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Fabrication of low cost fine-grained alumina powders by seeding for high performance sintered bodies

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Abstract

The effect of seeding into commercial aluminum hydroxide on the α-alumina transition temperature, powder characteristics and properties of sintered bodies was investigated, with the purpose of obtaining high performance sintered bodies from low cost raw material. A small amount of fine α-alumina seed addition, which was worn from wet ball milling, drastically lowered the α-alumina transition temperature. The particle size of the low temperature transformed seeded powder was smaller than non-seeded powder. This powder could be sintered to full dense at lower temperature. The abnormal grain growth, which is often observed in high temperature sintered usual purity alumina, occurred at lower temperature in the sintered low temperature transformed seeded powder. However, the abnormal grain size was small and the number of the grains was high. The sintered bodies with these microstructures show high bending strength and very high fracture toughness.

Keywords: Al_2O_3; Mechanical properties; Microstructure-final; Structural applications; Seeding

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1. Introduction

Alumina ceramics have been widely used in a variety of engineering fields, because of their excellent chemical stability, electric properties and good mechanical properties besides relatively low cost in the manufacturing process. Alumina powders for sintering are, in general, prepared by calcination of mother salts such as aluminum hydroxide, ammonium alum, and ammonium dawsonite at high temperature. In this calcination process, the mother salts are decomposed and finally transformed into α-alumina at high temperature above 1200 °C by way of different transitional phases χ, κ for gibbsite type aluminum hydroxide, and γ, δ, θ for boehmite type aluminum hydroxide, ammonium alum and ammonium dawsonite. Such calcination operation promotes not only the transformation from transition alumina to α-alumina, but also α-alumina particle growth and hard aggregates of α-alumina particles. Fine-grained sintered bodies are a fundamental requirement for strong ceramics, and they can be made only from fine raw powders by low temperature sintering. There have thus been many reports on the methods of preparing fine α-alumina powder by reducing the transformation temperature to α-alumina.[1–9] Additions of metal oxides, α-alumina seeds, liquid-phase formers, and non-organic compounds, as well as high energy ball milling are effective to reduce the α-alumina transformation temperature. In some of these studies, fine-grained sintered bodies were obtained[3,6,10] and high bending strength was acheived.[6,10] Although fine equiaxed grain structure increases bending strength, fracture toughness is not improved by fine equiaxed grain structure. Most of these studies have aimed at reducing the transformation temperature for obtaining fine α-alumina and obtaining strong sintered bodies. The raw materials used in these studies therefore tend to be very expensive reagent or high purity powders.

Fracture toughness of sintered alumina is greatly improved by large plate-like particles which are often formed in high temperature sintered alumina with impurities, though bending strength significantly decreases.[11] Recently, many studies designed to obtain high strength and high fracture toughness through microstructure control have been reported.[12–15] In these reports, small plate-like grains or rod-like anisotropic grains are used as reinforcement material. If fine-grained powders with impurities can be prepared, it is considered

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that such high strength and high fracture toughness can be obtained. In this study, α-alumina seeding in normal purity aluminum hydroxide was investigated. The aim of this study is to obtain sintered bodies with high fracture toughness and strength from a low cost raw material, through a combination of seeded fine-grained powder and impurities including in the raw material.

2. Experimental procedure

Fine-grained powder for sintering was made by low temperature calcination of seeded low cost commercial normal purity aluminum hydroxide, which was manufactured by the Bayer process and contained 0.46 mass% impurities. The crystal structure of the powder was gibbsite type, and the average particle size was about 0.6 μm. Seeding was conducted by tumbling ball milling under wet conditions. The process of fabricating alumina powders for sintering is shown in Fig. 1. During wet ball milling, part of the alumina balls was worn into very small particles and mixed into aluminum hydroxide as seeds. The aluminum hydroxide, 3000 g of 5 mmϕ high-purity alumina balls and 1200 g of distilled water were placed in a resin pot whose inner diameter and volume were 150 mm and 2600 cm^3. Dispersant addition or pH control was not conducted except for higher amounts of seed addition. The rotational speed of the mill pot was fixed at 98 rpm, which corresponds to 88% of critical speed, and the milling time was varied from 1 to 512 h. The amount of seed mixed into aluminum hydroxide was adjusted by the charged amounts of aluminum hydroxide and milling time, and was measured from the weight change of balls before and after the milling operation. The seeded aluminum hydroxide was dried, then calcined in air for 2 h at 50 °C intervals in the temperature range between 900 °C and 1300 °C. The calcination temperature was estimated from differential thermal analysis (DTA) data measured at a heating rate of 20 °C/min. The crystal structure of the calcined powders was identified by X-ray diffraction studies. The seeding conditions, seed amount and calcination temperature at which the sample was fully transformed to α-alumina are shown in Table 1.

