Experimental research on the effect of additives on the sintering process of alumina-based refractory materials

E M Vlad¹, R V Buzduga², M D Buzduga², V Caloian¹, E F Plopeanu¹, C Pandeleșcu¹, C Dobrescu¹ and N Constantin¹

¹Politehnica University of Bucharest, 313 Splaiul Independentei Street, Bucharest, 0600042, Romania
²SC CCPPR SA Alba Iulia, 33 Alexandru Ioan Cuza Street, Alba Iulia, 510001, Romania

E-mail: madalinavlad92013@yahoo.com

Abstract. This experimental study refers to the obtaining of refractory materials based on alumina, by adding different amounts of TiO₂ and MnO₂, as sintering agents, to the initial mixtures of raw materials (alumina, chamotte), followed by the sintering of the mass’s different temperatures between 1300 ºC and 1700 ºC. The effects of the use of additives on the sintering temperature, as well as on the microstructure and, consequently, on the properties of the sintered materials were analysed on both the added and non-added ceramic samples, considered as comparative benchmarks.

1. Introduction

Refractories are materials with a high melting temperature; conventionally, refractory materials are those that resist without melting at temperatures above 1500 ºC (in some countries, above 1580 ºC). Oxide refractories have the most important share in manufacturing and use. Refractories can be classified according to different criteria, among which we mention their refractoriness and their chemical nature.

Silicoaluminous refractory materials, semi-acid refractories, chamotte clay refractories and superaluminous refractories are distinguished by the ratio of Al₂O₃ and SiO₂ oxides, which are the basic components of such refractories.

The field of aluminosilicate masses extends beyond the range of compositions corresponding to burnt natural clays, by adding non-clay raw materials with high alumina content, such as sillimanite, distend (cyanite) and andalusite (the three forms of Al₂O₃.SiO₂), or corundum, Al₂O₃, etc. If the minor components that can form silicoaluminous refractories are neglected, they are in the Al₂O₃ – SiO₂ system.

The information provided by the phase diagram of the binary system Al₂O₃ – SiO₂ presents an exceptional theoretical and practical importance in the substantiation and management of the manufacturing processes of the respective ceramic materials. There are several points of interest in the Al₂O₃ – SiO₂ system:

- First, both silicon dioxide and alumina are compounds with high refractoriness, having melting points at 1710 º C and 2050 º C, respectively, but they form a eutectic mixture with a melting point of 1545 º C;

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- First, both silicon dioxide and alumina are compounds with high refractoriness, having melting points at 1710 º C and 2050 º C, respectively, but they form a eutectic mixture with a melting point of 1545 º C;
- Secondly, the composition of the eutectic is very close to the SiO2 component, namely, at 94.5% SiO2, 5.5% Al2O3, thus making the range of "silica" refractories very narrow, but leaving a wide range for aluminosilicate;

- Thirdly, under normal conditions of pressure, a single refractory compound is formed in the system, the mullite - 3Al2O3.2SiO2, which, however, melts incongruously at 1810 °C, with the formation of corundum and siliceous liquid phase.

All silica compositions in excess of that corresponding to the mullite composition begin to melt at 1545 °C, the amount of liquid phase formed being proportional to the excess silica present. Compositions richer in alumina than 3 Al2O3.2SiO2 begin to melt only at 1810 °C. Mullite refractories with additional pure alumina content show an improvement in hot load behavior, crack resistance and slag resistance [1-5].

Unlike traditional ceramic materials, which contain several solid phases connected by a glass matrix, modern refractory materials have a simpler phase composition, sometimes having a single component, which impresses on the material the properties that define it, for example, refactoriness, in the case of metals, oxides, boron’s, nitrides or carbides, which can be sintered in the presence of minimal amounts of impurities [6], [7].

The manufacturing process of alumina-based ceramic materials requires high sintering temperatures of 1600 - 1800 °C, thus being quite difficult to achieve economically. Alumina sintering is a solid-state process, for which a drop-in temperature is desirable without the incorporation of a enough flux to alter the essential properties of the material.

Sintering at lower temperatures can be accomplished by using high dispersion alumina, as well as by adding mineralizers such as: TiO2, MnO, Cu2O, GeO2, Fe2O3, CaO, MgO, BaO, Cr2O3, etc. These mineralizers allow densification by recrystallization, with or without the presence of the liquid phase [8].

