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Growth of Tabular α-Al_2O_3 Grains on Porous Alumina Substrate

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Gradient, porous alumina ceramics were prepared with the characteristics of microsized tabular α-Al_2O_3 grains grown on a surface with a fine interlocking feature. The samples were formed by spin-coating diphasic aluminosilicate sol on porous alumina substrates. The sol consisted of nano-sized pseudo-boehmite (AlOOH) and hydrolyzed tetraethyl orthosilicate [$Si(OC_2H_5)_4$]. After drying and sintering at 1150°–1450°C, the crystallographic and chemical properties of the porous structures were investigated by analytical electron microscopy. The results show that the formation of tabular α-Al_2O_3 grains is controlled by the dissolution of fine Al_2O_3 in the diphasic material at the interface. The nucleation and growth of tabular α-Al_2O_3 grains proceeds heterogeneously at the Al_2O_3/glass interface by ripening nano-sized Al_2O_3 particles.

I. Introduction

ANISOTROPIC grains with interlocking or texture structure are interesting because greater constraints among grains could enhance the bonding stress of ceramic matrixes. Al_2O_3 is one of the well-known structural ceramics with acceptable mechanical and chemical properties.[1] Tabular (or plate-like) alumina grains could be formed by an aluminosilicate gel method,[2] hot pressing and sinter forging processing,[3] or oxidation of Al metal with alumina powder.[4] Seabaugh and colleagues[5–7] have reported that anisotropic Al_2O_3 grains were formed by the addition of various oxides, for instance, SiO_2, CaO, and TiO_2. When the mixture was sintered above the eutectic temperature of the system (Al_2O_3–MO), a liquid phase was formed to help fast diffusion. Besides, a reduction of the surface energy of α-Al_2O_3 resulted in the fast grain growth of Al_2O_3 along specific crystalline planes. Without the doped material, there was no anisotropic growth of Al_2O_3 grains.[8] The key point of abnormal alumina grain growth is the presence of a multiple-component-oxide liquid phase during sintering.

Previous literature[9] has demonstrated mullite synthesis from diphasic aluminosilicate gels with stoichiometric and nonstoichiometric compositions. The pseudo-boehmite would convert to γ- and δ-Al_2O_3, at temperatures around 400° and 1050°C, respectively, and then react with amorphous SiO_2 to form mullite in stoichiometric diphasic gel at 1200°C. Mullite grains grew from the diphasic matrix with an equal-axis shape. Our previous study[10] found that tabular grains formed on porous Al_2O_3 substrate below the eutectic temperature, $T_e = 1570$°C. However, several important issues were not clarified, i.e., the formation mechanism and the crystalline phase of the tabular grains. This study identified the crystalline phase and investigated the formation mechanism of tabular α-Al_2O_3 grains. Microstructural observation revealed the formation of a glassy phase at processing temperatures below the eutectic point (T_e) and we reported the composition of the glass.

II. Experimental Procedure

The morphology and particle size of pseudo-boehmite (Remel-A-20, Remet, Utica, NY) by transmission electron microscopy (TEM) show a platy shape with a narrow size distribution. The size range was from 5 to 30 nm, and no particles were bigger than 50 nm. Porous Al_2O_3 substrate was made by slip casting a slurry containing alumina powder (A16-SG, Alcoa Co., Pittsburgh, PA) and dispersant (Darven-C, ammonium salt of polymethylacrylic acid, R. T. Vanderbilt Co., Norwalk, CT). The tape normally has a thickness of 0.5 mm and the processing details were reported in a previous study.[11] After heat treatment at 1100°C for 1 h, the sample had a granular microstructure (Fig. 1(a)) with a density of 63% ± 1% theoretical density, and designated as G11. The G11 tape was slightly sintered and the mean size of the Al_2O_3 grains was 0.5 μm.

Three coating sols were prepared by the same sol–gel process. Diphasic 60AS sol is composed of SiO_2/Al_2O_3 in a 2/3 molar ratio. Tetraethyl orthosilicate (TEOS, Art. 800658, Merck-Schuchardt, Hohenbrunn, Germany), pseudo-boehmite, ethanol (purity 99.5%, Nihon Shiyaku Industry Ltd., Osaka, Japan), and deionized water were used to prepare the 60AS sol. TEOS was dissolved in ethanol and hydrolyzed by H_2O in acidic condition (pH = 2.0) by HCl solution. After mixing for 30 min, the pseudo-boehmite colloids were added and stirred for 1 h. The formulation of the precursor mixture in molar ratio is SiO_2:Al_2O_3:H_2O:ethanol = 1.0:1.5:28.0:2.7. Experimental details have been described previously.[12] Pure SiO_2 sol and pseudo-boehmite sol were also prepared as the comparison cases, which were prepared either from acidic TEOS solution or the pseudo-boehmite precursor, respectively.