Sintering was carried out using powder calcined at 1100 °C, which contained 1.8 mass% seed before calcination (2.7 mass% in α-alumina). Since hard agglomerates were not formed in the low temperature calcined powder, the powder was not milled following the calcination, but was passed through a 60 mesh sieve. The powder was sintered using both conventional pressure-less sintering in air and hot pressing in vacuum. For pressure-less sintering, about 30 g of the powder was put into a 52 mm×44 mm cemented carbide die and uniaxially pressed under 40 MPa, followed by cold isostatically pressing under 200 MPa in a rubber tube. They were sintered using an electric heating furnace for 2 h in the temperature range between 1400–1700 °C. In the case of hot pressing, about 40 g of the powder was placed in a 42 mm×47 mm carbon die, and heated at 10 °C/min in vacuum to sintering temperature under 80 kN unidirectional load, held at sintering temperature for 1 h followed by furnace cooling. The hot press temperature was in the range of 1200–1500 °C. Pressure-less sintered and hot pressed samples were cut and ground by a diamond wheel into 4 mm×3 mm×32 mm mechanical test specimens. Mechanical properties of sintered samples were evaluated by three point bending test and single edge pre-cracked beam (SEPB) fracture toughness test. A scanning electron microscope (SEM) was used for observation of the calcined powders and microstructure of the sintered specimen.

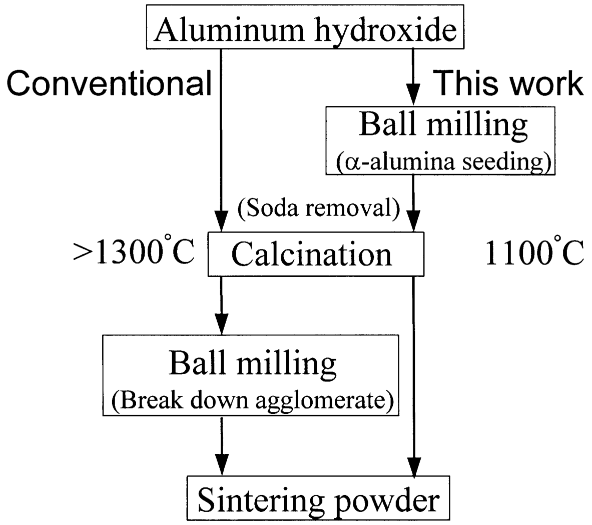

Fig. 1. Schematic diagram of conventional alumina sintering powder fabrication process and the process employed in this study.

Table 1
Ball milling conditions for seeding, amount of seed mixed into aluminum hydroxide by milling, DTA peak temperatures and calcination temperature to completely transform seeded aluminum hydroxide into α-alumina

Aluminium hydroxide/g	Milling time/h	Seed/ mass%	DTA peak temperature/°C	Calcination temperature/°C
100[a]	512	47	984	900
100	100	7.5	1027	1000
200	150	2.7	1060	1050
200	72	1.8	1078	1100
200	8	0.4	1165	1150
200	1	0.03	1229	1200
300	1	0.006	1253	1250
–	–	0	1301	1300

[a] Ph control.

3. Results and discussion

Fig. 2 shows DTA curves of aluminum hydroxide (upper) and magnification of the high temperature region for non-seeded and seeded aluminum hydroxide. The large endothermic peak at low temperature around 300 °C is due to the dehydration of aluminum hydroxide. The exothermic peaks at high temperature indicated by black arrows are attributed to the transformation from transition alumina to α-alumina. The curves correspond to the samples shown in Table 1 and the values in the figure show the amount of seed in the samples. It is clearly seen that the transition temperature decreases with increasing amount of seed. The transition temperature of non-seeded aluminum oxide is about 1300 °C. However, very small amount of seed addition, less than 0.1 mass%, reduces the temperature by more than 100 °C. The transition temperature of the sample including large amount of seed was below 1000 °C. The transition temperatures measured by DTA analysis are also given in Table 1.

