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Sintering of Composite Ceramic based on Corundum with Additive in the Al_2O_3-TiO_2-MnO System

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Abstract**—**In this paper, the effect of the additive content in the Al_2O_3-TiO_2-MnO system on the sintering of composite ceramics based on corundum was studied. The samples were pressed by uniaxial semi-dry pressing under 100 MPa and sintered at 1500 °C and 1550 °C. The properties of composite ceramics for porosity and flexural strength were studied. When the amount of additives increases, the properties of composite ceramic samples are better than samples without additives.

Keywords**—**Ceramic, composite material, sintering, corundum.

I. Introduction

CERAMIC materials are widely used in various industries, often under extreme conditions under the influence of thermal, mechanical and other types of loads. At present, technical ceramics is an independent class of materials and its increasingly used in various branches of technology and industry such as electrical engineering, power engineering, including nuclear, radio engineering, metallurgy, chemical engineering. It is practically impossible to produce high-quality products from such powders without the use of special additives. Therefore, one of the main problems in the technology of modern oxide ceramics is the development of methods for obtaining powders of specified dispersion, particle shape and activity for sintering [1]-[3].

From the theory and practice of solid-phase synthesis, it is known that sintering of powdery materials can be achieved by adding additives of foreign substances due to the formation of solid solutions and free vacancies in the lattice. From publications some additives strongly can accelerate the sintering of α-Al_2O_3. For example, TiO_2 and MnO can reduce the sintering temperature and MgO can regulate the crystallization of corundum or improve the individual properties of ceramics [4]. The addition of TiO_2 causes an intensive growth of grain of corundum ceramics up to 200-350 μm. The solubility of TiO_2 in α-Al_2O_3 is too low. This is determined by the shift in the lattice parameters of α-Al_2O_3. A solid solution of TiO_2 in α-Al_2O_3 is formed at a temperature of 1150 °C, and the solubility is 0.27% at 1300-1700 °C. Outside the solubility limit, excess TiO_2 coexisted with α-Al_2O_3 as rutile below 1350 °C and as Al_2TiO_5 above 1450 °C [5]. The role of MnO is very effective for controlling anomalous grain growth and achieving a density in the sintering of α-Al_2O_3. This leads to a decrease in the tendency to rupture of the pore-border and to adequate protection against abnormal grain growth. Combinations of manganese and titanium oxides were the most effective in lowering the sintering temperature, especially when present in equal amounts. The microstructure of such a ceramic usually consists of uniform dimensions and equiaxed grains of aluminum oxide [6], [7].

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State diagram of Al_2O_3-TiO_2-MnO system is a non-condensed one, in which the phase stability is determined not only by the temperature and composition but also by the oxygen partial pressure in the gaseous phase. In air, it was observed that the evolution of oxygen as the temperature rises is not easily reversed on cooling. In the other words, the high-temperature reduced forms tend to be retained at lower temperatures. This will be more the case when other components are present, with which the reduced oxide can react. Therefore, the phase equilibrium relationships in the system Al_2O_3-TiO_2-MnO_2-MnO can be approximated by those for the Al_2O_3-TiO_2-MnO system at temperatures above 800 °C [8].

Corundum ceramic based composite additives have been extensively studied because of their excellent properties such as high hardness, low electrical conductivity, good chemical stability, and oxidation resistance [9].

The purpose of this research is to obtain composite ceramics based on corundum α-Al_2O_3 with eutectic additives in the Al_2O_3-TiO_2-MnO system and to study its properties depending on the additive mass content and the temperature effect. To use as eutectic additives, a particularly suitable composite material with high strength and average pore size. Average pore size, porosity, density and mechanical strength of the ceramic materials are depending on concentration of the additive, pressing pressure and firing temperature.

When firing ceramic billets, various physical and chemical processes can occur: thermal decomposition of raw materials, chemical reactions between components or with the gaseous medium, polymorphic transformations, eutectic melting, dissolution of solid phases in the melt, crystallization from the melt of others. These processes can be accompanied by a change in mass, volume, chemical and phase composition, density and porosity.

II. Experimental

Corundum was obtained from alumina by melting in electric arc furnace and containing more than 98% α-Al_2O_3. Corundum is used as a structural ceramic due to having good mechanical properties and also excellent thermal properties at high temperatures. As base material powder was used corundum F600. The average particle size of corundum powder (F600) is D_{50} =10 мкм. Figs. 1 and 2 represent the microstructure and crystal structure of corundum powder F600 [9].

