FORMATION AND INFLUENCE OF MAGNESIUM-ALUMINA SPINEL ON THE PROPERTIES OF REFRACTORY FORSTERITE-SPINEL CERAMICS

TVORBA IN VPLIV MAGnezIT-ALUMINATNega ŠPINELA NA LASTnosti OGNjeVARne FORSTERIT-ŠPINELNE KERAMIKe

Martin Nguyen*, Radomír Sokolá

Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components, Volveť 331/95, 602 00 Brno, Czech Republic

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Forsterite refractory ceramic is mostly used in the cement industry as the lining of a rotary kiln and as the lining of metallurgical furnaces due to its high refractoriness of up to 1850 °C. Another significant property of forsterite is its coefficient of linear thermal expansion used in the electrotechnical industry for ceramic-metal joints. An addition of aluminium oxide to a raw-material mixture results in the creation of a magnesium-alumina spinel (MgO·Al2O3), which improves the sintering and mechanical properties of forsterite ceramics. An inexpensive source of aluminium oxide is fly ash. The utilization of fly ash, a secondary energy product of coal-burning power plants, is important for the environment and sustainable development. This paper evaluates the transformation of mullite (3Al2O3·2SiO2) from fly ash into a magnesium-alumina spinel, its influence during the synthesis and the resulting properties of a fired forsterite refractory ceramic body. Forsterite-spinel ceramics were synthesized from olivine, calcined magnesite and 0–20 % of fly-ash powders. XRD analyses were used to determine the mineralogical composition, thermal analyses were used to determine the formation of spinel and its behaviour during the firing, and scanning electron microscopy (SEM) was used to determine the morphology of crystal phases. The refractoriness of pyrometric cones, refractoriness under load, thermal-shock resistance, water absorption, porosity and mechanical properties of the fired test samples were also determined. The transformation of mullite resulted in small amounts of magnesium-alumina spinel in the forsterite ceramics. Test results showed that the presence of magnesium-alumina spinel improved the sintering microstructure, thermal-shock resistance and mechanical properties in comparison with pure-forsterite refractory ceramics.

Keywords: forsterite, magnesium-alumina spinel, refractory, fly ash

Forsteritna ognevarna keramika se najbolj pogosto uporablja v industriji cementa kot obzidava za rotacijske peči in kot notranja obzidava metalurških peči zaradi njene odlične termične stabilnosti pri visokih temperatureh, vse do 1850 °C. Druga pomembna lastnost forsterita je njegov koeficient linearnega toplotnega raztezanja zaradi česar se uporablja tudi v elektrotehniški industriji za izdelavo spojev keramika-kovina. Na koncu je rezultat dodajanja aluminijevega oksida, kot osnovne surovine v mešanici, nastane magnezitno-aluminatnega špinela (MgO·Al2O3), ki izboljša potek sinteze in mehanske lastnosti forsteritne keramike. Cenom aluminijevega oksida je dimniški pepel. Uporaba dimniškega pepela, ki je sekundarni produkt termoelektrarn na prenog, je pomembna z ekološkega vidika in trajnostnega razvoja. V članku avtorji opisujejo oceno pretvorbe mulita (3Al2O3·2SiO2), ki ga vsebuje dimniški pepel, v magnezitno-aluminatni špinel in njen vpliv na sintezo, kakor tudi na lastnosti zgnane na osnovi forsterita nastale ognevarne keramične opeke. Forsterito-špinelno keramiko so sinteizirali iz olivina, kalcinaranega magnezita in dodatka 0 % do 20 % prahu dimniškega pepela. Za določitev mineralološke sestave so uporabili rentgensko difrakcijsko analizo (XRD), termično analizo (TGA) pa so uporabili za določitev tveganje špinela in obnašanja med procesom zganja. Morfologijo kristalnih faz so določili z vrstičnim elektronskim mikroskopom (SEM). Na žiganj stožcih iz izdelane keramike, so določili njeno ognevarnost, na drugih preizkušanjih pa še njeno odpornost pod obremenitvami ter odpornost proti termičnim šokom, absorpcijo vode, poroznost in mehanske lastnosti. Rezultat pretvorbe mulita je bila majhna vsebnost magnezitno-aluminatnega špinela v forsteritni keramiki. Rezultat preizkuškov so še pokazali, da prisotnost magnezitno-aluminatnega špinela izboljša sintezu, mikrostrukturo, odpornost proti termičnim šokom in mehanske lastnosti v primerjavi s čisto forsterito-ognevarno keramiko.

