ISSN 1392 – 1231. CHEMINĖ TECHNOLOGIJA. 2009. Nr. 1 (50)

Influence of some additives on the properties of porous alumina ceramics

R. Svinka, V. Svinka, I. Zake, A. Butlers
Institute of Silicate Materials, Riga Technical University,
Azenes str. 14/24, LV-1048 Riga, Latvia
E-mail: svinka@ktf.rtu.lv

Received 2 February 2009; Accepted 17 February 2009

Production of porous alumina ceramics by the slurry casting method and pore formation by elimination of hydrogen as a result of a chemical reaction of aluminium powder with water is investigated. Such ceramics has a low mechanical strength. The purpose of the study was to determine various ways of producing high porosity alumina ceramics with a rather high mechanical strength and other properties significant for refractory ceramics. Some additives, both organic (Optapix) and inorganic (kaolin and silica), are used. The properties and structure of the obtained materials, such as bulk density, bending strength, porosity, pore size distribution, thermal shock resistance, depend on the grain size of raw materials, the viscosity of suspension, the type of additives and on the sintering temperature. Materials are sintered at a temperature of 1600 °C.

Introduction

Alumina ceramics is very important material, especially for high-temperature applications. Recently, there have appeared numerous works about porous alumina ceramics. Porous alumina ceramics is produced by different methods: pulse electric sintering with a porosity 30–50% [1], two-step heating schedule involving pulse electric sintering and pressure-assisted vacuum sintering, and the subsequent post-heat treatment in the air to produce porous alumina with a porosity of 28–38% [2], by slurry foaming combined with gel-casting [3], by adding albumin and starch with a porosity of 50–70% [4], starch alone with a porosity 6–47% [5], by the extrusion method using a plastic substance as a pore former with a porosity of 16–40%. [6]. The porous high-temperature materials presented in this work are produced by a direct foaming of ceramic suspension with a high content of solid particles according to the aerated concrete technology [7, 8]. The gas elimination reaction ability of metallic aluminium is the most important process in obtaining such ceramics. Besides, the viscosity of the suspension determines the possibility of forming spherical pores. A variation of viscosity and surface tension is also present, but it plays a minor role. A metastable pore structure is formed within 60 minutes in the pore formation reaction and in the solidification process [9].

Materials and methods

Various commercially available alumina with a different grain size distribution were used: Nabalox 115-25 (α-Al_2O_3) d_{50} 5.34 μ, Nabalox 201 (γ-Al_2O_3) d_{50} 81.03 μ, kaoline (Zettlitz Royal), milled amorphous SiO_2 d_{50} 6.993 μ, aluminum powder (Company Schlenk, Germany) 0.1 wt% from dry materials. Kaolin is a binder before sintering the green body. The primary pore structure in the green body during solidification of suspension is formed by a chemical reaction of aluminium powder with water, and kaolin catalyses this reaction. The suspensions contain 30–32 wt% of water.

Dispersing and mixing of raw materials with water are carried out within 20 min; after that, the suspension is cast in an open mould. The cast along with the mould is dried at 60 °C. The green body is sintered at a temperature of 1600–1700 °C by heating at the rate of 200 °C/h and keeping at the maximal temperature for 1 hour. The bulk density and open porosity are determined by DIN EN 993-1, the three-point bending strength with a *ZWICK BDO-FB 020 TN* by DIN 843-1. The bending strength is the average value from 8 samples with the dimensions 16 × 20 × 150 mm. Thermal shock resistance is determined for equal samples by putting into 1200 °C, keeping for 1 h at this temperature and the following cooling in the open air at 20 °C. After 1, 2, 3, 5 and 10 heating–cooling cycles, the elasticity modulus is determined by the *Buzz-o-sonic 05* ultrasound non-destructive method. Thermal expansion and the softening temperature are determined with a *NETZSH DIL 402 C* horizontal dilatometer. The microstructure of ceramic materials is investigated by SEM (Oxford Instrument) and the pore structure by optical microscopy (Leica 420) and mercury porosimetry (Quantachrome Pore Master). The phase composition is determined by X-ray analyses (X-ray Rigaku Ultra+ difractometer).

