SINTERING ENVIRONMENT INFLUENCE ON THE PROPERTIES OF ALUMINA – SILICON CARBIDE COMPOSITES

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Al_2O_3 matrix ceramic composites are permanently a challenging material due to their high compactness combined with increased mechanical properties. In our trials Al_2O_3 matrix composites with dispersed silicon carbide (SiC) particles were developed. The materials have been conventionally shaped by semi-dry pressing and heat treated in an electric furnace with graphite elements in argon at 1830°C, and in microwave field at 2.45 GHz at 1550°C respectively. The samples treated in argon to 1830°C showed the best physical and mechanical characteristics and therefore were investigated (the microstructure) by using a FEI, Quanta INSPECT F scanning electron microscope equipped with a system for energy dispersive analysis. The results are presented in backscattered electron images, obtained on the investigated surfaces, in conjunction with quantitative and qualitative micro compositional estimation.

Keywords: composites, alumina, silicon carbide, mechanical properties

1. Introduction

The physical properties of alumina ceramics, recommended them for special applications such as ceramic armor, grinding bodies, armor for mills and can be manufactured at a low cost, using a variety of methods, i.e., slip casting, pressing and injection moulding, without the use of expensive equipment, e.g., a kiln with special protective atmospheres. Despite elevated density (up to 3.95 g/cm^3), alumina ceramics can be used for ballistic protection. In general, non-oxide ceramics used for ballistic protection have exceptionally and relatively low density (except titanium diboride-based ceramics, and consequently, being more beneficial than the alumina ceramics. Generally, these ceramic-ceramic composites are usually manufactured with high densities by hot-pressing process because of the difficulty in densifying the composites. However, this process can only manufacture ceramic particles with simple geometrical shapes, and would be

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expensive and unsuitable for mass production. For many potential applications of these materials, pressureless sintering process would be preferable if full density is achieved by hot pressing that is relatively expensive and not productive. Nonetheless, hot pressing provides high mechanical properties. The mechanical properties of hot-pressed alumina ceramics are comparable with mechanical properties for non-oxide ceramics.

Structural ceramics such as alumina, mullite and silicon carbide have excellent resistance to high temperature, corrosion and wear resistance. However, fracture toughness is low. This low reliability has, limited their applications. Many investigators tried to improve the fracture toughness of structural ceramics by adding whiskers or fibres. On the other hand, to improve reliability of structural ceramics, some authors, [1 - 17], have proposed endowing the crack - healing ability by using oxidation of SiC. When ceramics admixed with SiC are kept in air at high temperature, SiC located on the crack surface reacts with O_2 in air and then crack is completely restored by the products and the heat of the reaction. Moreover, the restored part is mechanically stronger than the other parts, [18]. Development of ceramic - ceramic composites to provide exceptional mechanical properties and particularly a high fracture toughness is a challenge for researchers. The final purpose is to develop these materials as ceramic composite nanoparticles to be used as catalyst support applied for water nitrates removal.

2. Experimental researches

2.1. Raw materials

Basic raw material for the ceramic matrix composites was a special calcined alumina (ACS) with high purity and finesse, manufactured in the Pilot Station of ICEM-SA, starting from aluminium hydroxide (type ALOLT-01 produced by MAL ING. Alumina Brauch-Hungary). The hydrate was wetted (mineralized) with concentrated hydrochloric acid for sodium ions removal, shaped as briquettes and finally fired at 1550^{o}C in the tunnel kiln with a narrow section of the useful area.

The calcined material, slightly brittle, with an impurity content: 0.07% SiO_2 , 0.13% Fe_2O_3 and 0.01 to 0.09% Na_2O, had the chemical composition in accordance with the ICEM firm standard 17/1999 which allows: max. 0.15% SiO_2, max. 0.20% Fe_2O_3 and max. 0.15% Na_2O.