2. Experimental research in the laboratory phase

The raw materials used were a high purity tabular alumina and a commercially available super aluminous chamotte. Their properties are shown in Table 1.

| Table 1. Raw materials used [1] |
|-----------------------------|-----------------|-----------------|
| Powder characteristics   | Alumina         | Fireclay        |
| The manufacturer          | SIKEN           | RESIAL          |
| Tipe                      | ATAB 0 - 0,045 mm | SA 68A         |
| Composition               | α - Al2O3       | multiphase     |
| partial chemical analysis [%mass] | P0.             | Fe2O3          | Al2O3            |
|                          | 0,13            | 0,04            | 99,65            | 0,57            |
| Particle size             | > 45 μm [%mass] | 1,5             | 7,1              |
| average diameter [μm]     | 9,13            | 10,63           |
| Density [g/cm³]           | 3,85            | 3,00            |

High purity reagents were used as sintering additives, namely:
- very fine titanium dioxide with TiO2 > 99%; particle size: > 45 μm - 0.8%, average diameter - 0.385 μm,
- powdered manganese dioxide with MnO2 > 95%; particle size: > 45 μm - 3.4%, average diameter - 3,998 μm.

Preparation of experimental masses

In order to analyze the influences of the addition of TiO2 and MnO2, samples with different amounts of these additives were prepared, using the raw materials.

For comparison, samples without additives were also prepared.
The composition of the mixture of raw materials for the experimental masses is shown in Table 2.

| Name of the sample | Raw Material | Additive |
|--------------------|--------------|----------|
|                     | the name     | the name |
|                     | [% mass]     | [% mass] |
|                     | Series       | Sample   |
| I 0 I.0             | -            | -        |
| 1 I.1.1             | -            | 0,5      |
| 1 I.1.2 Alumina     | TiO₂         | 1,0      |
| 1 I.1.3 ATAB 100    | MnO₂         | 0,5      |
| 2 I.2.1 0-0,045 mm  | TiO₂         | 1,0      |
| 2 I.2.3             |             | 2,0      |
| 3 I.3.1 TiO₂ + MnO₂ | TiO₂, 1,0 MnO₂ - 1,0 |
| 3 I.3.2             | TiO₂, 0,5 MnO₂ - 1,5 |
| II 0 II.0           | -            | -        |
| 1 II.1.1 Chamotte   | -            | 0,5      |
| 1 II.1.2 SA 68A     | TiO₂         | 1,0      |
| 1 II.1.3 100        |             | 2,0      |
| 2 II.2.1            | -            | 0,5      |
| 2 II.2.2            | MnO₂         | 2,0      |
| 3 II.3.1 TiO₂ + MnO₂| TiO₂, 1,0 MnO₂ - 1,0 |
| 3 II.3.2            | TiO₂, 0,5 MnO₂ - 1,5 |
| III 0 III.0         | -            | -        |
| 1 III.1.1 Alumina   | -            | 0,5      |
| 1 III.1.2 ATAB      | TiO₂         | 1,0      |
| 1 III.1.3 0-0,045 mm|             | 2,0      |
| 2 III.2.1 +         | -            | 0,5      |
| 2 III.2.2 +         | MnO₂         | 2,0      |
| 3 III.3.1 Chamotte  | TiO₂ + MnO₂  | TiO₂, 1,0 MnO₂ - 1,0 |
| 3 III.3.2 SA 68A    | TiO₂ + MnO₂  | TiO₂, 0,5 MnO₂ - 1,5 |

For the preparation of each experimental mass, the starting materials were mixed with the respective number of additives by a conventional method of mixing the powders, which was carefully applied to ensure a uniform incorporation of the additives into the ceramic composition.

The test specimens, cylindrical in shape, with a diameter of 25 mm, were made from each experimental mass by hot casting under pressure (for this purpose, a mixture of organic binders was used).

The samples were subsequently burned: the first combustion, at a relatively low temperature (around 900 °C), to remove the organic binder; for the final combustion, samples from each experimental mass were subjected to different heat treatments, namely: at 1300, 1500, 1600 and 1700 °C, with a level of one hour at maximum temperature.

**Testing methods**

The chemical composition was determined by atomic absorption spectrometry.

The particle size was determined by a sedimentation method (Serigraphs 1500).

The linear contraction was calculated based on the measurements performed on the specimens before and after their heat treatment.
In order to determine the water absorption capacity, the apparent porosity and the apparent density, the samples were saturated with boiling water, which were weighed before and after immersion; the hydrostatic balance was used to determine the apparent volume.