Results and discussion

The stability of a ceramic suspension depends on the size, shape and surface properties of the particles. The surface properties may by characterised by the zeta potential induced among the interacting particles [10]. Compositions with the ratio of α- and γ-alumina from 1 : 3 to 3 : 1 are investigated. An organic binder with the properties of electrolyte optapix (Zschimmer & Schwarz)

in the amount of 0.2 wt% is added. The second series is compositions with the same ratio of α and γ alumina and an additive of 5 wt% kaolin. The bulk density of samples sintered at 1600 °C increases rises from 1.0 g/cm^3 to 1.2 g/cm^3 with increasing the α-Al_2O_3 content. The bulk density increases by adding kaolin (Fig. 1) depending on α and γ-alumina.

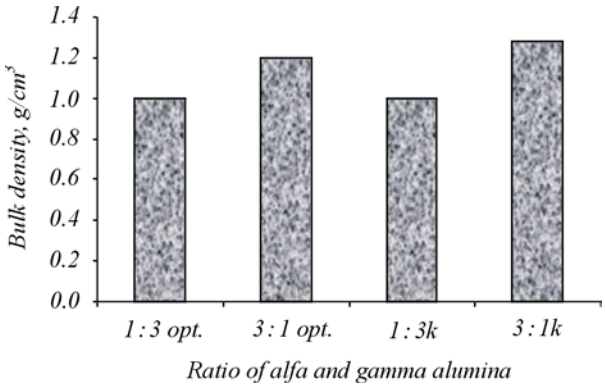

Fig. 1. Bulk density of samples. Opt. – Optapix additive; k – kaoline additive

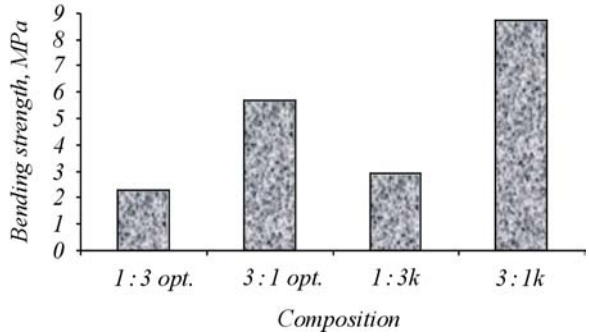

Fig. 2. Bending strength. Opt. – Optapix additive; k – kaoline additive

Addition of kaolin at the same ratio of α and γ-Al_2O_3 increases the bending strength of the obtained materials. Their mechanical strength increases two times with the prevalence of α-Al_2O_3 in comparison with the prevalence of γ-Al_2O_3 in the compositions (Fig. 2). X-ray phase analysis shows different diffraction results in these compositions. With the prevalence of α-Al_2O_3 in the composition with kaolin, by sintering at 1600 °C, besides corundum, also mullite is formed (Fig. 3, b), but in a similar composition with the prevalence of γ-Al_2O_3 there is only corundum α-Al_2O_3 (Fig. 3, a).

Phase formation reactions at a high temperature depend on the structure of raw materials, i.e. on the structure of alumina and not only on the chemical composition. The highest mechanical strength is shown by materials obtained from a mix of α- and γ-Al_2O_3 with the prevalence of α. The porosity of such materials is different. The porosity of ceramic obtained from raw powder with the prevalence of coarse-grained γ-Al_2O_3 (58.8%) is highest as compared with the porosity of materials with the prevalence of α-Al_2O_3 in the raw mix (49.7%). Different is also pore size distribution in the materials (Figs. 4 and 5).

