Fabrication and characterization of porous alumina with a surface layer composed of alumina platelet by direct-foaming method

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Porous alumina with the surface layer was fabricated from an alumina platelet/novolac-HexaMethyleneTetramine (HMT) composite. HMT was used as a blowing agent as well as a curing one for the novolac binder. When the alumina platelet/novolac composite was heated with covering its surface with filter papers, a porous structure formed inside the composite due to blowing from HMT. On the other hand, the blowing gas near the surface was evolved outward through the filter paper, which resulted in the formation of the surface layer composed of the aligned alumina platelets. Effct of the surface layer on the mechanical strength was examined by three-point bending measurement. The bending strength of the obtained porous alumina increased by 94% compared to the porous alumina without the surface layer.

Porous ceramics have numerous industrial applications, including structural components, thermal insulators, absorbents, and filters, due to a variety of specific properties, such as their heat and corrosion resistance, lightness, and low thermal conductivity. Among these specific properties, the lightness is one of the most important properties in the porous ceramics. While increasing porosity reduces the weight, it also degrades mechanical strength, which is critically important where the porous ceramics is used as structural materials.

We have previously proposed a direct-foaming approach for porous ceramics from ceramic/novolac-HexaMethyleneTetramine (HMT) composite, and using this approach we have fabricated porous alumina with the relatively dense surface layer. In this study, HMT was used as a blowing agent and as a curing one for the novolac resin. Gas blown from HMT led to the formation of a porous structure in the alumina/novolac composite with the expansion of the composite body, while it also resulted in swelling of the surface. This problem can be solved by covering the surface with a proper sheet and constraining the swelling using a mold during blowing. When using a plastic sheet for this purpose, coarse pores formed on the surface because the blowing gas accumulated around the surface, which led to degradation of mechanical strength. Instead, when employing a paper filter for the sheet, relatively dense layer was obtained since the blowing gas near the surface was released to the outside and to keep the surface flat, improving the mechanical strength 30% compared to that of porous alumina without the surface layer.

It has been known that dense alumina with microstructure of aligned platelets exhibits excellent mechanical property when stress is applied in the alignment direction. Therefore, if the surface layer composed of aligned alumina platelets parallel to the surface can be fabricated, then we can anticipate increase of the mechanical strength. However, to the best of our knowledge, there have been no studies on controlling microstructure of the surface layer with using alumina platelets via a direct-foaming method.

In this study, we fabricated the porous alumina with the surface layer composed of alumina platelets by means of the direct-foaming with using the filter paper. The alumina platelets were mixed with a novolac-HMT powder followed by preparing the alumina-platelet/novolac-HMT composite by the press molding. The composite was heated at 150°C with covering its surface with the filter papers. The porous alumina with the surface layer was obtained through de-binding and sintering process. The resulting porous alumina was characterized by mechanical strength measurements, X-ray diffraction measurements and microstructural observation.

Alumina platelets were obtained from the agglomeration of platelets alumina powder (D50 = 97 μm, Showa Denko Co.Ltd., Tokyo, Japan) after the ball-milling treatment using alumina balls (10 mm diameter). The obtained alumina powder was mixed with fine alumina powder (D50 = 0.55 μm; Showa Denko Co.Ltd., Tokyo, Japan) in a mass ratio of 80:20 (plate:finel. The mixed alumina powder was blended with the novolac-HMT powder (SPI101 novolac type with 9 wt.% of curing agent: HMT, D50 = 24.8 μm; Asahi Organic Chemicals Industry Co. Ltd., Tokyo, Japan) at a volume ratio of 40:60 (mixed alumina:novolac-HMT) for 1 h under dry conditions by a V-type mixer. Using a steel mold, disc-shaped alumina/novolac-HMT composites with a diameter of approximately 45 mm and a thickness of approximately 3 mm were formed at 20 MPa. Covering top and bottom surfaces of the composites with filter papers (pore size 2.7 μm), the composites were heated at 150°C for 1 h. After blowing, they were debound under flowing N2 gas at 800°C for 1 h and