The mineralogical composition was determined by X-ray diffraction, using Cu Kα radiation and Ni filter (DRON 3 diffractometer).

The microstructure was studied using the scanning electron microscope (SEM, Philips XL 30 ESEM TMP), and the local chemical analysis of the identified phases was performed with an energy dispersion X-ray emission spectrometer (EDS-EDAX), coupled with the electron microscope.

In order to follow the sintering behavior of the experimental masses, the following ceramic characteristics of the respective burned samples were determined, namely: linear shrinkage, water absorption capacity, apparent porosity and bulk density. The results obtained, for the different sintering temperatures, are illustrated in Tables 3-6 and Figures 1-3.

### Table 3. Burning contraction [1]

| Number Sample | 1300 °C | 1500 °C | 1600 °C | 1700 °C |
|---------------|---------|---------|---------|---------|
| I.0           | 1.7     | 3.07    | 4.09    | 6.06    |
| I.1.1         | 1.03    | 5.24    | 6.22    |         |
| I.1.2         | 3.02    | 5.12    | 5.83    |         |
| I.1.3         | 2.4     | 5.55    | 6.10    |         |
| I.2.1         | 1.02    | 3.72    | 5.76    |         |
| I.2.2         | 1.75    | 5.05    | 5.56    |         |
| I.2.3         | 2.74    | 4.40    | 5.07    |         |
| I.3.1         | 3.8     | 6.27    | 7.38    | 8.53    |
| I.3.2         | 3.8     | 6.36    | 7.12    |         |
| II-0          | 0.68    | 0.35    | 2.39    | 5.46    |
| II-1.1        | 1.66    | 1.68    | 4.14    |         |
| II-1.2        | 0.67    | 2.35    | 4.78    |         |
| II-1.3        | 1.03    | 3.48    | 6.85    |         |
| II-2.1        | 2.38    | 3.73    | 5.40    |         |
| II-2.2        | 1.69    | 3.07    | 6.48    |         |
| II-2.3        | 2.02    | 4.71    | 7.50    |         |
| II-3.1        | 2.33    | 4.83    | 7.71    |         |
| II-3.2        | 2.03    | 3.72    | 7.02    |         |
| III-0         | 1.36    | 2.42    | 4.36    | 6.44    |
| III-1.1       | 1.68    | 4.34    | 4.68    |         |
| III-1.2       | 1.37    | 4.36    | 5.36    |         |
| III-1.3       | 2       | 3.74    | 5.52    |         |
| III-2.1       | 2.73    | 4.49    | 5.80    |         |
| III-2.2       | 2.75    | 5.30    | 6.31    |         |
| III-2.3       | 3.79    | 5.70    | 8.78    |         |
| III-3.1       | 4.43    | 6.89    | 7.85    |         |
| III-3.2       | 3.41    | 5.21    | 8.53    |         |
Table 4. Shrinkage burning of samples [1]

| Number | Sample | 1300 °C | 1500 °C | 1600 °C | 1700 °C |
|--------|--------|---------|---------|---------|---------|
| I-0    |        | 11.83   | 9.11    | 9.40    | 8.22    |
| I-1.1  |        | 10.55   | 8.76    | 8.55    |         |
| I-1.2  |        | 10.68   | 7.69    | 7.22    |         |
| I-1.3  |        | 10.18   | 7.35    | 7.40    |         |
| I-2.1  |        | 11.94   | 9.51    | 9.01    |         |
| I-2.2  |        | 12.86   | 8.88    | 8.45    |         |
| I-2.3  |        | 12.65   | 9.09    | 8.45    |         |
| I-3.1  |        | 9.25    | 6.73    | 7.34    | 4.91    |
| I-3.2  |        | 9.75    | 8.18    | 7.76    |         |
| II-0   |        | 12.25   | 11.78   | 10.40   | 4.29    |
| II-1.1 |        | 13.42   | 11.97   | 9.48    |         |
| II-1.2 |        | 11.42   | 8.67    | 6.47    |         |
| II-1.3 |        | 10.68   | 7.80    | 4.47    |         |
| II-2.1 |        | 11.99   | 9.40    | 4.11    |         |
| II-2.2 |        | 11.93   | 8.77    | 4.23    |         |
| II-2.3 |        | 11.37   | 8.16    | 1.25    |         |
| II-3.1 |        | 11.03   | 7.64    | 3.89    |         |
| II-3.2 |        | 11.45   | 8.42    | 1.44    |         |
| III-0  |        | 11.85   | 10.40   | 7.74    | 6.05    |
| III-1.1|        | 11.06   | 9.52    | 8.19    |         |
| III-1.2|        | 11.52   | 9.42    | 7.40    |         |
| III-1.3|        | 11.88   | 9.67    | 7.66    |         |
| III-2.1|        | 11.48   | 9.06    | 6.65    |         |
| III-2.2|        | 10.5    | 7.86    | 6.56    |         |
| III-2.3|        | 10.47   | 6.39    | 3.70    |         |
| III-3.1|        | 9.79    | 6.88    | 5.53    |         |
| III-3.2|        | 9.57    | 6.51    | 4.82    |         |