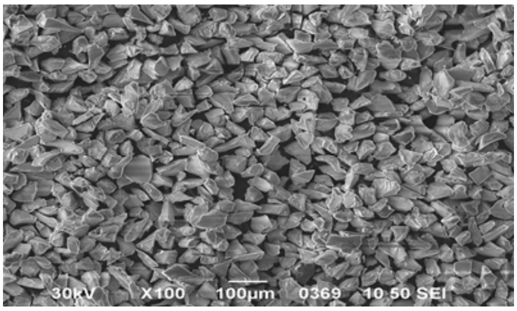


Fig. 1 Microstructure of corundum powder F600

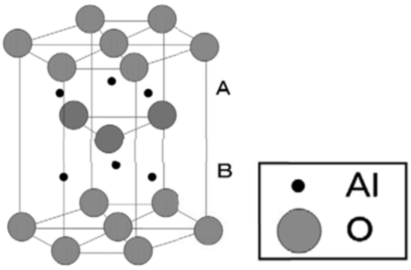


Fig. 2 Crystal structure of corundum powder F600

In the state diagram of Al_2O_3-TiO_2-MnO system, the concentrations of the eutectic materials were used as the following compositions (A) 30% Al_2O_3, 17% TiO_2, 53% MnO at eutectic temperature 1580 °C. Fig. 3 represents the state diagram of Al_2O_3-TiO_2-MnO system [10].

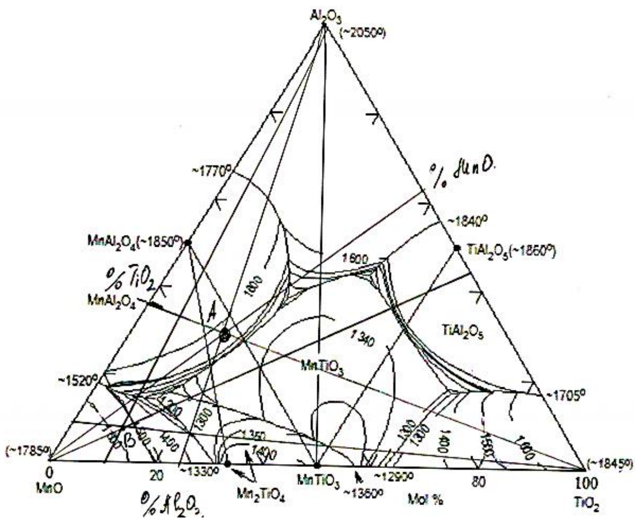
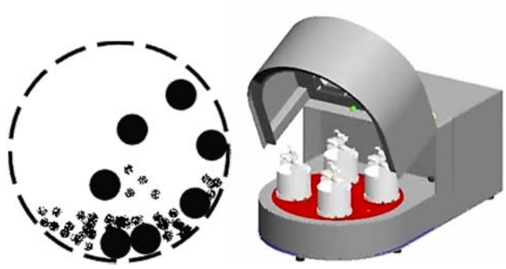


Fig. 3 The state diagram of Al_2O_3-TiO_2-MnO system

The raw materials powder components of eutectic additive were $Al(OH)_3$, $MnCO_3$, TiO_2. To obtain eutectic additive, the raw materials powder components were heated to high temperature at 1000 °C, in order to achieve constant mass, occurring reactions at high temperature, burning impurities and organic substances.

After heating, components of eutectic additive with constant mass were mixed in Teflon ball mill grinding pot, the ratio of grinding balls and material was 1: 1. The total mixing time was 24 hours. And then, synthesis was carried out combining eutectic additive powder at high temperature 1200 °C. After synthesis, eutectic additive was comminuted 30 minutes in planetary mill, the ratio of grinding balls: material: ethanol (polyvinyl alcohol) was 3: 1: 2.5. Liquid compound was drying for 48 hours at the temperature of 80 °C, and eutectic additive was obtained.



(a) (b)

Fig. 4 (a) Dry mixing eutectic additive in Teflon ball mill, (b) Wet mixing eutectic additive in planetary mill

The content of additives 1, 3, 5, and 7% were mixed with corundum in Teflon ball mill grinding pot by using dry milling method, the ratio of grinding balls and material was 1: 1. The total milling time of the charge was 1 hour. Composite ceramic powders with the ratio of corundum and additive 93/7, 95/5, 97/3 and 99/1 were formed a cylindrical disk shape (diameter=20 mm, high=4.9 mm and the mass of the sample was 4 g) in the uniaxial semi-dry pressing machine. The forming pressure was 100 MPa.

