Presence of magnesium-alumina spinel in forsterite ceramics and its influence during sintering and on resulting properties of fired body

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Abstract. The main objective of this paper is to describe the creation and behaviour of magnesium-alumina spinel (MA-spinel) phase from raw materials mixtures in forsterite refractory and its influence on resulting physical properties and mineralogical composition of fired body. Forsterite ceramics is mostly used for its high refractoriness as a refractory material in kilns and furnaces and also in electrotechnical engineering for its high coefficient of linear thermal expansion for ceramic-metal joints. Currently, forsterite is not produced in the Czech Republic. The primary objective is to synthesize forsterite ceramics via solid-state reaction utilizing various raw materials used in industry with stoichiometric ratio of forsterite. The resulting properties of fired body will be determined using X-ray diffraction analysis for mineralogical composition, thermal dilatometric analysis and vacuum water absorption method for physical properties of fired body and refractoriness of pyrometric cones will be conducted.

1. Introduction

Forsterite is a magnesium silicate mineral with chemical formula 2MgO·SiO₂. It is magnesium-rich end-member of the olivine solid solution series. Naturally occurring olivines are fairly abundant mineral in the earth’s crust but they contain about 10-15% of fayalite (iron silicate) with chemical formula 2FeO·SiO₂. While the melting point of forsterite is relatively high (1890 °C), the melting point of fayalite is relatively low (1205 °C) for refractory applications. The amount of fayalite up to 10% in olivine has not very significant impact on refractoriness. [1-2]

Forsterite ceramics primary use in the industry is for refractory bricks [3] due to the high refractoriness of forsterite (up to 1850 °C) and refractoriness under load above 1600 °C. [4] This is significant for utilization of forsterite as a lining of the sintering zone of rotary kilns for cement production and metallurgical furnaces, because forsterite practically does not react with clinker or iron at high temperatures. [1] Another significant attribute of forsterite is its coefficient of linear thermal expansion which has linear increase similar to coefficient of metals with increasing temperatures. [5] Due to this attribute, forsterite is also used in electrical engineering for joining the ceramics with metal. [4] Forsterite may even be suitable for biomedicine as a bone implant biomaterial. [6]

Addition of aluminium oxide into the raw material mixture results in a creation of MA-spinel (MgO·Al₂O₃) in addition to forsterite. MA-spinel in forsterite refractory improves its mechanical
properties and sintering while retaining its refractory properties. Inexpensive source of aluminium oxide is fly ash which is secondary energetic product in power plants combusting coal. [7-10]

2. Materials and methods

2.1. Raw materials

Raw materials used for synthesis of forsterite were raw magnesite (magnesium carbonate), talc, quartz sand, olivine, calcined caustic magnesite (CCM), fly ash from power plant Mělník and kaolin Zettlitz Ia. Pharmaceutical quality raw magnesite (purity 98%, d$_{50} = 2$ µm) and talc (purity 97%, d$_{50} = 5$ µm) were acquired from the company Fichema Ltd., micro-milled quartz sand ST9 (purity 99.6%, d$_{50} = 6$ µm) was acquired from the company Sklopísek Střeleč Inc., finely ground olivine was acquired from the company Olivin, Norway. CCM 85 (min. 85% of MgO) was acquired from the magnesite plants in Jelšava, Slovakia. Fly ash as a secondary energetic product of coal firing in power plant Mělník and kaolin Zettlitz Ia was used for better binding strength of a green body.

Five different raw material mixtures were designed with a stoichiometric ratio of forsterite. First mixture (REF) was intended as a reference value for other mixtures and was composed of pure pharmaceutical quality raw materials – magnesite and talc to form pure forsterite during synthesis. Second mixture (OLI-CCM) was composed of CCM 85 and olivine. Third mixture (FA-CCM) was composed of fly ash from power plant Mělník and CCM 85. Fourth mixture (OLI-QS-CCM) was composed of olivine, quartz sand ST9 and CCM 85. Fifth mixture (MAG-FA) was composed of raw magnesite and fly ash from power plant Mělník. All mixtures contained 10 wt% of kaolin Zettlitz Ia for improved binding strength of the green body and improved sintering during firing. Weight composition of raw materials with stoichiometric ratio of forsterite for all individual mixtures is presented in table 1. Chemical composition of used raw materials is presented in table 2.

