Fabrication of textured α-alumina in high magnetic field via gelcasting with the use of glucose derivative

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Textured ceramic materials arouse recently great interest due to the effective improvement of their physical and mechanical properties compared to those not crystalline oriented. Feeble magnetic ceramics, such as alumina can be textured under high magnetic field of 12T during shaping process. The connection between shaping by gelcasting method and crystalline orientation of α-alumina in high magnetic field is reported in this paper. Gelcasting allows obtaining high-quality complex-shaped elements with small quantities of organic binders. A new environmentally friendly compound on the basis of glucose (3-O-acryloyl-D-glucose) was synthesized and applied as a monomer in gelcasting process. The ceramic slurries of solid loading 30–50 vol % have been exposed to high magnetic field at the time of consolidation through an in situ polymerization of used monomer. The degree of crystalline orientation of sintered at 1600°C bodies was evaluated by X-ray diffraction (XRD).

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1. Introduction

Ceramic materials of textured structure have recently attracted much attention because of their improved mechanical, electrical, piezo- and ferroelectrical properties.1–4 The research to obtain textured materials have been performed for many compounds, such as α- and β-Al2O3, TiO2, ZnO, Bi4Ti3O12, Si3N4, AlN, SmO2, B4C, HAP, CNT, SiC and others.1–11 Textured ceramics can be obtained by application of variety of methods, including templated or seeded grain growth5–21 and hot forging22,23. The development of superconducting magnet technologies has enabled to introduce magnetic fields as high as 12T at laboratory scale. Under such strong magnetic field, magnetization force can be applied for nonmagnetic materials, for example alumina.

The development of textured microstructures in ceramics can be connected with shaping methods, especially by colloidal processes such as slip casting or electrophoretic deposition (EPD).25,26 Among these colloidal processes we can distinguish also gelcasting, which combines conventional moulding from slips with polymer chemistry. Gelcasting process allows obtaining high-quality, complex-shaped ceramic elements by means of an in situ polymerization, through which a macromolecular network is created to hold ceramic particles together.27 The key role in the whole process plays the suitable selection of an organic monomer, which is able to provide high mechanical strength of the gelled part.28 Thus the amount of organic additives needed in the suspension is reduced and the binder burnout clean.

In recent years gelcasting became a method willingly applied together with other ceramic processes, such as tape casting,25,32) production of porous ceramics33,34) and even with the methods of rapid prototyping.35) Therefore the authors decided to take advantage of gelcasting in fabrication of textured ceramics.

The aim of this study was the fabrication of oriented α-alumina bodies in a high magnetic field through shaping by gelcasting followed by sintering. The authors combined their knowledge concerning texturing of alumina and gelcasting with the application of new and environmentally friendly monomer synthesized on the basis of glucose (3-O-acryloyl-D-glucose). The synthesis route of 3-O-acryloyl-D-glucose (AkrG) and its application as monomer in gelcasting and as dispersing agent for nanoalumina was described in previous papers.30,36) In this paper the usability of 3-O-acryloyl-D-glucose in texture development in superconducting magnet is presented and compared with commercially available monomer 2-hydroxyethyl acrylate.

2. Experimental procedure

Single crystalline α-alumina powder TM-DAR (Tamei Chemicals, Japan) of an average particle size D30 = 0.21 μm, specific surface area 14.1 m2/g and of high purity > 99.99% was used. The gelcasting process was carried out with application of new low toxic monomer 3-O-acryloyl-D-glucose (AkrG), synthesized

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For comparison the commercially available 2-hydroxyethyl acrylate (Fluka) was used (Fig. 1). Diammonium hydrogen citrate (POCh, Poland) and citric acid (Sigma) were used as dispersants in ceramic slurries. \(N,N,N',N'-\text{tetramethyl-ethylene diamine} \) (Fluka) played the role of activator and ammonium persulfate (Aldrich) used as 1wt% aqueous solution was the initiator of polymerization reaction. In the case of commercial monomer, \(N,N'-\text{methylenebis(acrylamide)} \) (Fluka) was used as external cross-linking agent.