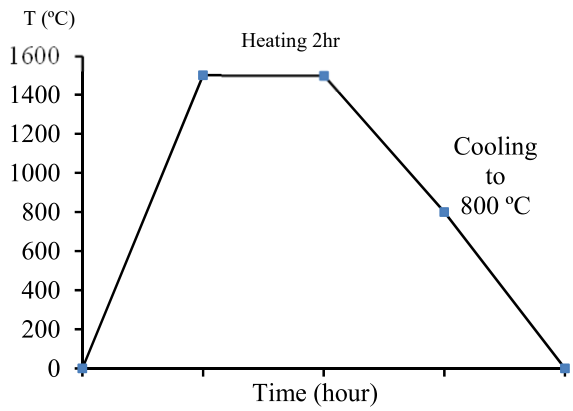


Fig. 5 Temperature range of sintering

To obtain samples of composite ceramics with improved density and sufficient strength, samples were sintered at 1500 and 1550 ºC in the furnace with lanthanum chromite heating rods. The samples were heated from room temperature to 1500 and 1550 °C. The temperature rate was 200 °C/hour, the holding time at 1500-1550 °C was 2 hours, temperature is reduced from 1500-1550 °C to 800 °C by the rate of 100 °C/hour.

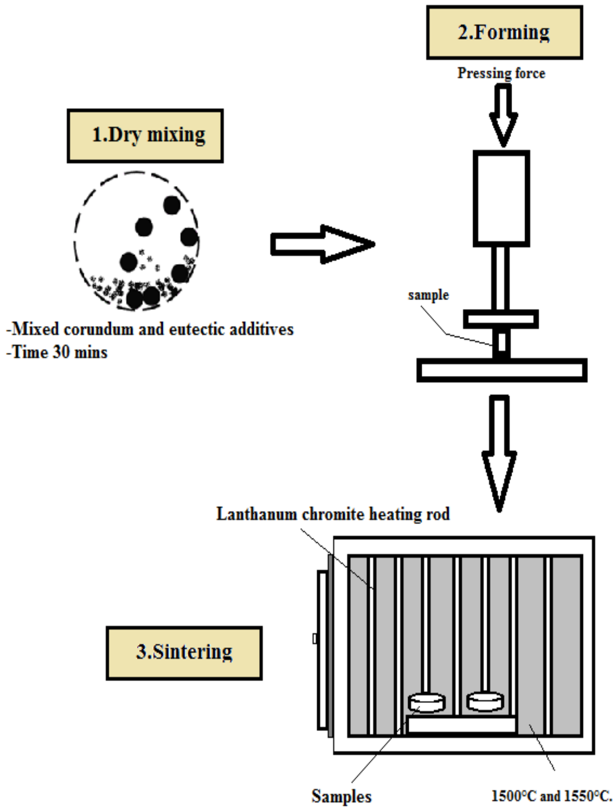


Fig. 6 Technological process of composite ceramic sintering

Open porosity of the composite ceramic samples was calculated by the following equations:

$$\Pi_0 = \varphi * W \quad (1)$$

$$\varphi = \frac{(M_{dry} * \rho_{water})}{(M_{wet} - M_{in\ water})} \quad (2)$$

$$W = \frac{M_{wet} - M_{dry}}{M_{dry}} * 100 \quad (3)$$

where Π_0 is the open porosity (%), φ is the true density of ceramic samples (g/cm^3), M_{dry} is the dry mass of sample (g), ρ_{water} is the density of the water (1g/cm^3), M_{wet} is the wet mass of sample (g), $M_{in\ water}$ is the mass in water (g), and W is the water absorption (%).

Flexural strength is the measure of the maximum stress per unit area that the specimen can withstand without breaking when it is bent. In the other words, it is defined as the ability of a material to withstand deformation under load. In Fig. 7, the three-point diagram of the flexural strength test is presented.

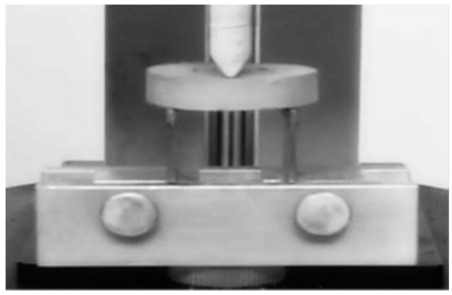


Fig. 7 Three-point diagram of the flexural strength test

To measure the flexural strength, a three-point bend was used in accordance with ASTM C1161-90 [11]. The flexural strength was calculated using the formula:

$$\sigma_{flexural} = \frac{3PL}{2bh^2} \quad (4)$$

where $\sigma_{flexural}$ is the flexural strength (MPa), P is the fracture load, L is the length between two span, b is the width, h is the high of sample.

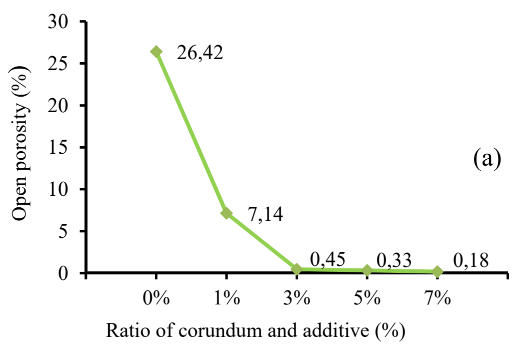
III. Results and Discussion

Samples containing 1, 3, 5 and 7 % by weight of the additive are already sintered at 1500 °C to a residual porosity of less than 0.5 %, at which the composition has a sufficiently high strength. With the increase in the content of the additive, the open porosity of the samples decreases from 7.14 to 0.16 % at a temperature of 1500 °C. The results on the sintering of samples with the addition of composition (A) in the Al_2O_3-TiO_2-MnO system are given in Table I.