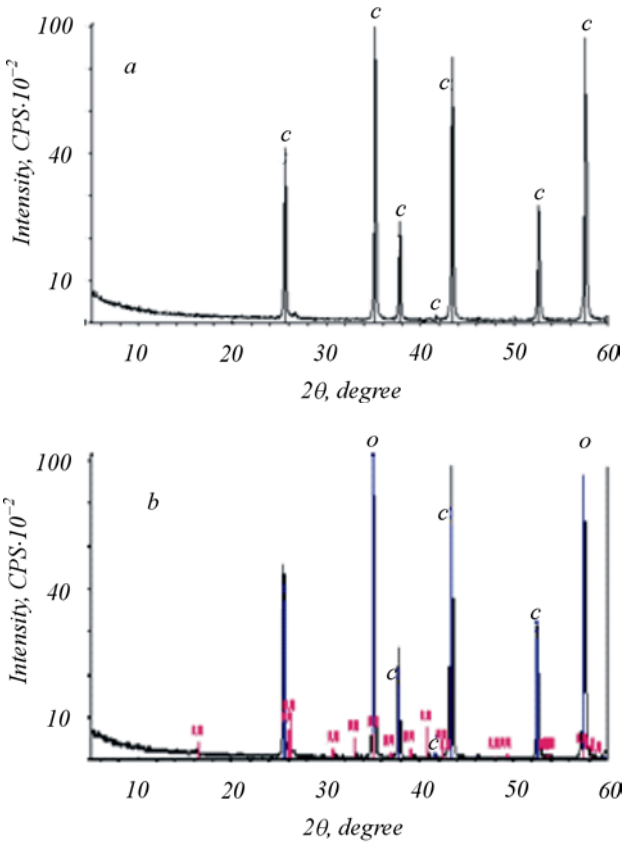

Fig. 3. X-ray diffraction of obtained materials: *a* – with prevalence of coarse-grained γ-Al_2O_3; *b* – with prevalence of fine-grained α-Al_2O_3

In the material with the prevalence of α-Al_2O_3 (Fig. 4), a pore size distribution column diagram shows two distinct pore size regions: the first with a large pore size (20–1000 μ), and the largest cumulative volume of pores (0.03 cm^3/g) has pores with the diameter of about 200 μ. Our experience shows that these pores are formed by elimination of hydrogen as a result of a chemical reaction of aluminium powder with water. Smaller pores in the second region are formed by the sintering of the material. The largest cumulative volume has pores 1–2 μ in diameter.

In the material with the composition 1 : 3k with the prevalence of coarse-grained γ-alumina, pore size distribution was of another nature. There are four regions in the column diagram (Fig. 5). The largest pores 100–1000 μ in diameter are formed similarly to the composition 3 : 1k (Fig. 4) by eliminating hydrogen. Pores in the second region (diameter 8–50 μ) may be formed as a result of chemical reaction as well by sintering. Pores in the third region (diameter 0.8–8 μ and 0.1–0.8 μ) are formed by sintering.

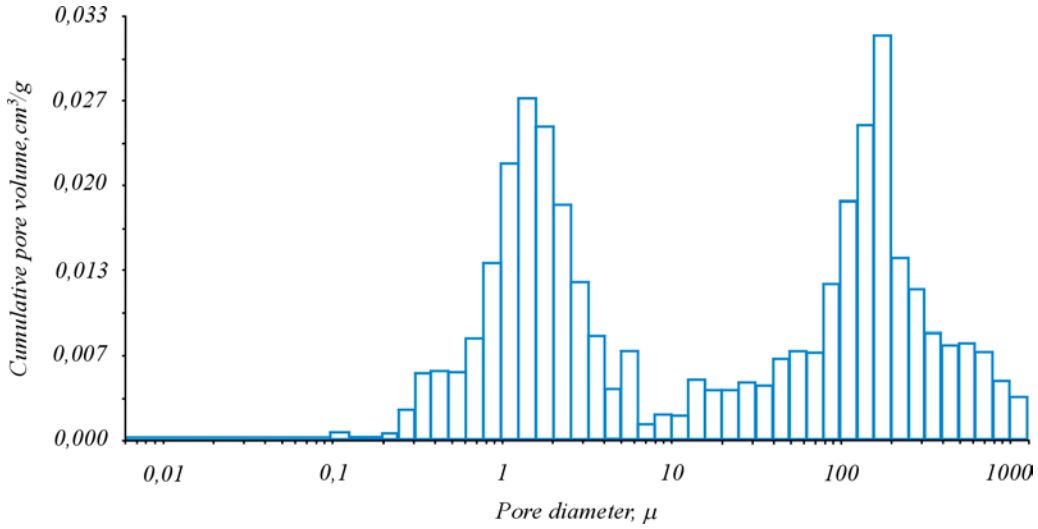

Fig. 4. Pore size distribution in the composition with the α-Al_2O_3 to γ-Al_2O_3 ratio 3 : 1 with the prevalence of fine-grained α-alumina