Physical-chemical characteristics of the used alumina powder are the following:

Al_2O_3, %, min.	99.50
SiO_2, %, max.	0.15
Fe_2O_3, %, max.	0.20

Alkali, %, max.	0.15
P.C., %, max.	0.20
Moisture, %, max.	0.50
Mineralogical composition	
Alfa-Al_2O_3, %, min.	98.00
Density, g/cm^3, min.	3.70

Advanced calcined alumina with high finesse was obtained by grinding in a tubular ball mill with continuous operation, during 30 hours. It was obtained a fine material with an average grain size of 2.0 μm (highlighted by laser grain size measurements).

The non-oxide component was carborundum (Silicon carbide (SiC).) of type M 600 Norton, corresponding to β-SiC structure with min. 98.5% SiC, with 3.00 g/cm^3 density and an average particle diameter of 1,2μm.

2.2. Experimental procedure

The alumina - SiC composites (abbreviated AS5, AS10, AS20, AS30) were obtained from special calcined alumina (SF no. 17/1993- ICEM) used as matrix, reinforced with 5%, 10%, 20% and 30-% by weight of silicon carbide powder. As mineralizing agent of the alumina matrix was used 0.5% MgO starting from $MgCl_2 \cdot 6H_2O$ (relative to the amount of calcined alumina). As referential was considered a special calcined alumina sample, denoted A0.

The dosage of the two components of alumina-carborundum mixtures was performed according to the weight amounts presented in Table 1.

Table 1

The dosage of the two components of Al_2O_3 - SiC mixtures

Simbol compozit / Composite symbol	%Al_2O_3	% SiC
A0	100	0
AS5	95	5
AS10	90	10
AS20	80	20
AS30	70	30

Wet homogenisation was done in attritor in isopropyl alcohol, by using corundum balls, for 2 hours. After drying in oven at 50 - 60^{o}C for 24 hours, the mixture was dispersed by passing through a 0.5 mm sieve. The mixtures of Al_2O_3 - SiC composite materials, thus prepared were shaped as cylinder with a diameter of 18 mm and 20 mm height. The samples were realized by hydraulic pressing, which provides a specific pressure of minimum 12 MPa.

The samples were heat treated in an electric furnace with graphite elements in Argon atmosphere (75 atm) at maximum temperature of 1830 ^{o}C –

with a soaking time of 30 minutes, respectively in microwave field at 2.45 GHz for 30 minutes at 1550^{o}C

2.3. Experimental methods

The particle size distribution of the ceramic powders was determined using a laser grain size measurement device from Retsch and the Fischer method. The bulk density after sintering was measured according to the method of the test for dense shaped refractory products – SR EN 993-1:1997.

The test for 3 points bending strength was performed according to SF no. 23:2003-ICEM, using a specially designed device to be adapted to the 20 kN press for prism-shaped (50 mm x 10 mm x 10 mm) specimens after sintering. A certain number of engineered alumina –SiC samples were pre-cracked in the center of the prospective tensile face by Vickers indentation using loads ranging from 10 N to 100 N before flexural test The mineralogical phases were investigated with a HZG type diffractometer using Cu-K_{α} radiation – 1500 W power, at 30 kW, with stabilized Seifert source and data acquisition software.

The composite samples were studied using a scanning electron microscope FEI, Quanta INSPECT F equipped with a system for energy dispersive analysis (EDS).