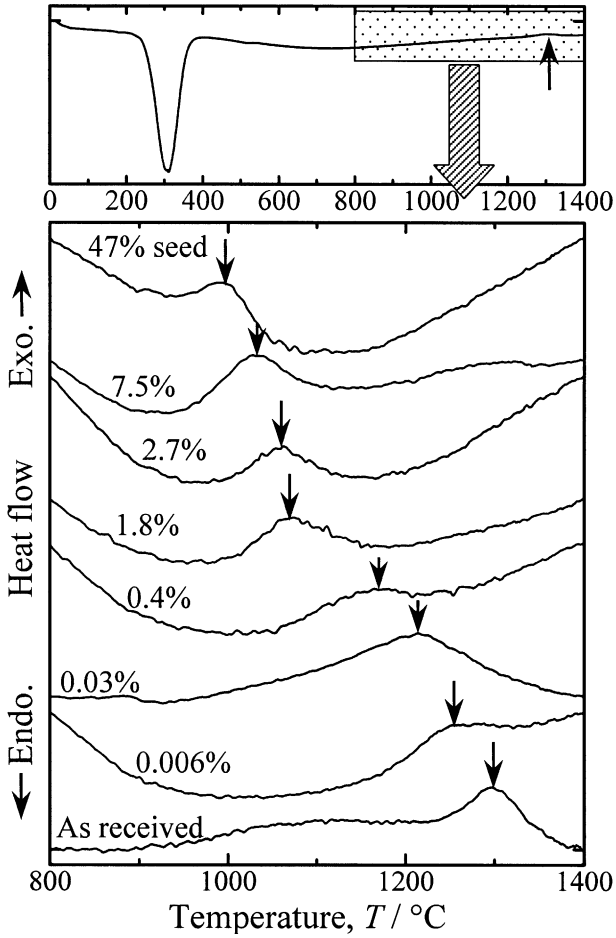

Fig. 2. DTA curve of aluminum hydroxide (upper) and the high temperature region for non-seeded and seeded aluminum hydroxide. The values in the figure shows the amount of seed in the samples and black arrows shows the α-alumina transition temperature.

Fig. 3 shows scanning electron micrographs of seeded aluminum hydroxide calcined at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C and (f) commercial easily sinterable low soda powder. The amount of seed is 47, 7.5, 1.8, 0.03 and 0% for (a), (b), (c), (d) and (e), respectively. It is clearly seen that the particle size increased with calcination temperature. The particle size of 900 °C calcined powder was very small around 60 nm. Even for the powder calcined at 1100 °C, the grain size was only 0.2 μm, which is almost comparable to the finest commercial high purity α-alumina powder. In the sample calcined at high temperature, not only large grains, but also formation of hard agglomerates were observed [Fig. 3(e)]. The particle size of non-seeded powder calcined at 1300 °C was about 0.5 μm, and is almost the same as commercial easily sinterable low soda powder. However, in commercial powder, large particles and also small grains are seen, and hard agglomerates were not observed. From these facts, it is supposed that the manufacturer milled this powder after a calcination process. Lower temperature calcined powder is very fine, however, the amount of seed is too high, so the sintering test was conducted using low temperature calcined powder at 1100 °C which included 1.8 mass% seed before calcination.

Low temperature calcined powder can be sintered at low temperature. The sintered densities of the powder are 3.75 and 3.86 Mg/m^3 by pressure-less sintering at 1400 and 1500 °C, respectively. Moreover, more than 3.90 Mg/m^3 density is obtained by hot press at only 1300 °C. The microstructures of low temperature calcined powder and commercial low soda powder sintered at low temperatures consisted of fine equiaxed grains and they show high bending strength. However, the microstructures of low temperature calcined powder sintered at slightly higher temperatures are different from sintered low soda powder. It has often been observed that large anisotropic grains formed in alumina with small amount of impurities sintered at high temperature.[16,17] Fig. 4 shows scanning electron micrographs of polished and thermally etched surfaces of (a) low soda alumina without MgO sintered at 1550 °C and (b) 1600 °C, pressure less sintered seeded low temperature calcined powder at (c) 1500 °C and (d) 1600 °C, hot pressed low temperature calcined powder at (e) 1430 °C and (f) 1480 °C. The photographs on the left-hand side of this figure [Fig. 4(a), (c), (e)] are the microstructure at the initial stage of anisotropic grain formation, and those on the right-hand side [Fig. 4(b), (d), (f)] are the microstructures where almost the entire structure is occupied by the anisotropic grains. In the microstructure of sintered low soda alumina powder at 1550 °C [Fig. 4(a)], very large plate-like grains whose grain size is more than 30 μm formed in a fine-grained matrix. This structure is typical "abnormal grain growth" structure, and the bending strength drastically