These sols were spin coated at a rate of 1000–5000 rpm for 10 s on porous Al_2O_3 substrates as the viscosity of the diphasic sol reached 35 cP. The Al_2O_3 substrates were named G11S, G11A, and G11M after being coated by a sol of silica, alumina, and 60AS, respectively. G11A and G11M showed coating layers about half to several micrometers in thickness. The coating layer on G11S can hardly be detected due to the filling of the low-viscous SiO_2 sol (ca. 35 cP) into the porous Al_2O_3 substrate. After coating, the samples were dried at 25°C for a day. Then the samples were heated at a rate of 10°C/min to 1150°–1450°C for 1 h. The sintering was conducted in a high-purity Al_2O_3 tube and no contaminants from low-melting salts, e.g., NaCl, were present.

The morphologies of the samples were observed by field emission scanning electron microscopy (Instrument 1530, Leo, Cambridge, U.K.) equipped with energy-dispersive spectrometry (EDS, DX4, EDAX Corp., Mahwah, NJ). Detailed microstructures and crystalline phase were also analyzed by analytical electron microscopy (AEM, TEM 100CX, JEOL Co., Akishima, Japan, and TECNAI F30 and TECNAI 20, Philips Co., Almelo, the Netherlands) and X-ray diffractometry (XRD, Philips PW1710, Eindhoven, the Netherlands).

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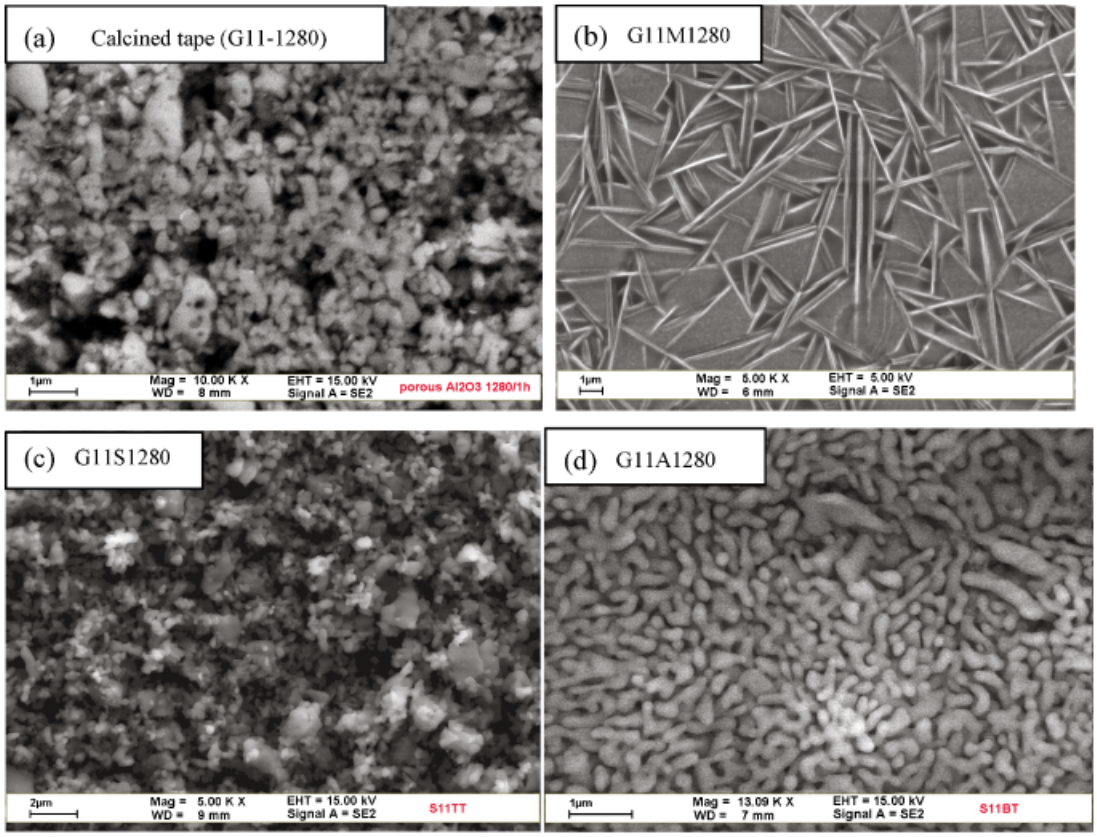