The mixing of the components in gelcasting process was carried out gradually. First, the components of ceramic slurry were dissolved in distilled water as follows: the dispersant as the mixture of diammonium hydrogen citrate (0.3 wt%) and citric acid (0.10 wt%), then 3.0 wt% of monomer and 2.0 wt% of activator (with regard to the quantity of monomer). The crosslinking agent (1.0 wt% with regard to the quantity of monomer) was used only in the case of the commercial monomer 2-hydroxyethyl acrylate (2-ha). Then the alumina powder was added and the slurry was mixed in ultrasonic magnetic stirrer for 30 min to achieve a good homogenization. Subsequently the slurries were deaired under pressure below atmospheric in vacuum desiccator connected with magnetic stirrer for 20 min. After that the viscosity of the slurries without the initiator was measured on cone/plate Brookfield CAP 2000 Viscometer. Then the initiator of polymerization was added to the slurry and mixed by magnetic stirrer for 5 min. The composition of all prepared slurries and their viscosity at shear rate 2667 s\(^{-1}\) are shown in Table 1. The mixture was then cast into polyethylene (PE) moulds of the same dimensions (20 mm diameter and 5 mm height) and placed in a superconducting magnet (Japan Magnet Technology, JMTD-10T100). Then a strong magnetic field of 12 T was applied to the suspensions (Fig. 2). The slurries with applied monomers are able to form a gel at room temperature. After 16 h gelled specimens have been unmolded, dried at 50°C for 24 h and

| Solid loading [vol %] | Applied monomer | Monomer content [wt %] | Cross-linking agent content [wt %] | Viscosity [mPas] at shear rate 2667 s\(^{-1}\) | Density of textured samples sintered at 1600°C [%TD] |
|----------------------|-----------------|------------------------|----------------------------------|-----------------------------|----------------------------------|
| 30                   | 3-O-acryloyl-D-glucose | 3          | 0       | 17.0  | 87.9 |
| 40                   | 3-O-acryloyl-D-glucose | 3          | 0       | 41.3  | 97.6 |
| 45                   | 3-O-acryloyl-D-glucose | 3          | 0       | 112.5 | 98.2 |
| 45                   | 2-hydroxyethyl acrylate | 3          | 1       | 97.0  | 97.9 |
| 50                   | 3-O-acryloyl-D-glucose | 3          | 0       | 217.5 | 98.0 |

Fig. 1. Molecular structure of a) 3-O-acryloyl-D-glucose (AkrG), b) 2-hydroxyethyl acrylate (2-ha).

Table 1. Composition and viscosity of prepared ceramic slurries placed in a superconducting magnet and density of sintered samples

![Schematic illustration of shaping by gelcasting carried out in superconducting magnet.](image)

Fig. 2. (Color online) Schematic illustration of shaping by gelcasting carried out in superconducting magnet.
preliminary fired at 800°C in order to burn out organic additives and not to lose the grains orientation during green machining. The sintering of samples was conducted at two temperatures 1300°C/2h and 1600°C/2h in air without applying magnetic field. The crystalline orientation of the alumina ceramics was evaluated by X-ray diffraction (XRD) on JEOL JDX-3500. The measurements were carried out for the cross-sectional planes which were perpendicular and parallel to the to the direction of the magnetic field, designated as TOP and SIDE, respectively. The resulting microstructures were observed by SEM JEOL JSM-6500F. The densities of specimens sintered at 1600°C were measured by the Archimedes’ method in water.

3. Results and discussion

3.1 Suspensions characterization

Four alumina suspensions of increasing solid loading: 30, 40, 45 and 50 vol% with new monomer AkrG were prepared as shown in Table 1. Additionally, one suspension of 45 vol% alumina content with commercial monomer 2-hydroxyethyl acrylate was also prepared. For commercial monomer the solid loading of 45 vol% was chosen as thereabout in the middle of the range of powder content of investigated slurries. The viscosities of all prepared slurries as a function of shear rate are shown in Fig. 3. The lowest viscosity exhibit the slurry with 30 vol% solid loading and as it was expected, the increase of viscosity is observed with the increase of alumina content. The differences in viscosity values do not differ much for the first four slurries, but the suspension with solid loading 50 vol% has almost two times higher viscosity that those of 45 vol% alumina content with monomer AkrG. If these research would concentrate only on gelcasting process of alumina, the viscosity of the 50 vol% slurry would be very satisfactory in order to obtain high-quality, non-defected ceramic body, but for texture development in high magnetic field it may be too high. On the other hand, although the very low viscosity of 30 vol% slurry is perfect for particles so that they could freely rotate in high magnetic field, the solid loading is definitely not sufficient for shaping ceramic powders by gelcasting method. In gelcasting the water from the suspension is either bonded in nascent polymeric network or evaporated during exothermic reaction of an in situ polymerization. For that reason, too low solid loading can result in obtaining highly defected samples. The situation would look completely different in shaping by slip casting method, where water is drawn in by porous substrate, mainly in one direction. The received green body would be less defected even with low solid loading, but serious defects could appear after sintering, due to large distances between particles.

The subsequent experiments carried out in superconducting magnet were the trial to obtain well oriented alumina crystals while maintain high-quality ceramic bodies.

