Sintering of Al_2O_3 ceramics based on different sizes powders

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It have been studied the structure, phase composition and the specific surface of alumina-based powder systems produced by the method of thermal decomposition of hydroxide aluminum and the plasma-spray pyrolysis method. It was shown that in the plasmochemical powder there is a sharp transition to the α-form in a narrow temperature interval (1150–1200 °C) while for another powder this transition is occurred in wide temperature interval (600–1200 °C). Thus, transformation in plasma-spray powders has an "explosive-like" character. This transition is accompanied by destruction foam-like agglomerates and an increase in the specific surface, which during sintering leads to recrystallization and activation of diffusion processes and high properties.

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1. Introduction

It is well known that ceramics is a wide used material for production various engine parts possesses high strength, hardness, wear resistance [1, 2], a wide range of thermal and electrophysical properties, chemical and corrosion resistance [3]. However, the presence of pores in the ceramics structure results in a significant decrease of its mechanical strength. One of the ways of increasing the strength of structural ceramic materials is to use nanosized powders with a particle size of several tens of nanometers [4].

The above nanosize powders can be produced using the technique of salt denitration in high-frequency plasma [5, 6]. However, there are not enough data on the properties, morphology and the structure of such powders, in particular alumina, relative to the powder (coarsely crystalline, as a rule), produced by conventional methods [7], although these data are critical at sintering such systems. This is due to the fact that the surface morphology, the fine crystalline structure parameters, the specific surface area and the phase composition of the powder system depend both on the crystallite size, the shape of the particles and the degree of their agglomeration. Therefore, sintering may have various features.

The present work is aimed at studying the features of the phase composition, the specific surface area and the surface morphology of the alumina powder synthesized in the plasmochemical reactor with respect to conventional alumina and sintered ceramics with various contents of the plasmochemical Al_2O_3 powder.

2. Materials and experimental procedure

Two types of alumina powders have been investigated: alumina produced using the conventional method of thermal decomposition of aluminium hydroxide and the plasma spray pyrolisis of salt water solutions of aluminium (PSP) produced using thermal decomposition of these solutions in high-frequency plasma.

The powders were annealed at the temperatures of 600, 800, 1100 and 1200 °C for one hour. The X-ray studies were carried out using a DRON-UM1 diffractometer with filtered CuK_α radiation. The phases were identified by comparison of the X-ray patterns with the ASTM table. The average crystallite size was calculated from widening on small angle peaks [8]. Specific surface area was measured using the BET method on the "Sorbi" unit, with an error of no more than 3%. The SEM studies of powders were taken using the Philips–505 scanning electron microscope.

The mixtures were prepared within the concentration interval from the conventional Al_2O_3 to the PSP powder. The powders were mixed in a ball-mill unit for 24 hours, before moulding a 5 wt% polyvinyl alcohol was added into the mixture. A sintering process was carried out at 1200, 1300, 1400, 1500 and 1650 °C for one hour. Density was measured using the method of hydrostatic weighting, with the residual porosity derived from the density values. Shrinkage was calculated from geometric changes of the samples before and after sintering. An "Instron–1185" unit was used to determine the ultimate compressive strength.

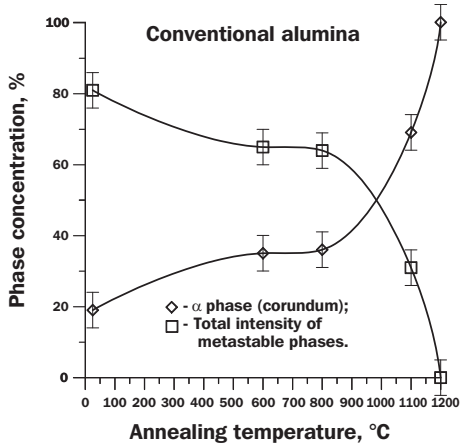
3. Results and discussion

Powders

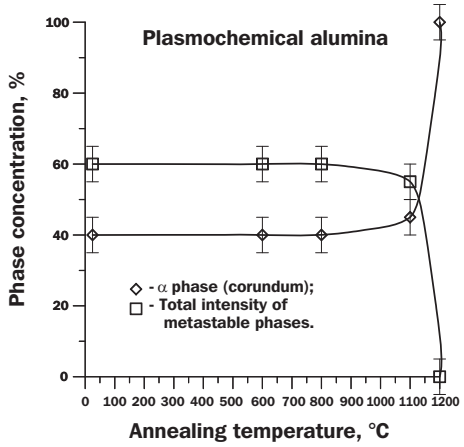
Phase analysis of the initial powders was indicated the presence of rhombic (α), cubic (γ), FCC (γ'), hexagonal (ε) and tetragonal phases. Annealing of powders at various temperatures leads to a change in the phase content: at an annealing temperature of 1200 °C all metastable phases transform into the rhombic modification.