Fig. 1. Scanning electron microscopy micrographs showing (a) calcined porous Al_2O_3 substrate, G111280, (b) G11M1280, (c) G11S1280, and (d) G11A1280. The samples were precalcined at 1100°C before coating and then sintered at 1280°C for 1 h after coating.

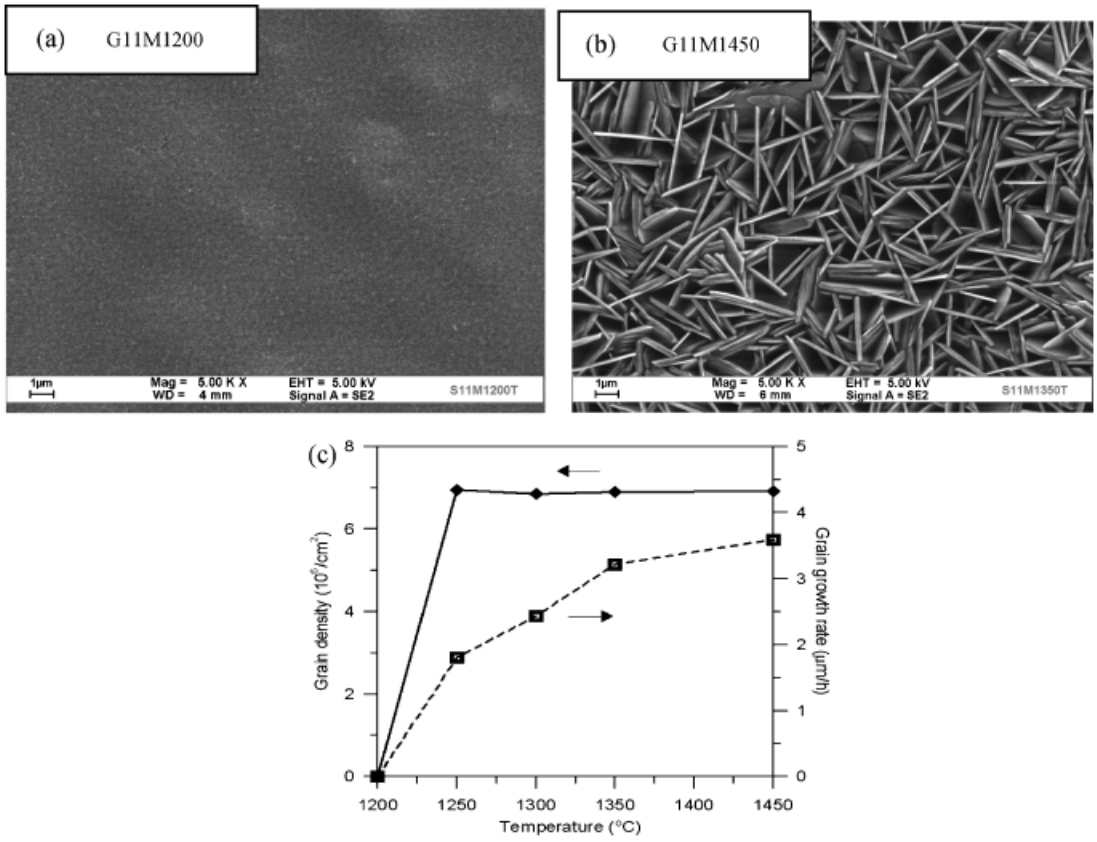

Fig. 2. Scanning electron microscopy of the surface morphology of (a) G11M1200, (b) G11M1450, and (c) the grain density and grain growth rate plotted against sintering temperature.

III. Results and Discussion

Figure 1(b) shows the top view of G11M1280, illustrating tabular α-Al_2O_3 grains in the coating film grown in a direction perpendicular to the surface and interlaced. The tabular grains were up to 8 μm in length, about 0.2-μm thick, with aspect ratios from 3 to 20.