| Raw materials | REF (wt%) | OLI-CCM (wt%) | FA-CCM (wt%) | OLI-QS-CCM (wt%) | MAG-FA (wt%) |
|---------------|----------|---------------|--------------|-----------------|-------------|
| Magnesite     | 53.8     | -             | -            | -               | 62.2        |
| Talc          | 36.2     | -             | -            | -               | -           |
| CCM 85        | -        | 42.2          | 50.0         | 49.9            | -           |
| Quartz sand ST9 | -        | -             | -            | 15.6            | -           |
| Olivine       | -        | 47.8          | -            | 24.5            | -           |
| Fly ash       | -        | -             | 40.0         | -               | 27.8        |
| Kaolin Zettlitz Ia | 10.0 | 10.0         | 10.0         | 10.0            | 10.0        |

| Raw materials | MgO (%) | SiO$_2$ (%) | CaO (%) | Fe$_2$O$_3$ (%) | Al$_2$O$_3$ (%) | K$_2$O+Na$_2$O (%) | LOI* (%) |
|---------------|---------|-------------|---------|-----------------|-----------------|-------------------|----------|
| Magnesite     | 44.2    | 0.1         | 0.4     | 0.0             | 0.0             | 0.0               | 52.0     |
| Talc          | 31.5    | 59.1        | 1.0     | 0.7             | 1.0             | 0.2               | 6.5      |
| CCM 85        | 85.0    | 0.5         | 5.2     | 7.3             | 0.8             | 0.2               | 1.0      |
| Quartz sand ST9 | 0.0    | 99.6        | 0.1     | 0.1             | 0.2             | 0.1               | 0.0      |
| Olivine       | 24.1    | 64.7        | 0.7     | 8.8             | 1.0             | 0.5               | 1.0      |
| Fly ash       | 1.4     | 57.3        | 2.2     | 5.1             | 29.3            | 1.7               | 1.2      |
| Kaolin Zettlitz Ia | 0.5  | 46.8        | 0.7     | 0.9             | 36.6            | 1.2               | 13.2     |

* Loss on ignition
It is apparent from figure 1 that major crystal phases in raw fly ash from power plant Mělník are mullite and quartz. The curved background of diffraction curve also indicates the presence of amorphous glass phase and iron oxide. Figure 2 contains XRD analysis of raw and heat-treated olivine. Crystal phases present in raw olivine are forsterite, fayalite, enstatite, quartz and serpentine. Crystal phases present in heat treated olivine at 1300 °C are forsterite, enstatite, quartz and hematite. And in heat treated olivine at 1400 °C are forsterite, periclase, magnetite and enstatite.

2.2. Preparation of test samples
All mixtures were subjected to homogenization in a mechanical rotary homogenizer for 24 hours to ensure homogeneity of all mixtures. Homogenized mixtures were then mixed with water to gain an optimal viscosity of plastic paste for plastic moulding of test samples. Dimensions of test samples were approximately 20 × 25 × 100 (mm³). Pyrometric cones were also prepared from the same plastic paste as test samples according to the official standard EN 993-13:1995. Green bodies and pyrometric cones were then dried in a laboratory dryer at 105°C. After drying, all test samples and pyrometric cones were fired in an electrical laboratory furnace with air atmosphere and controlled environment.
Maximum firing temperature was set to 1300 °C with heating rate of 4 °C per minute and soaking time of 2 hours at maximum temperature.

### 2.3. Experimental procedures

Several laboratory tests were performed on test samples and pyrometric cones after firing. Apparent porosity, water absorption and bulk density were determined utilizing the vacuum water absorption method described in the official standard EN 993-1:1995. Change in dimension (length) of test samples during firing was determined according to the official standard EN 993-10:1997. Refractoriness of pyrometric cones was determined according to the official standard EN 993-12:1997 using an electrical laboratory furnace with an observation opening which enables the use of a digital camera to record the real time behaviour of pyrometric cones during increasing temperature up to 1800°C, considering optical properties. Thermal dilatometric analysis was done in accordance with the official standard EN 993-19.