In *Fig. 1*. it has been plotted the dependences of the α-phase intensity and the total intensity of the metastable phases vs. the annealing temperature. As one can see, the powders produced

by the conventional method (Fig. 1*a*) are characterized by a smooth transition to the α-form starting at 600 °C, while in those obtained by the PSP method (Fig. 1*b*) the volume of the metastable phases lasts up to much higher temperatures and then, in the narrow temperature range of ≈ 1150–1200 °C a sharp transition to the rhombic lattice occurs, i.e. the transition has an "explosive-like" character.



a



b

Fig. 1. Changing of phase content in powders vs. annealing temperature
1. ábra A porok fázisösszetételének változása a hőkezelési hőmérséklet függvényében

Calculation of the average crystallite sizes in the powders at various annealing temperatures showed that in the initial alumina powder the average crystallite size was 23 ± 5 nm, whereas in the PSP powder the average crystallite size was 18 ± 5 nm, i.e. the average crystallite size in both types of powders does not depend on the method of production and is about 20 nm. Annealing of powders at a temperature of 600 °C results in a slight decrease in the average crystallite size values, while at annealing temperatures of 800, 1100 and 1200 °C a slight increase in the crystallite size is observed in both powder systems. At an annealing temperature of 1200 °C the average crystallite size was 30 ± 8 nm for both systems.

The specific surface areas of powders are shown in *Fig. 2*. In the initial powders conventional and the PSP Al_2O_3 the specific surface area is 75 m^2/g and 60 m^2/g, respectively and as one can see from the plots (Fig. 2.), in the first case, a smooth decrease in the specific surface area is observed, whereas the for PSP powder is characterized firstly by an increase in the specific surface area at 600–800 °C with the following decrease. Annealing of powders at 110 °C results in a sharp decrease of the specific surface area for both systems, 25.5 m^2/g and 27 m^2/g, correspondingly, and at 1200 °C the specific surface area was about 1 m^2/g for both systems.

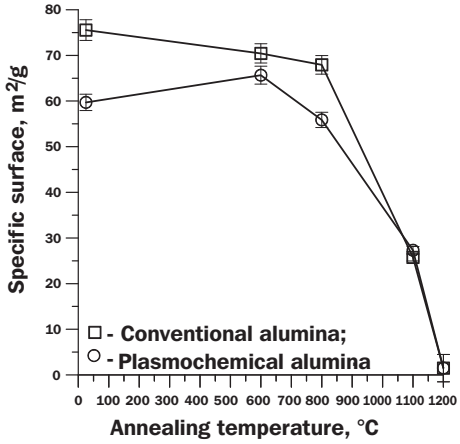


Fig. 2. Specific surface of powders vs. annealing temperature
2. ábra A porok fajlagos felületének változása a hőkezelési hőmérséklet függvényében

Using these data on specific surface area we are calculated the average diameter of the alumina particles assuming the spherical particle shape, these values was 20 ± 3 nm and 26 ± 3 nm for conventional and PSP correspondently. Annealing at the temperatures of 600 and 800 °C practically has no effect on the average particle diameter, but annealing at 1200 °C leads to increase in the size practically 60 times as compare to the initial state. This means that the powders are sintered into dense polycrystal agglomerates thus decreasing the specific surface area of the powders.

These results are confirmed by the scanning electron microscopy, which showed that the initial alumina powder obtained by conventional methods is represented by various porous agglomerates with a size of 30 to 100 μm consisting of dense particles with regular faces. There are also individual dense particles of 5 to 30 μm with a distinctly developed surface relief. The initial alumina PSP powder consists of foam-shaped agglomerates with a very smooth surface whose size varies from tens of nanometers to tens of micrometers. Individual particles are not observed. Fragments both hollow and filled can be seen, with the wall thickness of the hollow fragments being no more than 10 nm. Annealing of alumina at 1100 °C contributes to the destruction of the agglomerates along the interior grain boundaries. Individual particles are destroyed and distinct layer-like structure can be observed. In the PSP powder all the material after annealing at a temperature of 1100 °C is in the aggregated state, with a particle size from 1 to 50 μm. There are also sintered agglomerates consisting of dense filled spherical elements with a size about 200 μm.