3. Results and discussions

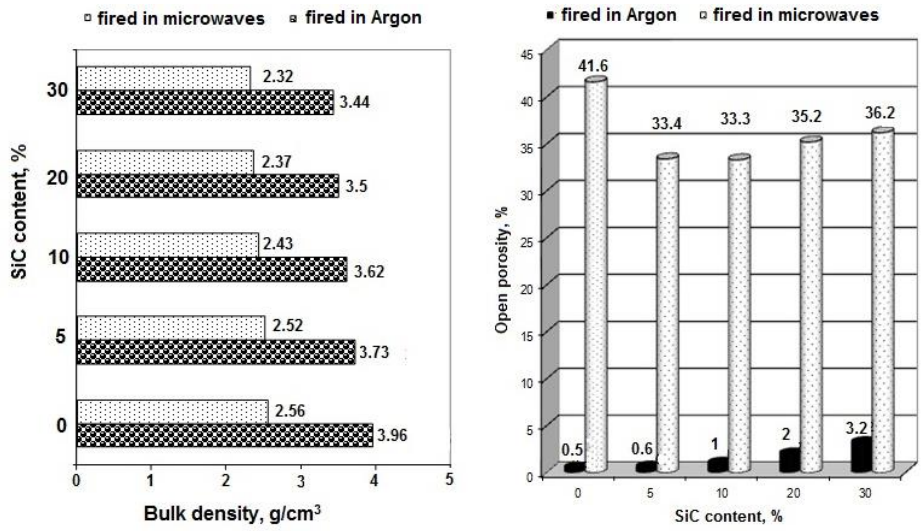
3.1. Physical and mechanical properties

After the sintering performed in a furnace with argon atmosphere and in a microwave field respectively, on the obtained ceramic - ceramic composites were determined: bulk density, apparent porosity (Figures 1) and mechanical strength. (Fig. 2), as well.

The ceramic properties and the mechanical properties of composite mixtures were better for the samples heated in argon at 1830^{o}C, compared with the microwave field firing at 1550^{o}C. For this reason, microstructural investigations were focused on the samples fired in argon.

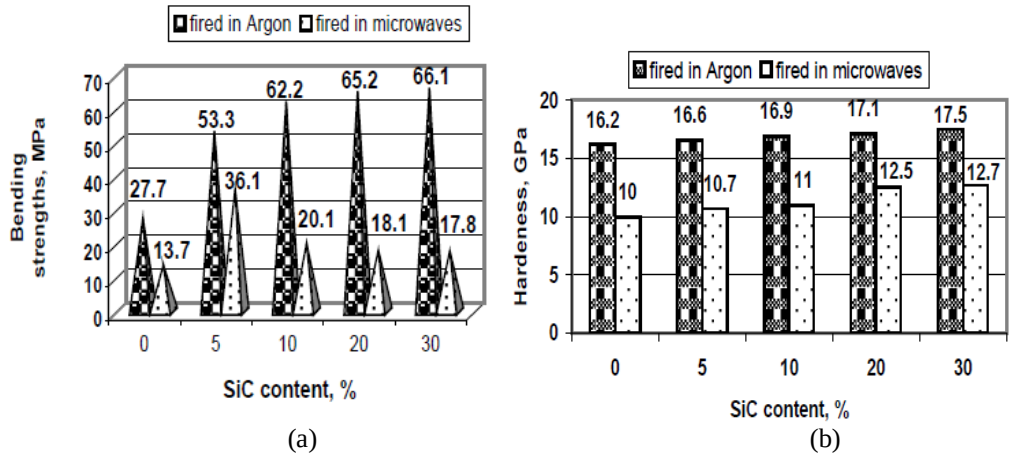
For the alumina – carborundum composites it was found, that the addition of SiC leads to increased mechanical strength than for the reference sample A0. An increase of SiC content to 20% and 30%t led to an improvement in mechanical strength (Fig. 2 a). The observed increase in failure stress with SiC content can be accounted for by the transformation of the fracture propagation from intergranular in pure alumina samples to transgranular in composites containing larger amount of silicon carbide as shown in Fig. 2 b; such effect of matrix weakening and grain boundary strengthening is a consequence of the tensile residual stresses field which develops upon cooling in the matrix around SiC particles because of the

thermo-elastic mismatch between Al_2O_3 and SiC. The reduction of critical defect size associated to smaller grain size obtained with SiC additions, that inhibit the grain growth of Al_2O_3, can also be considered for the observed increase of strength. It is also noted the decrease of the samples density when they are treated in argon at 1830^{o}C (Fig. 1) as the SiC content increases, in terms of advanced compactness of the composites, confirmed by the open porosities which are close to 0%. (Fig. 1). It is found in the same case deviation for the bulk densities and open porosity of the samples treated in microwave, probably due to temperature gradients that occur in the samples.



(a) (b)

Fig. 1. Evolution of (a) bulk density for alumina-SiC composites and (b) open porosity for alumina-SiC composites



(a) (b)

Fig. 2. Evolution of (a) bending strength for the alumina -SiC composites and (b) hardness for alumina-SiC composites

3.2. Structural and microcompositional analysis of Al_2O_3-SiC composites after sintering in argon at 1830°C

The three ceramic composites after being sintered in argon at 1830°C were studied to establish the morphology and microcomposition, through techniques of scanning electron microscopy and micro-analysis.