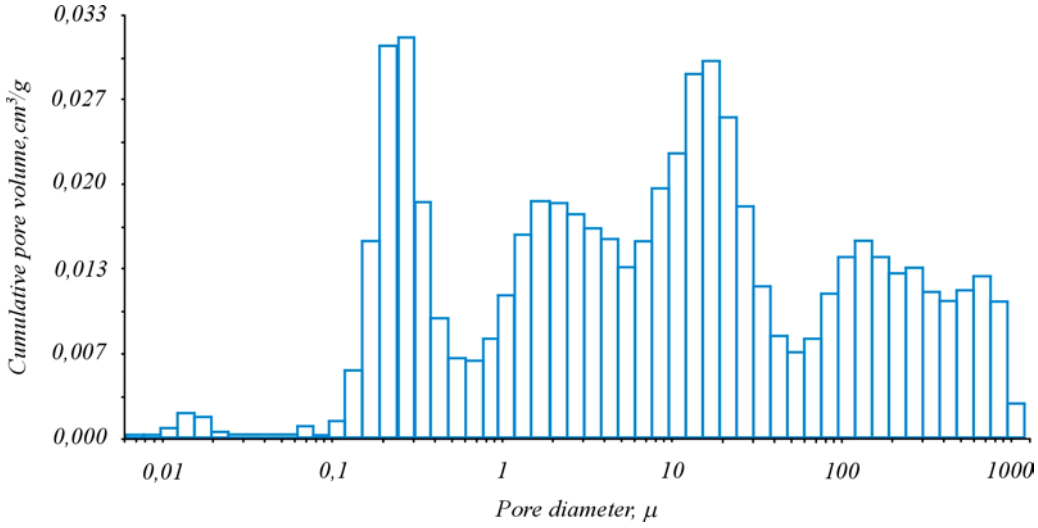

Fig. 5. Pore size distribution in a composition with the α-Al_2O_3 to γ-Al_2O_3 ratio 1 : 3k with the prevalence of coarse-grained γ-Al_2O_3

The microstructure of the materials depends on the grain size of raw materials. In a sample with the α-Al_2O_3 to γ-Al_2O_3 ratio 1 : 3 with the prevalence of coarse γ-Al_2O_3 there are large crystals with a little specific surface of powder, and the cohesion among such particles is weak in comparison with a sample with the α-Al_2O_3 to γ-Al_2O_3 ratio 3 : 1 with the prevalence in raw powder mix of fine-sized α-Al_2O_3 with a larger specific surface area. Mullite crystals, formed from kaolin by sintering, meet the cohesion among the particles (Fig. 6).

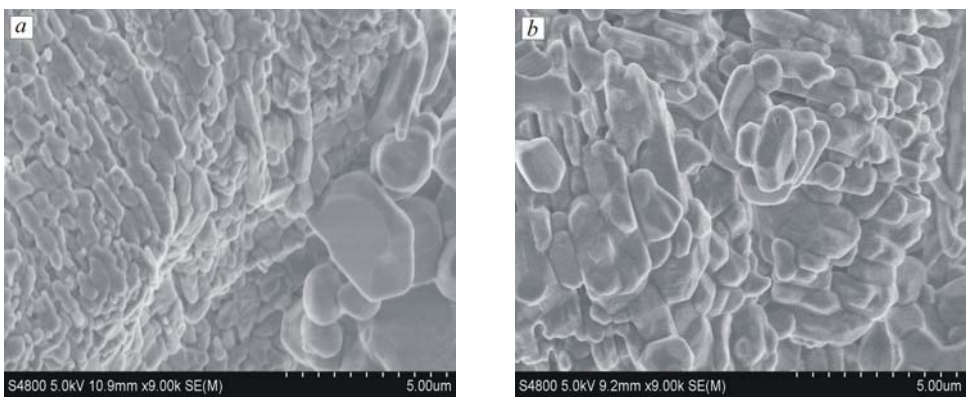

Fig. 6. SEM pictures of materials sintered at a temperature of 1600 °C: *a* – with prevalence of coarse-grained γ-Al_2O_3; *b* – with prevalence of fine-grained α-Al_2O_3