Mineralogical composition of fired test samples was identified using X-ray diffraction analysis (PANALYTICAL Empyrean XRD) with Cu cathode as a radiation source, Kα2/Kα1 ratio of 0.5, accelerating voltage 45 kV, beam current 40 mA, diffraction angle 2θ in the range from 15° to 70° with a step scan of 0.01°. Acquired XRD patterns were then evaluated using a PC software Match! version 3.8 and Crystallography Open Database (COD). Semi-quantitative analysis of all fired samples was obtained by means of the reference-intensity ratio (RIR) method using the same software. Final chemical composition of all mixtures after firing is presented in table 3.

| Mixture     | MgO (%) | SiO₂ (%) | CaO (%) | Fe₂O₃ (%) | Al₂O₃ (%) | K₂O+Na₂O (%) |
|-------------|---------|----------|---------|-----------|-----------|--------------|
| REF         | 53.6    | 39.1     | 0.9     | 0.54      | 5.6       | 0.29         |
| OLI-CCM     | 48.8    | 36.4     | 2.7     | 7.53      | 4.2       | 0.37         |
| FA-CCM      | 44.8    | 28.9     | 3.6     | 6.17      | 15.6      | 0.91         |
| OLI-QS-CCM  | 49.8    | 37.0     | 2.9     | 6.03      | 4.0       | 0.26         |
| MAG-FA      | 44.8    | 32.3     | 1.4     | 2.65      | 17.9      | 1.04         |

### 3. Results and discussion

The presence and influence of MA-spinel (MgO·Al₂O₃ or MgAl₂O₄) in forsterite ceramics were studied to understand the decomposition and crystallization of various minerals from raw material mixtures via solid-state reaction and the impact on resulting properties of forsterite ceramics. Firing shrinkage is apparent from table 4. Relatively high firing shrinkage of mixtures REF and MAG-FA is due to decomposition of magnesite (magnesium carbonate) into magnesium oxide and carbon dioxide. Released carbon dioxide also lead to high porosity and water absorption of these mixtures and created very porous structure of those test samples.

Opposite phenomenon occurred in the mixture FA-CCM which also had relatively high firing shrinkage, however apparent porosity and water absorption of these test samples were the lowest of all samples. This phenomenon occurred due to the creation of eutectic melt in the mixture in the presence of flux oxides (Fe₂O₃, Na₂O and K₂O). Flux oxides created optimal conditions for creation of amorphous glassy phase and enhanced sintering. Firing shrinkage of mixtures OLI-CCM and OLI-QS-CCM was relatively low (1.5% and 2.9%) even though the amount of iron oxide was similar to the mixture FA-CCM. This phenomenon occurred because significant amount of iron oxide in these mixtures is from olivine, bound in the form of fayalite 2FeO·SiO₂ (confirmed by XRD analysis in figure 2) which conducts differently with increasing temperature. R. Michael et al. [11] also confirmed this behaviour of olivine in high temperatures.
Table 4. Test results performed on fired test samples from all mixtures.

| Test sample       | Firing temperature (°C) | Firing shrinkage (%) | Apparent porosity (%) | Water absorption (%) | Bulk density (kg·m⁻³) |
|-------------------|-------------------------|----------------------|-----------------------|----------------------|-----------------------|
| REF               | 1300                    | 26.9                 | 56.8                  | 41.6                 | 1340                  |
| OLI-CCM           | 1300                    | 1.5                  | 40.3                  | 20.0                 | 2010                  |
| FA-CCM            | 1300                    | 13.3                 | 24.4                  | 10.6                 | 2310                  |
| OLI-QS-CCM        | 1300                    | 2.9                  | 39.4                  | 19.8                 | 1990                  |
| MAG-FA            | 1300                    | 36.5                 | 40.4                  | 23.7                 | 1680                  |

Figure 3. Thermal dilatometric analysis of all designed mixtures.