Figure 1. Water absorption capacity for burned samples [1]
All the refractory materials studied are relatively porous materials, the water absorption values are not less than 4.91% (series I), 1.25% (series II), 3.70% (series III), as illustrated in Table 4 and Figure 1.

**Table 5. Apparent porosity**

| Number Sample | 1300 °C | 1500 °C | 1600 °C | 1700 °C |
|---------------|---------|---------|---------|---------|
| I-0           | 1300 °C | 1500 °C | 1600 °C | 1700 °C |
| I-1.1         | 30.84   | 24.90   | 26.68   | 24.05   |
| I-1.2         | 28.8    | 25.71   | 25.30   |         |
| I-1.3         | 29.39   | 23.03   | 21.80   |         |
| I-2.1         | 28.18   | 22.12   | 22.45   |         |
| I-2.2         | 31.22   | 26.59   | 25.68   |         |
| I-2.3         | 33.38   | 25.49   | 24.65   |         |
| I-3.1         | 32.66   | 26.13   | 24.94   |         |
| I-3.2         | 26.12   | 20.74   | 22.35   | 15.85   |
| II-0          | 27.24   | 24.19   | 23.16   |         |
| II-1.1        | 27.32   | 26.37   | 24.22   | 11.16   |
| II-1.2        | 28.79   | 26.93   | 22.40   |         |
| II-1.3        | 25.36   | 20.74   | 16.42   |         |
| II-2.1        | 24      | 19.01   | 11.67   |         |
| II-2.2        | 26.48   | 22.29   | 10.87   |         |
| II-2.3        | 26.41   | 20.84   | 11.07   |         |
| II-3.1        | 25.61   | 19.83   | 3.72    |         |
| II-3.2        | 24.82   | 18.65   | 10.34   |         |
| III-0         | 25.63   | 20.34   | 3.86    |         |
| III-1.1       | 29.34   | 26.63   | 21.00   | 17.46   |
| III-1.2       | 28.39   | 25.63   | 22.84   |         |
| III-1.3       | 29.51   | 25.56   | 21.03   |         |
| III-2.1       | 29.65   | 25.84   | 21.44   |         |
| III-2.2       | 29.58   | 25.90   | 19.33   |         |
| III-2.3       | 27.35   | 22.43   | 19.50   |         |
| III-3.1       | 26.89   | 19.16   | 11.76   |         |
| III-3.2       | 25.87   | 20.30   | 16.65   |         |

**Figure 2.** Apparent porosity of burned samples [1]
The studied refractory materials are relatively porous materials, the apparent porosity values are not less than 15.85% (series I), 3.72% (series II), 11.76% (series III), as illustrated in Table 5 and Figure 2.