Ključne besede: forsterit, magnezitno-aluminatni špinel, ognevarnost, dimniški pepel

1 INTRODUCTION

Forsterite is magnesium silicate with the chemical formula 2MgO·SiO2. The melting point of forsterite is 1890 °C, which makes it very useful for refractory ceramics.1 Forsterite is used in the industry as the lining of the sintering zone of rotary kilns and metallurgical furnaces.2–3 Another significant attribute of forsterite ceramics is a high coefficient of linear thermal expansion, which is similar to the coefficients of metals. For this reason, forsterite is used in electrical engineering for joining ceramics with metals.4 Because of a high coefficient of linear thermal expansion, forsterite has a low thermal-shock resistance. This attribute can be improved through an addition of aluminium oxide, creating a magnesium-aluminate (MA) spinel. With the addition of spinel to a forsterite ceramic, the microstructure is improved, leading to higher mechanical properties.5

*Corresponding author's e-mail: nguyen.m@fce.vutbr.cz (Martin Nguyen)
Traditionally, spinel ceramics are sintered from alumina and magnesium oxides. However, fly ash as a secondary product from power plants can also be a source of aluminium and silicon oxides that can be utilized as raw materials for sintering forsterite-spinel ceramics. The formation of MA spinel from the mixtures with fly ash also occurred in our previous work. The main objective of this work is the clarification of the formation and influence of an MA spinel on the resulting properties of forsterite ceramics. Thermal analyses, microstructure, phase composition, physico-mechanical properties and refractory properties are investigated and compared with the forsterite ceramics without MA spinels.

2 EXPERIMENTAL PART

Three different raw-material mixtures were designed for the synthesis of forsterite refractory ceramics. Raw materials used for the synthesis of these mixtures were olivine (A/S Olivin, Norway), calcined caustic magnesite (CCM 85, min. 85% of MgO, SMZ, a.s. Ješava, Slovakia), fly ash (power plant Mělník, Czech Republic) and kaolin Sedlec Ia (Sedlecý kaolin a.s., Czech Republic). Designation of individual mixtures was based on the fly-ash content of the concerned mixture. Mixture OCF-0 had 0.0% of fly ash, OCF-10 had 10.0% of fly ash and OCF-20 had 20.0% of fly ash. Compositions of all raw-material mixtures are presented in Table 1. X-ray diffraction analysis (XRD) of the used raw materials is presented in Figure 1. The major crystal phase in CCM 85 (calcined caustic magnesite) is periclase and the minor phase is magnetite. The major crystal phases in olivine are forsterite and fayalite with minor traces of quartz and serpentine. The crystal phases in fly ash Mělník are mullite and quartz. The curved background of diffraction patterns also indicates the presence of an amorphous glass phase and iron oxide. The major crystal phases in kaolin Sedlec Ia are kaolinite and the minor phase is biotite.