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the swelling of the composite. Because the swelling was con-

strained by the mold, the surface layer where blowing gases were released outward through the filter paper was subjected to compression in direction perpendicular to the surface. The alumina platelets had the high aspect ratio and were able to flow in the molten novolac during the swelling, they were aligned parallel to the surface. Figure 2 shows XRD patterns of specimens when the X-ray irradiated the top surface of the specimens (A) with the surface layer and (B) without the surface layer. In (B) the surface layer was removed by polishing around 100 μm from the surface, and the spherical pores were exposed on the surface. All the diffraction peaks from (A) and (B) were assigned as typical diffraction of α-alumina (JCPDS 46-1212). The (006) was the basic crystal plane. The (116), (018), (1010) and (119) were also defined as a similar plane group. Diffraction peaks from (006), (116), (018), (1010) and (119) were strongly detected on the XRD pattern of (A) compared to the XRD pattern of (B). This indicated alignment of the alumina platelets parallel to the surface in the surface layer.19) The Lotgering factor (f) proved to be of good use as the simplicity of the representation for the orientation degree.19)-21)

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f = \frac{p - p_0}{1 - p_0}
\]

where p denotes the fraction of the summation of the peak intensities corresponding to the preferred orientation axis to that of the summation of all diffraction peaks in the specimen. p_0 is p of a standard material and standard α-alumina powder is used in this case. Since the peak intensity of (006) was small, the Lotgering factor f was calculated using the peak intensities from

Figure 1. Particle size distribution of alumina platelets.

Figure 2. SEM images with different observation positions on the specimen (a) top view on the surface, (b) cross-section of the surface layer, (c) cross-section of the specimen and (d) wall between spherical pores.

Figure 3. XRD patterns of the specimen (A) with the surface layer, and (B) without surface layer.
mina have been investigated by several researchers.\(^1\),\(^1\),\(^2\),\(^3\),\(^4\),\(^5\),\(^6\),\(^7\),\(^8\) The \(f\) values from (A) and (B) were calculated to be 0.16 and 0.06, respectively. The \(f\) of (A) was almost three times higher than that of (B), which indicated that the alumina platelets of the surface layer were well aligned parallel to the surface.

**Figure 4** shows the result of three-point bending strength of the specimen with (A) the surface layer and (B) without the surface layer. The porosities were both around 60%. The bending strength of (A) and (B) was 32 ± 5 and 17 ± 2 MPa, respectively; the former was 94% higher than the latter. Furthermore, the bending strength of (A) was also substantially high compared with that of the reference specimen which had a bending strength of 9.3 ± 0.9 MPa with porosity of 65% and the surface layer thickness of around 60 \(\mu\)m, while the porosity and the thickness of the surface layer were similar to each other. It could be concluded that the improvement of bending strength was largely contributed to the aligned alumina platelets in the surface layer. Ray et al.\(^2\) reported about 14 MPa for the bending strength of porous alumina with the porosity of about 48% and the average particle size of 7 \(\mu\)m, and Kritikaki et al.\(^3\) did about 22 MP for that of porous alumina with the porosity of 52% and the average particle size of 5 \(\mu\)m. Note that the particles of these materials are isotropic ones. Compared to these values, the strength of the specimen with the surface layer in this study was high, in spite of the higher porosity.

Strengthening and toughening behaviors of textured alumina have been investigated by several researchers.\(^1\),\(^3\),\(^5\),\(^7\),\(^8\),\(^9\) Yoshizawa, et al.\(^5\) investigated the mechanical properties of a textured alumina made by high-temperature deformation of normal-purity sintered alumina, where plate-like grains were aligned perpendicularly to the pressed direction, and found very high bending strength as well as extremely high fracture toughness when stress is applied in the alignment in one direction. They attributed the excellent fracture toughness to enhancement of the grain bridging effect by the large number of aligned plate-like grains and the full grain boundary fractures (or crack deflections) in the textured structure. This effective toughening behavior led to rapid increment of fracture resistance, which could result in increase of fracture strength.\(^10\) Furthermore, the aligned grains reduce the apparent size of the fracture origin defect, also leading to high strength. Because the microstructure of the surface layer in this study is very similar to that of theirs, it can be assumed that the same toughening and strengthening mechanisms work, leading to the substantially high fracture strength.

We have fabricated the porous alumina using the alumina platelet derived from alumina platelet/novolac-HMT composite by the direct-foaming method. The resulting porous alumina indicated different microstructure between the surface layer and the inside. In the surface, the alumina platelets were aligned parallel to the surface, which formed the surface layer up to 60 \(\mu\)m of thickness without pores. In the inside, the alumina platelets were randomly oriented and the spherical pores were formed. The XRD study revealed that the degree of alignment of the platelets in the surface layer was almost three times higher than that of those inside the specimen. The aligned platelets in the surface layer played an important role in improving bending strength of the porous alumina, which increased the bending strength by 94% compared to that of the porous alumina without the surface layer.

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