Figure 3 contains thermodilatometric curves of all mixtures. Mixtures REF and MAG-FA contained magnesite which started decomposing around 400 °C. Shrinkage of these test samples was too high that it exceeded the measuring range of the testing equipment. Sintering of the mixture FA-CCM occurred around 1200 °C. Sintering of the mixtures OLI-CCM and OLI-QS-CCM started around 1350 °C.

Figure 4 contains the X-ray diffraction analysis patterns of all test samples from all mixtures. Major crystal phase in all mixtures is forsterite. Minor crystal phases are periclase (MgO) in mixtures OLI-CCM, FA-CCM, OLI-QS-CCM and MA-spinel (MgO·Al₂O₃) in all mixtures except reference (REF) mixture. REF mixture is composed of pure forsterite with no traces of minor crystal phases. Mixture FA-CCM contains forsterite as a major crystal phase with periclase and MA-spinel as minor crystal phases. These minor crystal phases formed from mullite (3Al₂O₃·2SiO₂) which is present in fly ash (figure 1) and decomposes at temperatures above 1200 °C due to the presence of flux oxides (Fe₂O₃, Na₂O, K₂O) and with magnesium oxide forms MA-spinel and also amorphous glass phase which is presented as curved background of XRD patterns. No traces of mullite were found in the XRD patterns after firing test samples with fly ash as a raw material. Due to the lack of sufficient amount of silicon dioxide, unreacted magnesium oxide (periclase) is present in this sample.

Similar phenomenon also occurred in mixture MAG-FA. Mullite from fly ash decomposed and formed MA-spinel with magnesium oxide from magnesite and the remaining magnesium oxide...
reacted with quartz (figure 1) from fly ash into forsterite. Amorphous glass phase was also created. Mixture OLI-QS-CCM also contained minor crystal phases of periclase and MA-spinel. MA-spinel was created from aluminium oxide contained in kaolinite. Due to the presence of flux oxides, amorphous glass phase was also formed and therefore there was a surplus of magnesium oxide which remained unreacted.

![Figure 4. X-ray diffraction analysis of test samples from all mixtures fired at 1300°C.](image)

Table 5 contains the semi-quantitative analysis by means of the reference-intensity ratio (RIR) method confirmed the results of X-ray diffraction analysis. Major crystal phase (73-100%) in all mixtures is forsterite and minor crystal phases are periclase (10-16%) and MA-spinel (5-20%). Quantities of these minor phases are in relation to the chemical composition of raw materials mixtures and consecutive chemical reactions between oxides during solid-state reactions.

| Mineral quantity          | REF (%) | OLI-CCM (%) | FA-CCM (%) | OLI-QS-CCM (%) | MAG-FA (%) |
|---------------------------|---------|-------------|------------|----------------|------------|
| Forsterite ($2\text{MgO-SiO}_2$) | 100.0   | 83.3        | 72.5       | 78.6           | 80.4       |
| Periclase ($\text{MgO}$)   | -       | 11.1        | 9.7        | 16.3           | -          |
| MA-spinel ($\text{MgO-Al}_2\text{O}_3$) | -       | 5.6         | 17.8       | 5.1            | 19.6       |

![Figure 5. Refractoriness test of first set of pyrometric cones.](image)
Figure 5 represents the first set of pyrometric cones for refractoriness test and was comprised of mixtures REF, OLI-CCM and OLI-QS-CCM. Both pyrometric cones from mixtures OLI-CCM and OLI-QS-CCM bent at 1685 °C meanwhile pyrometric cones from REF mixture endured up to the maximum achievable temperature of laboratory furnace which is 1800 °C. Refractoriness of pure forsterite is 1850 °C. [1] Lower refractoriness of mixtures OLI-CCM and OLI-QS-CCM was probably because of creation of eutectic melt due to the presence of impurities CaO, Fe$_2$O$_3$ and alkalis (Na$_2$O, K$_2$O). These two mixtures have one of the highest amount of CaO, Fe$_2$O$_3$ of all mixtures.