Thermal shock resistance is an important property of high temperature materials. The bending strength of the obtained materials is determined before and after the thermal shock test. The bending strength of samples with the composition 1 : 3k with the prevalence of γ-alumina decreases from 3.4 MPa to 2.0 MPa after 10 thermal test cycles. With the prevalence of α-Al_2O_3 in a raw mix (composition 3 : 1k, Fig. 7), the bending strength of a sintered material is 8.6 MPa, but after the thermal shock test it increases to 12.0 MPa (Fig. 7).

A similar cohesion among the alumina particles is obtained by using fine milled silica. Addition of silica in the amount of 0.5–10 wt% to the composition with the α-Al_2O_3 to γ-Al_2O_3 ratio 1 : 2 allows obtaining porous alumina ceramics with the bending strength of up to 12 MPa. Determination of pore structure by mercury porosimetry shows that the amount of small pores is reduced to 0.1 cm^3/g, but the cumulative volume of large pores formed by solidification of a suspension remains in the same limit of about 0.06 g/cm^3 (Fig. 8).

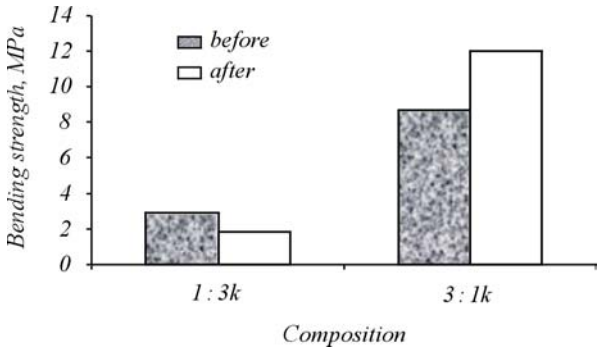

Fig. 7. Bending strength of materials with the prevalence of γ-Al_2O_3 (composition 1 : 3k) and of α-Al_2O_3 (composition 3 : 1k) before and after thermal shock testing

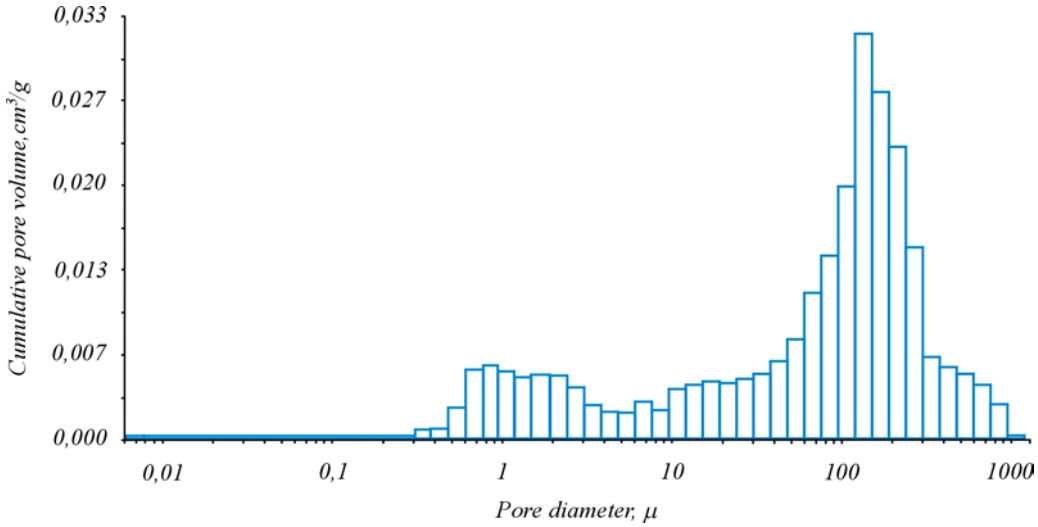

Fig. 8. Pore size distribution in the material with the α-Al_2O_3 to γ-Al_2O_3 ratio 1 : 2 after addition of 5 wt% of kaolin and 5 wt% of silica

At the same time the properties of the suspension remain constant, shrinkage decreases to 0.2%, the bulk density is the same as without silica additive.