TABLE I
PROPERTIES OF COMPOSITE CERAMIC SAMPLES AT TEMPERATURE 1500°C

Ratio of corundum and additive (%)	Open porosity (%)	Average density (g/cm^3)	Flexural strength (MPa)
Pure corundum	26.42	3.03	75±10
99/1	7.14	3.58	157±10
97/3	0.45	3.87	219±10
95/5	0.33	3.92	225±10
93/7	0.16	3.94	248±10

At a temperature of 1500 ºC, the flexural strength of pure corundum is 75 MPa. But, the flexural strength increases 248 MPa with an additive content of 7%.



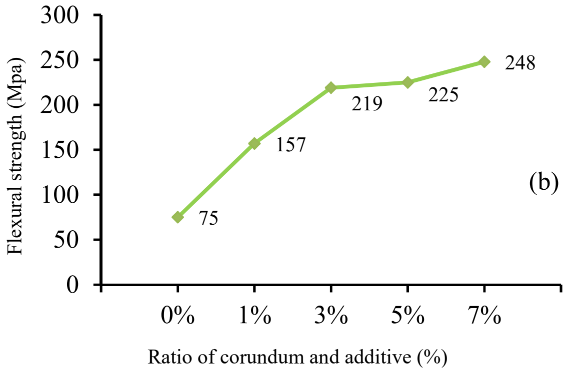
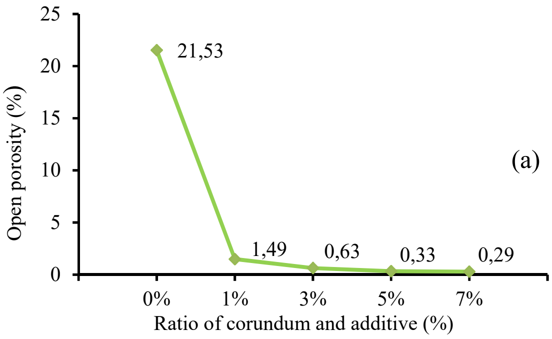


Fig. 8 Properties of composite ceramic samples at temperature 1500 °C: (a) – Average open porosity of composite ceramic samples (%), (b) – Flexural strength of composite ceramic samples (MPa)

At a temperature of 1550 °C with the increase in the content of the additive, the open porosity of the samples decreases from 1.49 to 0.29%. The results on the sintering of samples with the addition of composition (A) in the Al_2O_3-TiO_2-MnO system are given in Table II.

TABLE II
PROPERTIES OF COMPOSITE CERAMIC SAMPLES AT TEMPERATURE 1550 °C

Ratio of corundum and additive (%)	Open porosity (%)	Average density (g/cm^3)	Flexural strength (MPa)
Pure corundum	21.53	2.95	87±10
99/1	1.49	3.74	207±10
97/3	0.63	3.82	210±10
95/5	0.33	3.85	218±10
93/7	0.29	3.87	223±10



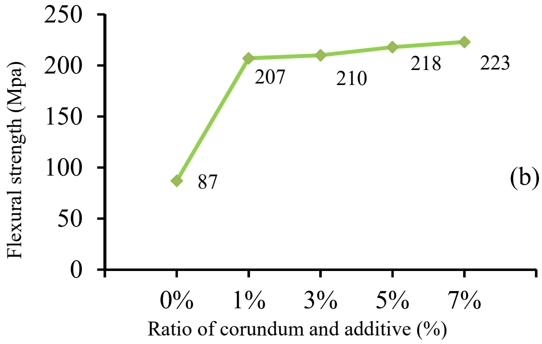


Fig. 9 Properties of composite ceramic samples at temperature 1550 °C: (a) – Average open porosity of composite ceramic samples (%), (b) – Flexural strength of composite ceramic samples (MPa)

IV. CONCLUSION

When sintering occurred, the shape of the grain changes by densification and mass transport occurs by volume and grain boundary diffusion. But, eutectic additive powder must be occurred the formation of a viscous liquid (liquid + solid) that filled the pore spaces and combined with corundum powder. So, the use of a dispersed powder as an additive to the eutectic composition in the Al_2O_3-TiO_2-MnO system makes it possible to produce a dense material with a residual porosity of less than 0.1%, a flexural strength of more than 250 MPa using corundum.

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