Figure 6 represents the second set of pyrometric cones for refractoriness test and was comprised of mixtures MAG-FA and FA-CCM. Pyrometric cone from mixture MAG-FA bent at 1580°C meanwhile pyrometric cone from mixture FA-CCM bent at 1600°C. Lower refractoriness of these mixtures was probably because of creation of eutectic melt due to the presence of impurities in the mixtures – CaO, Fe$_2$O$_3$ and alkalis Na$_2$O and K$_2$O. Mixtures MAG-FA and FA-CCM had higher amount of alkalis, so the refractoriness was even lower than that of mixtures OLI-CCM and OLI-QS-CCM.

4. Conclusion

Forsterite ceramics was successfully synthesized from all designed mixtures at 1300 °C. X-ray diffraction analysis confirmed presence of forsterite in all mixtures and periclase and/or MA-spinel in some mixtures. RIR method confirmed results of XRD and revealed that forsterite was major crystal phase in all mixtures with amounts from 72.5% to 100%. Minor crystal phases present in test samples were unreacted magnesium oxide (periclase) and MA-spinel (MgO·Al$_2$O$_3$).

Unreacted magnesium oxide was present in mixtures which contained caustic calcined magnesite (CCM) as a raw material, namely mixtures OLI-CCM, OLI-QS-CCM and FA-CCM. In mixtures which contained magnesite as a raw material (mixtures REF and MAG-FA), periclase was not found. This was probably because all magnesium oxide from magnesite reacted to form either forsterite or MA-spinel. The MA-spinel was formed due to the recrystallization of mullite (present in fly ash) and subsequent reaction with magnesium oxide in mixtures with fly ash (FA-CCM and MAG-FA) in larger quantity (18-20%) or from kaolin in mixtures OLI-CCM and OLI-QS-CCM in smaller quantity (5-6%). All mixtures also contained certain amount of amorphous glass phase and iron oxide which can be distinguished by curved background in XRD patterns.

Test results of vacuum water absorption method revealed that test samples from mixtures which contained magnesite as a raw material (REF and MAG-FA) had high firing shrinkage, apparent porosity and water absorption due to the decomposition of magnesite which has high loss on ignition. These samples were very porous with relatively low bulk density, which is suitable for example for thermal insulation purposes.

Sample from mixture FA-CCM also had relatively high firing shrinkage, however its apparent porosity and water absorption were the lowest. This was caused due to the presence of fly ash in the mixture which has impurities that enabled sintering and densification of the sample. Samples which contained olivine as a raw material had relatively low firing shrinkage while their apparent porosity, water absorption and also bulk density were relatively high. Due to the presence of flux oxides, samples were densified and solid-state reaction to form forsterite occurred, while their dimensions were almost unchanged.
Refractoriness of all mixtures was conducted on pyrometric cones from these mixtures. The lowest refractoriness had mixture MAG-FA at 1580°C, followed by mixture FA-CCM at 1600 °C, followed by mixtures OLI-CCM and OLI-QS-CCM at 1685 °C. Highest refractoriness had mixture REF which consisted of pure forsterite and its value was over 1800 °C which is maximum achievable temperature of laboratory furnace. Impurities such as CaO and flux oxides FeO, NaO and KO had negative impact on refractoriness in the rest of the mixtures. These mixtures contained 1.4-3.6% of CaO, 2.65-7.53% of FeO and 0.26-1.04% of alkalis NaO and KO.

Utilization of secondary energetic product – fly ash can be very beneficial for synthesis of forsterite-based ceramics. Fly ash as a raw material is a source of silicon dioxide SiO₂ in the form of quartz for forsterite synthesis and also source of aluminium oxide Al₂O₃ in the form of mullite which forms small quantity of MA-spinel in forsterite ceramics which improves both mechanical properties and also enhances formation of amorphous glass phase which lowers apparent porosity and water absorption while increases bulk density of test samples at firing temperature of 1300 °C. The only disadvantage appears to be lower refractoriness caused by impurities which can be improved by lowering the amount of fly ash in the mixture.

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