| Number Sample | 1300 °C | 1500 °C | 1600 °C | 1700 °C |
|---------------|---------|---------|---------|---------|
| I-0           | 2.61    | 2.73    | 2.84    | 2.93    |
| I-1.1         | 2.73    | 2.93    | 3.02    |         |
| I-1.2         | 2.75    | 3.00    | 3.03    |         |
| I-1.3         | 2.61    | 2.80    | 2.85    |         |
| I-2.1         | 2.59    | 2.87    | 2.92    |         |
| I-2.2         | 2.58    | 2.87    | 2.95    |         |
| I-2.3         | 2.82    | 3.08    | 3.04    | 3.24    |
| I-3.1         | 2.8     | 2.96    | 2.98    |         |
| I-3.2         | 2.23    | 2.25    | 2.33    | 2.6     |
| II-0          | 2.15    | 2.25    | 2.36    |         |
| II-1.1        | 2.22    | 2.39    | 2.54    |         |
| II-1.2        | 2.25    | 2.44    | 2.61    |         |
| II-1.3        | 2.21    | 2.37    | 2.64    |         |
| II-2.1        | 2.21    | 2.38    | 2.62    |         |
| II-2.2        | 2.25    | 2.43    | 2.98    |         |
| II-2.3        | 2.25    | 2.44    | 2.66    |         |
| II-3.1        | 2.24    | 2.42    | 2.68    |         |
| II-3.2        | 2.47    | 2.56    | 2.71    | 2.89    |
| III-0         | 2.57    | 2.69    | 2.79    |         |
| III-1.1       | 2.56    | 2.71    | 2.84    |         |
| III-1.2       | 2.49    | 2.67    | 2.80    |         |
| III-1.3       | 2.57    | 2.75    | 2.90    |         |
| III-2.1       | 2.6     | 2.85    | 2.97    |         |
| III-2.2       | 2.56    | 2.99    | 3.18    |         |
| III-2.3       | 2.64    | 2.95    | 3.01    |         |
| III-3.1       | 2.74    | 2.98    | 3.06    |         |
| III-3.2       | 2.82    | 2.98    | 3.04    |         |

Figure 3. Apparent density of burned samples [1]
The density values of the studied refractory materials (Table 6 and Figure 3) are lower than the theoretical density of the material or, respectively, of the mixture of initial materials.

Samples with sintering additives show a higher degree of densification than samples without additives in that series of samples.

3. Results and discussions
As can be seen in Figure 4, the addition of 1.0% TiO$_2$ and 1.0% MnO$_2$ led to a sintered material (sample I.3.1-1500°C) whose density represents 80% of the theoretical density (3.85 g/cm$^3$), while the respective sample without additive (sample I.0), after burning at 1700°C, does not reach more than 76% of the theoretical density.

The addition of 2% MnO$_2$ was found to be most effective for the densification of series II and III samples. Thus, for sample II.2.3 - 1600°C a relative density of 99.3% was obtained, while for the respective sample without additive (sample II.0) burned at 1700°C only 86.70% of the theoretical density was obtained (3.00 g/cm$^3$). In series III, the highest relative density, 87.4%, was obtained for sample III.2.3 - 1600°C, compared to the value of 79.4% of the theoretical density (3.64 g/cm$^3$) obtained for the respective sample without additive (sample III.0), burned at 1700°C.

The X-ray diffraction spectra of the samples selected from those that reached the highest level of compactness after sintering, from the three experimental series, are shown in Figure 6. These spectra show that the only crystalline phase present (or at least, detectable with the X-ray diffractometer used), in the case of series I samples, is corundum (JC PDS 46 - 1212). Series II samples consist of mullite (JC PDS 15 - 0776), as the majority phase, while the crystalline corundum phase was difficult to detect. The XRD spectra of the series III samples indicate the presence of two crystalline phases - corundum and mullite, corundum being the predominant phase.
The SEM electron microphotographs of the selected samples are shown in Figures 5-7, which also show the X-ray emission spectra characteristic of some identified phases, as well as the respective local elemental analysis.

In general, the studied ceramic materials have a heterogeneous microstructure, which contains several solid phases and pores, especially closed.

The size of the granules depends on the initial composition of the mixture of raw materials, the size of the granules of the initial materials and their particle size distribution.

The size of the granules is larger for ceramic materials that have a higher glass phase content, such as in the case of samples burned at a higher temperature, as well as in the case of samples with sintering agents, which causes a more abundant development of the liquid phase; In both cases, the ceramic materials have a less uniform and relatively coarse microstructure.
4. Conclusions
Currently, alumina-based ceramic materials are the most widely used in practice. Each additive used, both alone and in combination, increases the density of the sintered samples.
For the samples of alumina (series I) with 1.0% TiO$_2$ + 1.0% MnO$_2$ a relatively high degree of densification was obtained, while for the samples of chamotte (series II) and those composed of alumina and chamotte (series III) the addition of 2.0% MnO$_2$ led to a density close to the theoretical one (especially for the series II samples) at a temperature 100-200 ºC lower than the one necessary to reach the same sintering level in the case of the respective samples without additives.

The microstructure of the studied ceramic materials was influenced by the addition of TiO$_2$ and MnO$_2$. It has been shown that the presence of these additives favors the more abundant development of the liquid phase, as well as a greater growth of the crystals.

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