Conclusions

The structure and properties of materials obtained at 1600 °C depend on the grain size of the raw material, on the ratio of α- and γ-alumina, viscosity of suspension, types of additives. It is possible to reduce the amount of water by employing an organic additive, but the mechanical strength is low and the bulk density depends only on the ratio of alumina with a different grain size. Kaolin increases the bending strength of the material and its thermal shock resistance. These properties depend on the ratio of alumina with a different grain size. Bending strength and thermal shock resistance increase at the prevalence of fine-grained α-Al_2O_3. The bulk density of the study materials increases at the prevalence of fine-grained α-Al_2O_3. Similar results were obtained by adding fine milled silica. The bending strength and thermal shock resistance increase, and the amount of small pores decreases. Addition of silica, in contrast to kaolin, reduces the shrinkage of materials to 0.2%.

Production of porous ceramics by the slurry casting method and pore formation by eliminating hydrogen in the solidification process result in an oriented pore structure. Such structure decreases the loading deformation the materials at a high temperature, and it is possible to use these materials both as thermal insulating and high temperature building materials.

References

1. **Jauaseelan D. D., Ueno S., Ohji T., Kanzaki S.** // Sc. Techn. Adv. Mat. 2004. N 5. P. 387–392.

2. **Jauaseelan D. D., Kondo N., Brito M. E., Ohji T.** // J. Amer. Ceram. Soc. 2002. Vol. 85, N 1. P. 267–269.
3. **Jung-Soo Ha, Byong Gu Lim.** // Adv. Sc. Technol. 2006. Vol. 45. P. 829–834.
4. **Sarama Bhattacharjee, Laxmidhar Besra, Bimal B.** // Singh. J. Eur. Ceram. Soc. 2007. Vol. 27. P. 47–52.
5. **Živcova Z., Gregorova E., Pabst W., Smith D. S., Michor A., Poulier C.** // J. Eur. Cer. Soc. 2009. Vol. 29. P. 347–353.
6. **Isobe T., Kameshima Y., NakajimaA., Okada K.** // J. Eur. Ceram. Soc. 2007. Vol. 27. P. 61–66.
7. **Svinka V., Mörtel M., Krebs S.** // Proceed. of 10th Intern. Cer. Congr., Florence, 2002. Part F: Refractories: Trends in research and applications. Faenza, 2002. P. 149–160.
8. **Jüttner T., Mörtel H., Svinka V., Svinka R., Krebs S.** // Proceed. of 48th Intern.Colloquium on Refractories, Aachen, Germany, Stahl und Eisen (Special), 2005. P. 62–65.
9. **Svinka R., Svinka V., Bula G., Jüttner T., Palcevskis E.** // Adv. Sc. Technol. 2006. Vol. 45. P. 2266–2271.
10. **Lewis I. A.** // J. Amer. Ceram. Soc. 2000.Vol. 83. P. 2341.

R. Svinka, V. Svinka, I. Zake, A. Butlers

KAI KURIŲ PRIEDŲ ĮTAKA PORĖTOS ALIUMINIO KERAMIKOS SAVYBĖMS

S a n t r a u k a

Darbe tirta porėtos aliuminio keramikos gamyba, liejimo iš suspensijų būdu, ir porų susidarymas pasišalinant vandeniliui, kai vykdoma cheminė aliuminio miltelių reakcija su vandeniu. Tokios keramikos mechaninis stiprumas yra mažas. Šio darbo tikslas yra ištirti porėtos aliuminio keramikos, kuri pasižymėtų didesniu mechaniniu stiprumu ir kitomis geresnėmis ugniai atsparių medžiagų savybėmis, gamybos būdus. Tyrimuose naudojami organiniai (*Optapix*) ir neorganiniai (*kaolinas ir kvarcas*) priedai. Nustatyta, kad produktų savybės – tankis, stiprumas, porėtumas, porų pasiskirstymas, terminis atsparumas – ir struktūra priklauso nuo žaliavų smulkumo, suspensijos klampos, naudojamų priedų ir sintezės temperatūros. Medžiaga sintetinta 1600 ^{o}C temperatūroje.