Sintered ceramics

The studies of the density of sintered ceramics depending on the ratio between the conventional and PSP powders in the mixture are shown on *Fig. 3*. One can see that after sintering at 1200–1400 °C its density practically does not change and is

1.5 ± 0.2 g/cm^3, its increase after sintering at 1500 °C and after sintering at 1600 °C the densities of the samples are equal up to 3.2 g/cm^3 for samples containing 90% PSP powder. Thus, the concentration dependence of the density looks like a curve with a maximum whose position varies with changing of sintering temperature.

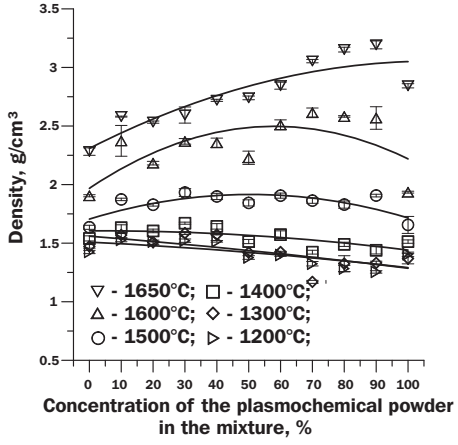


Fig. 3. Density vs. concentration of the PSP powder in the mixture at various sintering temperatures
3. ábra A plazmatermikus por sűrűség-koncentráció összefüggése különböző szinterelési hőmérsékleteken

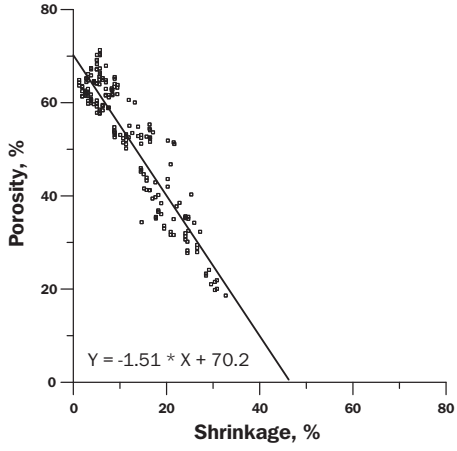


Fig. 4. Porosity vs. shrinkage in ceramics based on alumina
4. ábra Az Al_2O_3 kerámiák porozitás – zsugorodás görbéi

The dependences of the porosity vs. shrinkage are shown on *Fig. 4* for studied ceramics. As one can see this plot is linear and suggests a possibility of creating both shrinkage-free ceramics and ceramic with almost theoretical density.

The dependences of the synthesized ceramics density vs. the initial densities are shown in *Fig. 5*. After sintering at 1200 and 1300 °C densification of compacts does not practically occur and all dependences are linear. All lines changes its slopes from the positive to the negative and extrapolation of the straight lines in Fig. 5 (dashed lines) shows them to cross at an initial density value about 2 g/cm^3. Thus, we can suppose that if the method of cold pressing is used to achieve the pressing density of 2 g/cm^3, then after sintering its density will not change, which suggests a possibility of creating such ceramics free from shrinkage. This is likely to be due to the fact that during pressing, as a result of a high pressure, agglomerates and particles in the powder are destroyed and deform losing the excess free energy and reducing the surface of the substance-pore interface. Consequently, during the sintering process the diffusion transport of a substance will be hindered owing to the low vacancy concentration gradient on the grain surfaces.

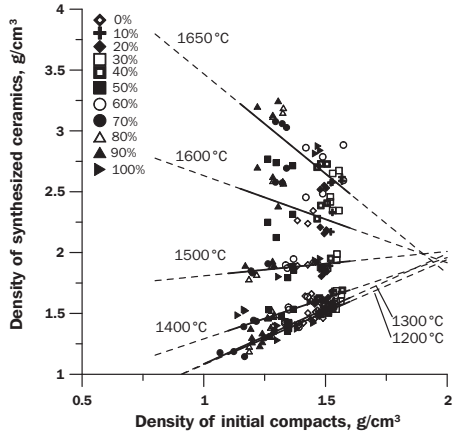


Fig. 5. Dependences of the sintered ceramics density vs. green body density with various concentration of the PSP powder in the mixture
5. ábra A szinterelt testek sűrűségének változása a nyers sűrűség függvényében különböző mennyiségű plazmatermikus port tartalmazó elegyeknél