Samples were studied using a scanning electron microscope FEI, Quanta INSPECT F equipped with a system for energy dispersive analysis (EDS). The results are presented in backscattered electron images, obtained on the investigated surfaces, in conjunction with quantitative and qualitative micro compositional estimation.

Sample AS5

Backscattered electron images of the figures below highlight specific aspects relating to quality of material from which the sample is made. Fig. 3 shows the microstructure of the material referred to the polished surface, which can be characterized as porous and homogeneous in terms of microcomposition (backscatter electron images shows microstructural features with different compositions from the matrix). One can see (Fig. 3) that the sample contains a heterogeneous grain shape and size. Qualitative chemical microanalysis is given in Fig. 4.

Sample AS10

In sample AS10 were outlined the carbides, carbides are observed in backscatter electron images of Fig. 5. On the X-ray spectrum shown in Fig. 6, one can see a tendency to increase of C content for a high percentage of Si. Carbides have a low density and are distributed unevenly as can be observed from X-ray spectrum from Fig. 6 (Si peak intensity of characteristic X radiation element is small) which represents a qualitative estimation of the global chemical micro-composition. In terms of porosity, the sample similar to sample AS5, can be characterized as porous in this regard, a detail of grain and porosity being shown in Fig. 5 b.

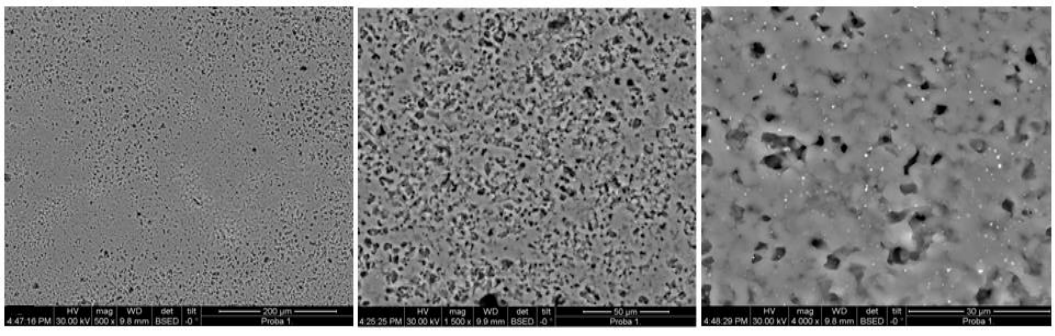


Fig. 3. General appearance of the microstructure (x.500), detail (x.1500) and detail of grain size (x.4000) – sample AS5