Test samples were prepared from all designed mixtures and were subjected to homogenization in a rotary mechanical homogenizer for 24 hours to ensure homogeneity. The mixtures were then mixed with water to gain the optimal viscosity of plastic paste for the plastic moulding of the test samples. Approximate dimensions of the test samples were (20 × 25 × 100) mm³. Pyrometric cones for the refractoriness test were also prepared from the same plastic paste according to the official standard EN 993-13:1995. Green bodies were then dried in the laboratory dryer at 105 °C. All the test samples were then fired in an electrical laboratory furnace with air atmosphere at two different firing temperatures of 1400 °C and 1500 °C, with a heating rate of 3 °C / min.
Several experimental procedures were performed on the test samples after the firing. The apparent porosity, water absorption and bulk density were determined utilizing the vacuum water-absorption method described in the official standard EN 993-1:1995. Thermal analyses DTA/TG and DSC of all the mixtures (SN 72 1083) were carried out. A change in a dimension (length) of the test samples was noticed during the firing (EN 993-10:1997). Other observations included: the refractoriness of the pyrometric cones (EN 993-12:1997), refractoriness under load (ISO 1893:2007) and thermal-shock resistance (EN 993-11:2007). A thermal dilatometric analysis (EN 993-19:2004) was carried out. The modulus of rupture was tested using a Testometric M350-20CT (EN 993-6:1995).

The mineralogical compositions of the fired test samples were identified using the X-ray diffraction analysis (XRD; PANALYTICAL Empyrean) with Cu-Kα as the radiation source, an accelerating voltage of 45 kV, a beam current of 40 mA, a diffraction angle of 2θ in a range of 5–80° with a step scan of 0,01°. Scanning electron microscopy (SEM) with an EDX probe (Tescan MIRA3) was used to determine the morphology and elemental analysis of the crystal structure.

### 3 RESULTS

The creation and influence of the MA spinel in forsterite ceramics are studied in this paper to understand the process of recrystallization of aluminium oxide bearing minerals to the MA spinel. The XRD analysis presented in Figure 1 confirmed the presence of kaolinite (Al₂O₃·2SiO₂·2H₂O) in kaolin Sedlec Ia and mullite (3Al₂O₃·2SiO₂) in fly ash Mlénik as the sources of Al₂O₃. In the presence of magnesium oxide, they formed the MA spinel (MgO·Al₂O₃). This phenomenon is supported by the XRD analysis and SEM with the EDX probe used on the fired samples containing fly ash and kaolin as reported in the reference literature.8

Residual MOR is the quantity of the thermal-shock resistance of the test samples, heated to 950 °C and then quickly cooled down with air while this cycle is repeated 4 times. After all the cycles, the MOR of the tested samples is measured and compared with the MOR of the non-tested samples. Refractoriness is decreased for the samples with a higher amount of fly ash due to a higher amount of flux oxides such as Fe₂O₃, Na₂O and K₂O; however, the decrease is less than 5 %.

Figure 2 displays the behaviour during the sintering of all the samples with a varying amount of fly ash (0, 10 and 20 %). The sintering process can be divided into three stages. The first stage is the shrinkage at 1100–1250 °C, the second stage is the expansion at 1250–1350 °C and the third stage is re-shrinkage (>1350 °C).

Figure 3 displays the determination of refractoriness under load of the fired samples. With the increasing amount of fly ash in the mixture, the temperature at 0.5 % deformation (T₀.5) is decreasing due to the increased amount of flux oxides; however, the decrease is less than 3 %.

The microstructure of the test samples was evaluated using SEM with an EDX probe. Mixture OCF-0 without fly ash had large forsterite crystals interlocked into the