3.2 Texture development in high magnetic field

The prepared ceramic slurries with addition of polymerization initiator were poured into polyethylene moulds and placed in a superconducting magnet of 12T for 16 h. The samples of 30 and 40 vol% solid loading were defected after removing from magnet. The samples of 45 and 50 vol% solid loading were of good quality. The samples have been then fired at 800°C in order to remove organic additives and then green machined in order to prepare specimens for XRD analysis. XRD patterns for specimens sintered at 1300°C did not differ much from patterns for alumina bodies without applying high magnetic field sintered at the same temperature. As it was proved in previous works (10,11).

Figure 5 shows the XRD patterns of the α-Al₂O₃, textured at 12T from slurry with 45 vol% solid loading by gelcasting with new monomer AkrG followed by sintering at 1600°C for 2h. The presented sections have been perpendicular and parallel to the direction of the magnetic field, designated as TOP and SIDE, respectively. In order to characterize the XRD peaks, the interplanar angles 𝜃 for planes of [hkl] and the basal plane (001) were calculated for the hexagonal unit cell of α-Al₂O₃ on the basis of equation presented in previous paper. (11) The significant difference is observed between the XRD patterns of the TOP and the SIDE. The diffraction peak of the plane (001) where 𝜃 = 90° is observed only for the TOP. The peaks of the planes where 𝜃 < 25° which are (1010), (018), (104) and (116) of the TOP are stronger than those of the SIDE. In contrast, the diffraction peaks of the planes (110) and (030) where 𝜃 > 60° of the SIDE are stronger than those of the TOP. The XRD data clearly show the crystallite orientation of the α-alumina prepared in the strong magnetic field of 12 T. It is also confirmed that the c-axis is easy to align along the magnetic field. Nevertheless some texturing degree for so high solid loading was achieved.

There is additional important observation form the carried out research. The time needed for complete in situ polymerization of monomers in the slurries placed in superconducting magnet was few times longer than without applying magnetic field. The polymerization of all samples outside superconducting magnet with 0.3 wt% (with regard to the quantity of monomer) of initiator was completed after half hour. The sample prepared with the commercial monomer 2-hydroxyethyl acrylate (2-ha) did not gel completely and while removing from the magnet was still a bit fluid. This could be due to the fact that some organic monomers
also willingly align in high magnetic field thus they are not able to create a cross-linked polymeric network. As a result the obtained alignment of alumina particles could be lost during transportation from the magnet if the samples are not strongly consolidated as in the case of 2-hydroxyethyl acrylate.

Figure 6 shows SEM microstructures of SIDE plane of samples sintered at 1600°C from four different slurries. The most elongated and aligned grains are visible for specimen from slurry with 45 vol% solid loading and with monomer AkrG [Fig. 6(c)]. Grains alignment is visible also for specimen from slurry with 40 vol% solid loading [Fig. 6(a)] but in green stage some defects were observed. The visible grains alignment is not evident for slurry with 45 vol% solid loading and monomer 2-ha [Fig. 6(b)]. This is because the specimen removed from the superconducting magnet did not gel completely and the obtained texturing could be lost during transportation. The microstructure of sample from slurry with 50 vol% solid loading [Fig. 6(d)] corresponds with the results from XRD analysis and texture development is not satisfactory enough. On SEM image elongated grains are visible but not well aligned. Then, although the alignment of specimens obtained from 40 vol% solid loading was achieved, the defects in the samples disqualified them from further applications. The samples with high solid loading of 45 and 50 vol% (especially for TM-DAR of an average particle size 210 nm) were of good quality, however the samples of 45 vol% of alumina concentration were better textured that of 50 vol%. The values of relative densities for samples sintered at 1600°C are presented in Table 1. The lowest density (87.9% of the maximum theoretical value) exhibited samples casted from slurry with 30 vol% solid loading. This was due to the fact that these samples were defected in a green state, as was wider described in section 3.1. The highest values of density (around 98% of TD) had samples casted from slurries with 45 and 50 vol% solid loading with both monomers. Slightly lower density (97.6%) had samples casted from...
slurry with 40 vol%, as was expected. Nevertheless densities of textured and sintered alumina bodies are satisfactory.

4. Summary

The application of superconducting magnet together with shaping by gelcasting method allowed obtaining textured α-alumina. The compromise between low viscosity of slurries which ensure easy rotation of particles in high magnetic field and enough high solid loading which ensure obtaining ceramic bodies of good-quality was found. The application of alumina slurry of 45 vol% solid loading with low-toxic monomer on the basis of glucose under high magnetic field followed by sintering results in obtaining non-defected, well densified textured α-alumina specimens.

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Fig. 6. SEM micrographs of SIDE plane of samples oriented in high magnetic field and sintered at 1600°C received from slurries: a) 40 vol% with AkrG b) 45 vol% with 2-ha c) 45 vol% with AkrG d) 50 vol% with AkrG.
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