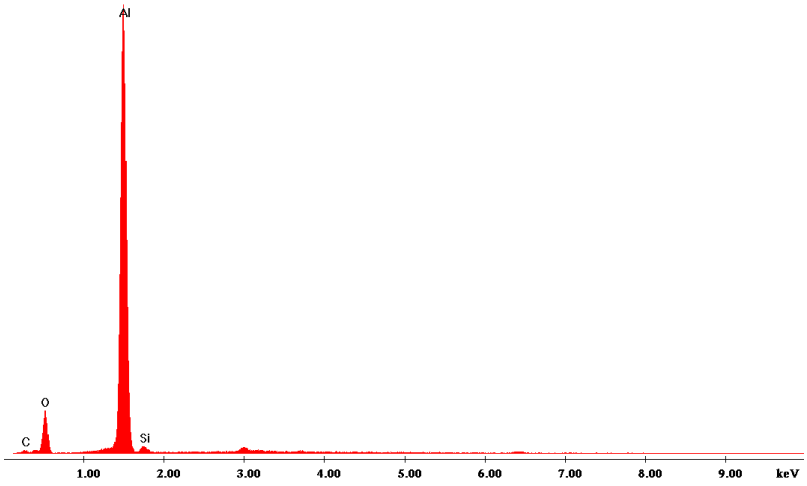
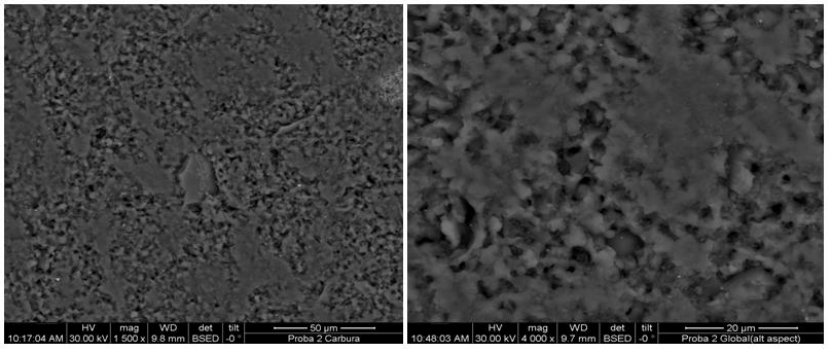
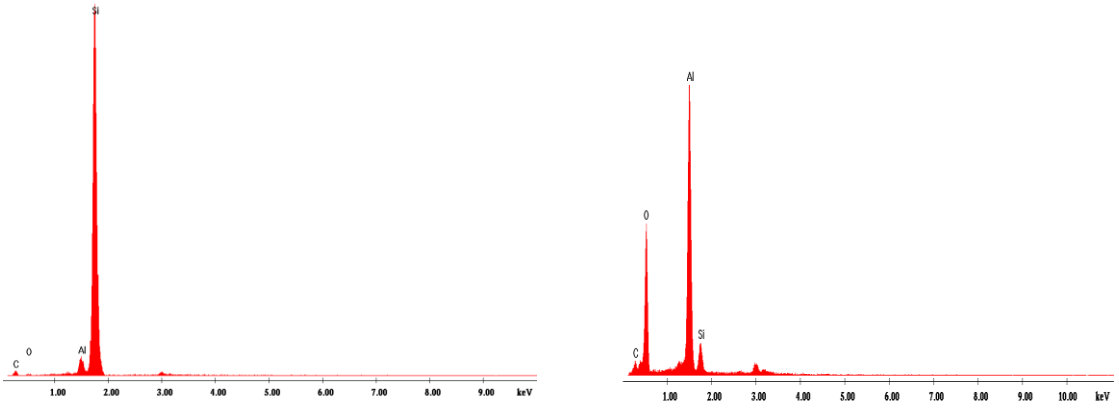


Fig. 4. Global qualitative chemical microanalysis – sample AS5



(a) (b)

Fig. 5. Appearance of the microstructure (carbide), x.1500, detail on grain size, x.4000– sample AS10



(a) (b)

Fig. 6. (a) Related qualitative chemical microanalysis Figure 6 (carbide); (b) globally qualitative chemical microanalysis – sample AS10

Sample AS20

The images in Fig. 7 (BEI images) show the characteristic microstructure features of the sample; being also noticed a tendency to increase the density of carbides.

Qualitative chemical microanalysis performed on a zone containing carbides (related to Fig. 7) is shown in Fig. 8, where Al being the major element and the X-ray peak intensity for Si showing an upward trend compared to sample AS10.

One can see the pore density is high with the mention that their sizes are generally in the range of 1 -3 µm.

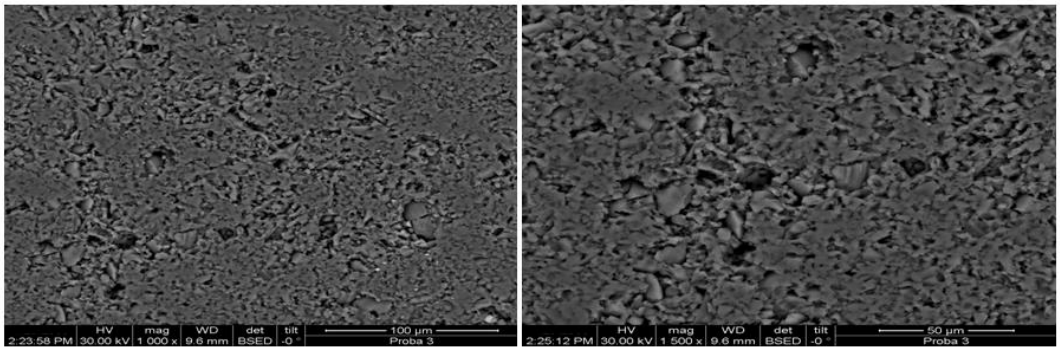


Fig. 7. Microstructure showing the carbides (x.1000), on the right detail of the microstructure (x.1500) – sample AS20