The other two samples, G11S1280 and G11A1280, are shown in Figs. 1(c) and (d), respectively. G11S1280 with SiO_2 sol coating showed no apparent coating. On the G11A1280 sample, a vermicular structure was seen on the surface of the coating.

The crystal structures of the coatings were analyzed by XRD. The coating samples had only α-Al_2O_3 except for sample G11M1280, which showed an additional very small peak at 20.3°, possibly belonging to cristobalite (SiO_2).

Figure 2 shows the surface morphologies of G11M sintered at 1200°–1450°C for 1 h. No tabular grains were observed on the sample sintered at 1200°C. As the sintering temperature increased to 1350°C, the glassy surface was replaced with porous structure consisting of tabular α-Al_2O_3 grains with an interlocking configuration.

The grain density of tabular α-Al_2O_3 grains on the surface of the G11M sample sintered at different temperatures is shown in Fig. 2(c). Below 1250°C, the grain density was zero because there were no tabular α-Al_2O_3 grains on the surface. The grain density on the surface of the G11M above 1250°C is almost the same, 7×10^6 cm^{-2}. This means that instant heterogeneous nucleation of tabular α-Al_2O_3 grains occurred at $\geq$ 1250°C. Nucleus formation takes place seemingly independent of the temperature at $\geq$ 1250°C. However, we believe some nuclei have formed at as low as 1150°C (as shown in Fig. 3(b)). The grain growth rate of tabular α-Al_2O_3 grains on the surface increased from 1.8 to 3.6 μm/h when the sintering temperature was raised from 1250° to 1450°C.

Nucleus formation and growth of tabular α-alumina is controlled by the solubility of alumina in glass, which is dependent on temperature. Nucleus formation of tabular α-alumina takes place at the interface of glass/α-alumina. Further growth of the nucleus is hindered due to insufficient space existing around the grains. That is why we observed nearly identical grain density on the surface of G11M above 1250°C.

Figure 3 shows the cross-sectional TEM morphologies of G11M1150, illustrating a typical structure of a few tabular α-Al_2O_3 grains grown at the interface of glass/α-Al_2O_3 grain. Porous substrate, tabular α-Al_2O_3 grains (A_T), and acicular nano-grains could be observed at the interface. The tabular grains were in the middle of growth, but not large enough to reach the surface of the coating layer. Hence the morphology of the top view on the G11M1150 sample was covered by diphasic materials, similar to that of G11M1200 (Fig. 2(a)). There are some small grains (A_P) that have nontabular characters, which develop faceted low-index surfaces. The grain coalescence of the A_{P1} grain with its neighboring A_T grain could result in large tabular grains as those in the middle region of Fig. 3(a). Grain coalescence was also occasionally found in the G11M1280 samples. A few tabular α-Al_2O_3 grains that contained small angle boundaries and dislocations have been characterized previously.[13] These observations reveal the rearrangement of small Al_2O_3 grains to the lowest surface energy and then the formation of tabular α-Al_2O_3 grains.

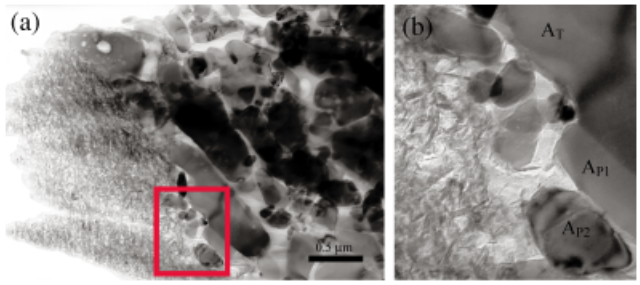

Fig. 3. Cross-sectional transmission electron microscopy morphologies of G11M1150. (a) The interface of diphasic (left) and porous Al_2O_3 (right) regions and (b) the region of interest, showing pretabular grains (A_P) next to tabular grains(A_T), nano-acicular grains, and glassy phase.