<table>
<thead>
<tr>
<th>Test samples</th>
<th>OCF-0-1400</th>
<th>OCF-10-1400</th>
<th>OCF-20-1400</th>
<th>OCF-0-1500</th>
<th>OCF-10-1500</th>
<th>OCF-20-1500</th>
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<tr>
<td>Fly ash amount (w/%)</td>
<td>0.0</td>
<td>10.0</td>
<td>20.0</td>
<td>0.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Firing temperature (°C)</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Firing shrinkage (%)</td>
<td>3.4</td>
<td>4.1</td>
<td>3.2</td>
<td>5.7</td>
<td>7.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>32.7</td>
<td>36.1</td>
<td>41.2</td>
<td>27.0</td>
<td>31.1</td>
<td>35.2</td>
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<tr>
<td>Water absorption (%)</td>
<td>14.4</td>
<td>16.7</td>
<td>20.7</td>
<td>10.9</td>
<td>13.3</td>
<td>16.1</td>
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<td>2160</td>
<td>1990</td>
<td>2470</td>
<td>2340</td>
<td>2190</td>
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<tr>
<td>Modulus of rupture (MPa)</td>
<td>9.1</td>
<td>10.0</td>
<td>11.6</td>
<td>11.4</td>
<td>13.5</td>
<td>17.4</td>
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<tr>
<td>Residual modulus of rupture (%)</td>
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<td>14.9</td>
<td>19.9</td>
<td>3.5</td>
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<td>Refractoriness (°C)</td>
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<td>1692</td>
<td>1665</td>
<td>1730</td>
<td>1693</td>
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matrix with few periclase crystals. On the left bottom image there is a rounded patch of forsterite crystals. Mixtures OCF-10 and OCF-20 with fly ash also contained orthorhombic dipyramidal crystals of the MA spinel (bottom middle and right images), located in the patches between the forsterite crystals and in the space between them, creating a more compact microstructure.

The XRD analysis confirmed the presence of forsterite in all the mixtures. Mixture OCF-0 (without fly ash) had a major crystal phase of forsterite and minor phases of periclase, magnetite and monticellite. Mixture OCF-10 and OCF-20 (with 10 % and 20 % of fly ash, respectively) had a major crystal phase of forsterite and minor phases of periclase, MA spinel and monticellite.

The thermal analyses (Figures 6 to 8) performed on the test samples were DTA/TG and DSC using a Mettler Toledo TGA/DSC1 device up to 1350 °C at a heating rate of 10 °C/min.

Figure 4: SEM of different mixtures with magnifications of 2000× (top) and 15000× (bottom)

Figure 5: X-ray diffraction patterns of all the mixtures with different amounts of fly ash
4 DISCUSSION

The increased firing shrinkage (Table 3) of the mixtures with higher amounts of fly ash is due to the presence of accessory oxides (Fe$_2$O$_3$, K$_2$O, Na$_2$O and CaO), which promote the densification of the samples and creation of an amorphous glass phase, which can be seen as a curved background of the XRD patterns. With the increased amount of fly ash in the mixtures, the porosity and water absorption also increase while the bulk density decreases (Table 3). This phenomenon can be explained with the results of a thermodilatometric analysis (Figure 2) where, in the temperature interval of 1250–1350 °C, the expansion stage of the samples with fly ash occurred, followed by the re-shrinkage stage. Y. Dong, S. Hampshire et al. also reported this behaviour in their work. This expansion is attributed to the formation of an amorphous phase with a lower density (around 17 %) than that of quartz.\textsuperscript{1–2}
In the thermal analyses (Figures 6 to 8), the SDTA and DSC curves exhibit strongly exothermic reactions, starting at around 1100 °C, indicating the oxidation of fayalite into magnetite and amorphous silica (Equation 1) in all the samples and also a simultaneous crystallization of the MA spinel from mullite and periclase (Equation 2) in the samples with fly ash. These results are also confirmed by the XRD analysis (Figure 5) and SEM with the EDX probe (Figure 4, bottom). The surplus silicon dioxide then reacts with periclase to form forsterite according to Equation (3).14

\[
3(2\text{FeO} \cdot \text{SiO}_2) + \text{O}_2 \xrightarrow{1205^\circ C} 2\text{Fe}_2\text{O}_3 + 3\text{SiO}_2 \tag{1}
\]

fayalite+oxygen \rightarrow magnetite+silicone dioxide

\[
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 3\text{MgO} \rightarrow 3\text{MgO} \cdot \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \tag{2}
\]

mullite+periclase \rightarrow MA – spinel+silicone dioxide

\[
2\text{MgO} + \text{SiO}_2 \rightarrow 2\text{MgO} \cdot \text{SiO}_2 \tag{3}
\]