Compression testing for sintered ceramics showed (*Fig. 6*) that after sintering at temperatures below 1500 °C the samples were very brittle, and their compressive strength, practically, did not depend on the PSP content in the system and lay within the range of 5 to 50 MPa. Sintering at 1600 and 1650 °C resulted in a considerable increase in the compressive strength. After sintering at 1650 °C in the case when the plasmochemical powder prevailed in the compacts, compressive strength increased significantly and the maximum (500 MPa) was achieved in the samples containing 80 wt.% PSP powder.

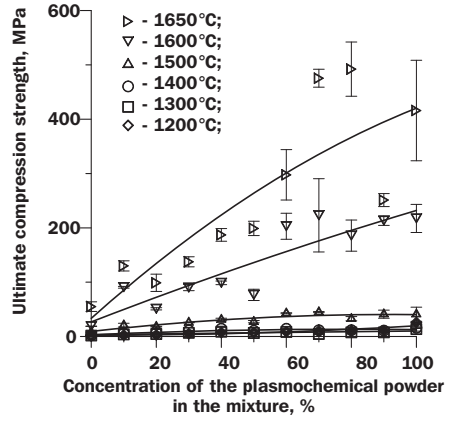


Fig. 6. Ultimate compression strength vs. concentration of the PSP powder in the mixture at various temperatures of sintering
6. ábra A végső nyomószilárdság alakulása a plazmatermikus por koncentrációjának függvényében különböző hőmérsékleteken szinterelt porelegyeknél

So, substitution of the conventional alumina for the PSP Al_2O_3 powder leads to increasing the density and strength of corundum ceramics. Apparently, it may be related to the fact that over the range of sintering temperatures from 1200 to

1400 °C in the powder compacts from the plasmochemical powder an "explosive" phase transition to the stable α-form takes place. This "explosive-like" transition is accompanied by the destruction of the foam-like agglomerates and an increase in the specific surface area, which during sintering results in recrystallization and an increase in the substance-pore interface surface. Thus, as new grain boundaries appear during the sintering process activation of diffusion mass transfer occurs due to an increase in the gradient of vacancy concentrations on the additionally formed grain surfaces, i.e. there is activation of the processes which take place during sintering [9].

The composition of 80 wt.% plasmochemical Al_2O_3 powder – 20 wt.% alumina allows to produce corundum ceramics with the best properties after sintering. It is likely to be related to the fact that under similar conditions of cold pressing alumina particles, uniformly distributed in the volume of the compact from the PSP powder and ensure a high initial compact density.

4. Conclusions

In the plasma-spray Al_2O_3 powder the transition from the nonequilibrium state to the stable one has an "explosive-like" character and lies within a narrow temperature range (1150–1200 °C). During sintering the "explosive" transition in the plasmochemical Al_2O_3 powder results in the activation of the diffusion processes of mass transfer as well as sintering.

Linear dependence of porosity on shrinkage has been found for corundum materials with various morphology of the initial particles at various sintering temperatures, which suggests a possibility of creating both shrinkage-free ceramics and that with a density close to theoretical.

The dependences of the final densities of alumina ceramics vs. initial densities are linear and cross at the one point $\approx 0.5\rho/\rho_{theor}$ for various sintering temperatures, which imply a possibility of producing shrinkage-free ceramics.

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Különböző szemcseméretű porokból előállított Al_2O_3 kerámiák szinterelése

Alumínium-hidroxid termikus bontásával, illetve plazaszórásos pirolízisével készített Al_2O_3 porrend-szerek szerkezetét, fázisviszonyait és fajlagos felületét vizsgáltuk. Azt találtuk, hogy hőkezeléskor a plazmatermikus por már viszonylag szűk (1150-1200 °C) hőmérséklet-tartományban átalakul α-Al_2O_3-dá, míg a másik pornál ez az átalakulás sokkal szélesebb (600-1200 °C) tartományban megy végbe. A plazmatermikus porból tehát „robbanásszerűen" alakul ki α-Al_2O_3. A fázisátmenet során szétesnek a habszerű agglomerátumok, növekszik a fajlagos felület, és ez a szinterelés során átkristályosodáshoz, a diffúziós folyamatok felgyorsulásához, ezáltal a tulajdonságok javulásához vezet.

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