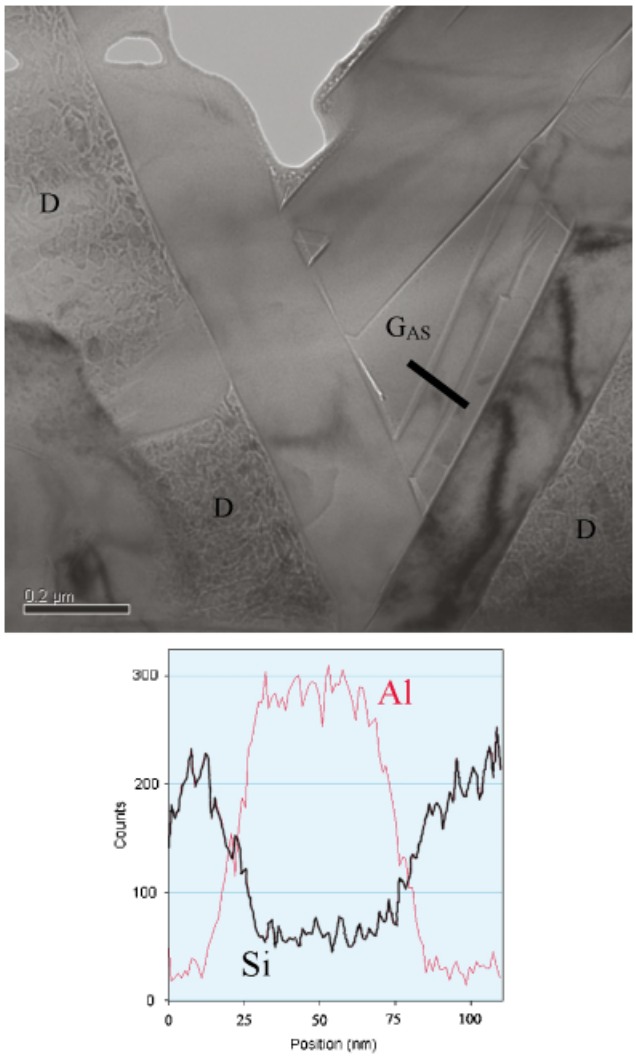

Fig. 4. Transmission electron microscopy micrograph of G11M1250 illustrating the elemental scanning results of Al and Si contents. The D regions are diphasic, containing fine Al_2O_3 grains.

The composition of an amorphous region near tabular α-Al_2O_3 grains (Fig. 4) was analyzed by analytical TEM. The composition of the tabular α-Al_2O_3 grains in the coating layer was confirmed. Moreover, there were two types of grain boundary phases. One (marked D in Fig. 4(a)) was a diphase region with cuboid nano-sized Al_2O_3 grains. These could be δ- or θ-Al_2O_3,[14] with a SiO_2/Al_2O_3 molar ratio of about 17/83. This is higher in Al_2O_3 content than in mullite, 40/60. No other elements, e.g., Na_2O or MgO, were detected. The other type of grain boundary phase was glass marked as G_{AS} in Fig. 4. The composition of the glassy phase was about 4.7-mol% Al_2O_3 and 95.3-mol% SiO_2. EDS results from a number of glassy regions showed an Al_2O_3 content of 5 ± 2 mol%. As the temperature increases, more Al dissolves in the glass. This may play a role in enhancing diffusion during the growth of tabular grains.

The AEM result of electron diffraction analyses (not shown here) in Fig. 4 indicates that there are no crystalline phases in the glassy region G_{AS}. Minor Al_2O_3 (by EDS) was detected, which implies Al–O dissolution into amorphous SiO_2. This provides decisive evidence that transient glassy phases exist in the Al_2O_3–SiO_2 system below the eutectic temperature.

IV. Conclusions

In summary, analysis of nano-Al_2O_3 particles transformed from pseudo-boehmite resulted in the following conclusions. First, alumina dissolves into a glassy SiO_2 phase and acts as the source of growing tabular Al_2O_3 grains. During particle ripening, small alumina particles dissolve into the glass and then precipitate on the large faceted Al_2O_3 particles. In addition, the coalescence of neighboring particles could be an additional grain growth mechanism.

The growth of tabular grains is mainly along the basal plane of α-Al_2O_3. The glassy phase contains about 5.0-mol% Al_2O_3 content. The glass offers the route of heterogeneous nucleation of Al_2O_3 grains preferentially taking place at the interface. Only the perpendicular growth of the Al_2O_3 grains can reach the surface of the coating layer. A maximum grain growth rate of 3.6 μm/h was measured at a temperature of 1450°C.

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