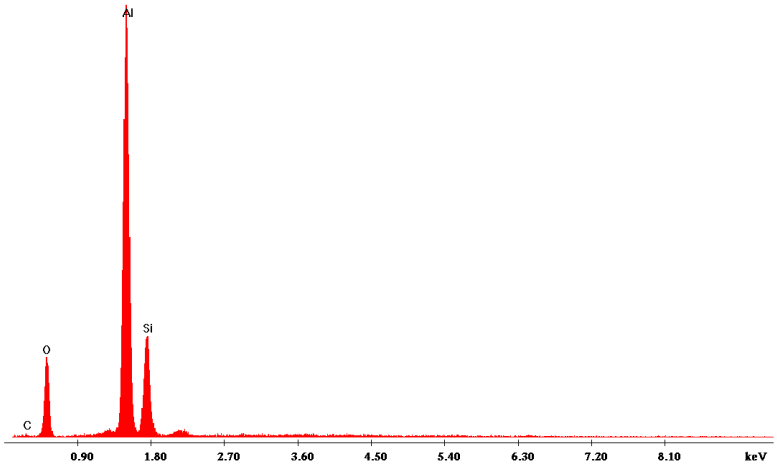


Fig. 8. Qualitative chemical microanalysis on a carbide zone – sample AS20

For the surfaces investigated were not observed significant microcompositional differences, which leads to the conclusion (as well as in the case of samples AS5 and AS10) that in terms of chemical composition the samples are homogeneous, in accordance with the confirmed level analysis global X-ray spectrum presented in Fig. 9.

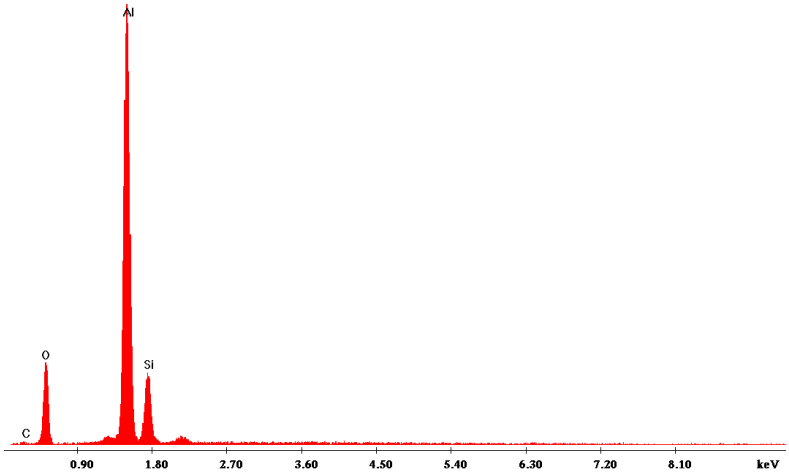


Fig. 9. Qualitative chemical microanalysis, carried out globally

XRD analysis performed on AS0 and AS30 samples did not point out the presence of any impurity and confirmed the expected composition by showing only α-Al2O3 peaks for the first one and α-Al2O3 and α-SiC peaks for the second one. The formation of mullite is very limited considering the amount of silica normally present as surface layer on SiC powder or formed during the pre-sintering step.

4. Conclusions

Experimental tests carried out by two sintering techniques: electric oven with argon, the microwave field in oxidizing atmosphere (air) revealed the possibility of obtaining some types of alumina-SiC composites.

Al_2O_3-SiC composites develop potential improved mechanical strength by using an electric oven with argon sintering atmosphere at 1830^{o}C.

An increase of the SiC content may lead to the improvement of mechanical strength according to higher compactness as determined by ceramic properties and SEM analysis.

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