periclase+silicon dioxide \rightarrow forsterite

With the increased amount of fly ash in the mixture, the MOR (Table 3) of the test samples is also increased due to the positive effect of MA spinel, improving the mechanical properties of the forsterite ceramics.14 MA spinel is formed as small crystals of 2–4 μm in diameter on the edges of large forsterite crystals or in the connecting space between the patches of forsterite crystals and the amorphous glass matrix, as seen in the SEM images of the microstructure (Figure 4). This attribute allows the test samples with MA spinel to have a higher MOR due to the interconnection between the MA spinel crystals and the forsterite matrix, which improves the microstructure.

MA spinel has a lower thermal-expansion coefficient than forsterite, leading to an improvement of the thermal-shock resistance of the mixtures with fly ash.5 The residual MOR (Table 3) characterizes the thermal-shock resistance according to standard EN 993-11:2007 method B. The residual MOR of mixture OCF-0 without fly ash was, on average, 3 %; for mixture OCF-10 with 10 % of fly ash, it was, on average, 19 % and for mixture OCF-20 with 20 % of fly ash, it was, on average, 25 %. It can be concluded that MA spinel significantly improved the thermal-shock resistance. With the increased amount of fly ash in the mixture, the thermal-shock resistance is higher due to the presence of MA spinel crystals interlocking the forsterite patches with the amorphous glass matrix (the SEM analysis) and due to a higher amount of flux oxides, promoting the creation of the amorphous glass phase and sintering of the test samples.

The thermal analyses (Figures 6 to 8) confirmed the results of the XRD analysis and SEM with the EDX probe. There are several endothermic peaks on the DTG (the 1st derivation of TG) curve. The first broad peak up to 200 °C is due to the loss of adsorbed water, the next peaks at around 370 °C and 440 °C are due to the de-hydroxylation of water from serpentine.15,16 The peak at 525 °C is due to the modification from β-quartz to α-quartz. The endothermic peak at around 690 °C is due to the decomposition of kaolinite into metakaolin and water1 and also the subsequent decomposition of serpentine. The last peak is between 1255–1275 °C and is due to the decomposition of fayalite, which melts at 1205 °C, and an amorphous silica phase is formed.1–2

There is a strong exothermic peak on the SDTA curves (Figures 6 to 8), which starts at 1100 °C and continues up to 1350 °C. This exothermic reaction is due to the crystallization of MA spinel from mullite and periclase and also the solid-state reaction needed for the formation of forsterite.5 MA spinel was identified with the XRD analysis and the EDX probe of SEM while no traces of mullite were found.

5 CONCLUSIONS

Refractory forsterite ceramics were sintered at 1400 °C and 1500 °C from calcined magnesite, olivine, fly ash and kaolin. Different amounts of fly ash were used to evaluate the creation of MA spinel from aluminium and magnesium oxides and its influence and properties after firing. An XRD analysis confirmed the presence of forsterite as the major crystal phase with minor phases of periclase, magnetite, monticellite and MA spinel in the mixtures with fly ash. Spinel formed dipyramidal crystals (2–4 μm in diameter) on the edges and in the space between large forsterite crystals in the matrix. The formation of spinel improved the modulus of rupture and thermal-shock resistance while only a minor decrease in the refractoriness and refractoriness under load occurred.

In the samples with fly ash, the expansion stage occurred in the temperature interval of 1250–1350 °C, which is attributed to the creation of an amorphous silica phase. Flux oxides contained in fly ash promoted the creation of this amorphous phase. Therefore, with the increased amount of fly ash, more amorphous phase was formed and this resulted in a higher shrinkage, porosity, water absorption and a lower bulk density.

In conclusion, the addition of fly ash into the raw-material mixture of forsterite ceramic resulted in the creation of a small amount of MA spinel that improved the mechanical properties, microstructure and thermal-shock resistance of forsterite ceramic. Simultaneously, the refractory properties were impaired only by less than 5 %.

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6 REFERENCES