumina, 10.2 wt% andalusite, 15 wt% kyanite, 2.6 wt% (3 mol%) TiO_2, and 3.1 wt% (2 mol%) P_2O_5.
The aggregate/matrix volume ratio was 7:3. The maximum and minimum grain sizes of 6 mm and 2 µm, respectively, were the same for all formulations.
Various aggregate systems were evaluated, but only the two most suitable systems are detailed in this paper. The first system used a combination of andalusite (0.1–1.6 mm) and high alumina chamotte (1–6 mm) aggregates, while the second system used fused zirconia–mullite (FZM; 0.1–6 mm) aggregates.
After a total mixing time of 30 min, the batch was pressed to bricks using a uniaxial pressure of 150 MPa. Finally, the bricks were dried overnight at 110 °C and fired at 1500, 1550, or 1600 °C. The heating rate and dwell time were 2.5 °C/min and 3 h, respectively.

➢ *Choice of aggregates*

To successfully transfer the good matrix properties to the brick, the choice of aggregate is important.
Representative microstructures of the bricks with andalusite/Mulcoa 60 and FZM aggregates are depicted in Fig.6 (a) and (b). In both cases, the zirconia particles are well distributed and there are no large gaps between the aggregates and matrix. However, fine cracks appeared at the matrix/aggregate interface when using andalusite/Mulcoa 60 aggregates, which were absent when using the FZM aggregates.

- FZM aggregates suited well; the chemical similarity of the matrix and aggregate materials led to strong cohesion at the matrix/aggregate interface.

- In contrast Mulcoa 60 had a loose interface with the matrix and therefore bestowed relatively poor strength. The loose bonding probably had two origins :
First, there is a thermal expansion mismatch between the matrix and chamotte, which provoked cracking. Second, the TiO_2 impurities in Mulcoa 60 caused higher matrix shrinkage.
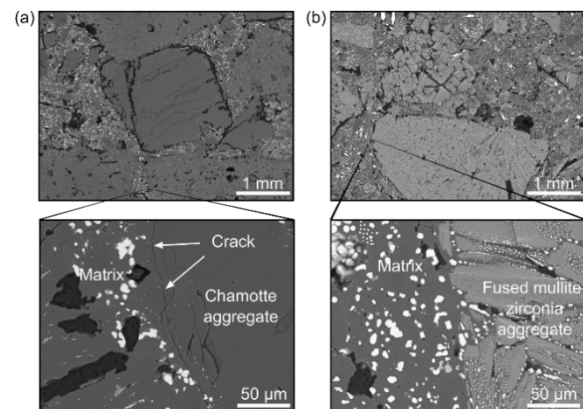

Fig 6. SEM images of mullite–zirconia-bonded refractory bricks made with (a) andalusite/Mulcoa 60 aggregates and (b) fused zirconia–mullite aggregates (FZM). Both bricks used the same matrix (31.3 wt% zircon, 37.8 wt% alumina, 10.2 wt% andalusite, 15 wt% kyanite, 2.6 wt% (3 mol%) TiO_2, and 3.1 wt% (2 mol%) P_2O_5) and sintering temperature (1550 °C).

➢ *Role of phosphate*

Just a few percent of phosphate precursors assures sufficient green strength and plasticity, forming chemical bonds at ambient temperature [9]. At high temperatures, $AlPO_4$ is formed [10], which reinforce the mullite–zirconia bonding.
In the investigated materials, P_2O_5 considerably reduced the porosity and increased the mechanical strength (Fig.7)
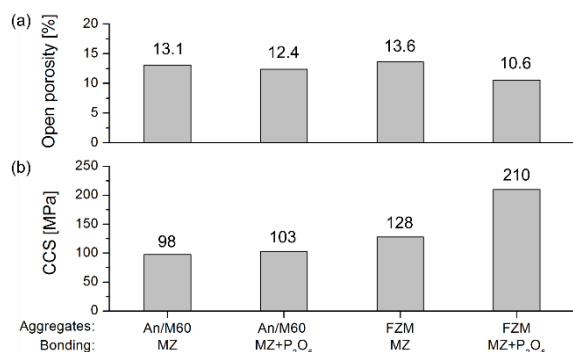
Fig. 7. Comparison of (a) open porosity and (b) cold crushing strength of mullite–zirconia bonded bricks with and without 2 mol% P_2O_5. Andalusite/Mulcoa 60 (An/M60) and fused zirconia–mullite (FZM) aggregates were used. All bricks were sintered at 1550 °C.

The liquid phase accounts for 3.9 wt% of the matrix at 1550 °C, which is only 0.9 wt% more than that in the additive-free mixture.

However, P_2O_5 has a slight retarding effect on the liquid phase formation.

> ➤ *Sintering curve*

The sintering temperature had a clear impact on the mechanical properties of the bricks (Fig. 8).
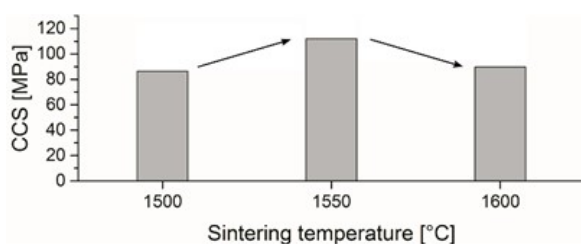

Fig. 8. Cold crushing strength (CSS) vs. sintering temperature of a mullite–zirconia-bonded brick (Aggregates: andalusite/Mulcoa 60).

Because the andalusite/kyanite ratio and additive content were respectively designed to give zero matrix shrinkage and complete zircon dissociation at 1550 °C, a maximum in strength was obtained when sintering at 1550 °C. If the sintering temperature is above or below this designed temperature, the desired matrix properties are no longer guaranteed.

The understanding of the high temperature phase transformations suggests applying low heating and cooling rates, for the following reasons:

- Slow heating rates, or a dwell at 1400 °C, should help to develop primary mullite crystals before zircon decomposition. A well-developed primary mullite network may inhibit zirconia coalescence and eventually reduce the zirconia grain size.

- Slow cooling rates or, if possible, a dwell at 1300 °C are recommended to encourage the 3:2 → 2:1 mullite transformation and reduce the amorphous phase fraction.

CONCLUSION

A novel mullite–zirconia bonded refractory material has been produced and field-tested in a rotary kiln incinerator, where the material was exposed to thermal shock and mechanical load. The material persisted much longer than mullite- bonded refractories.

We believe similar success could be achieved in other refractory areas, especially if alternative and more cost-effective aggregates could be found that are compatible with this matrix.

ACKNOWLEDGEMENTS

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