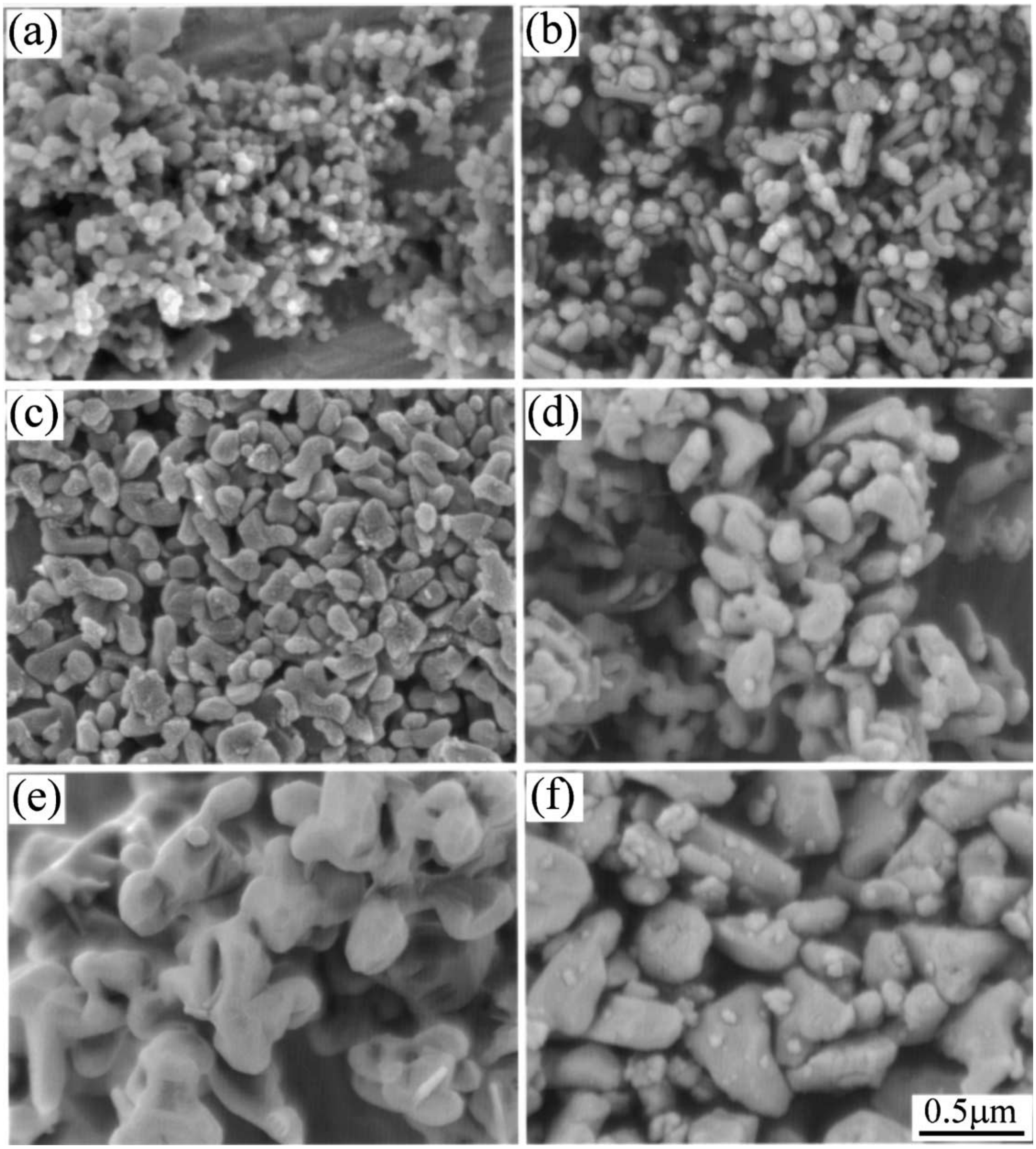

Fig. 3. Scanning electron micrographs of seeded aluminum hydroxide calcined at (a) 900, (b) 1000, (c) 1100, (d) 1200, (e) 1300 °C and (f) commercial easily sinterable low soda powder. The amount of seed is 47, 7.5, 1.8, 0.03 and 0% for (a), (b), (c), (d) and (e), respectively.

declines.[11] These large plate-like grains increase and almost the whole structure is occupied by the grains in the microstructure sintered 1600 °C [Fig. 4(b)]. The bending strength of this structure is very low around 250 MPa, but fracture toughness is greatly improved.[11] The microstructures of sintered low temperature calcined powder [Fig. 4(c), (e)] are also composed of fine grains and anisotropic grains, which are of course abnormal grain growth structures. However, the grain size of the anisotropic grains is small about 5 μm, and the size and the distribution of the anisotropic grains are much more uniform than the microstructure of sintered low soda powder [Fig. 4(a)]. The size of the anisotropic grains in the microstructures where almost all the structure is occupied by the grains [Fig. 4(d), (f)], is still small around 10 μm. The reason why these small anisotropic grains formed instead of large plate-like grains, is considered to be as follows. It has been reported that the abnormal grain growth starts just after the densification in normal purity alumina.[16] If the sinterability of the raw powder is not good, high temperature sintering is necessary to obtain a dense body. Since material flow such as diffusion is very fast at high temperature, small numbers of nuclei of anisotropic grains grow rapidly, so very large grains are formed at high temperature. On the contrary, using easily sinterable raw powder, dense sintered bodies can be obtained by sintering at low temperature. The growth rate of the grains is slow at low temperature, and results in the formation of a large number of small anisotropic grains.

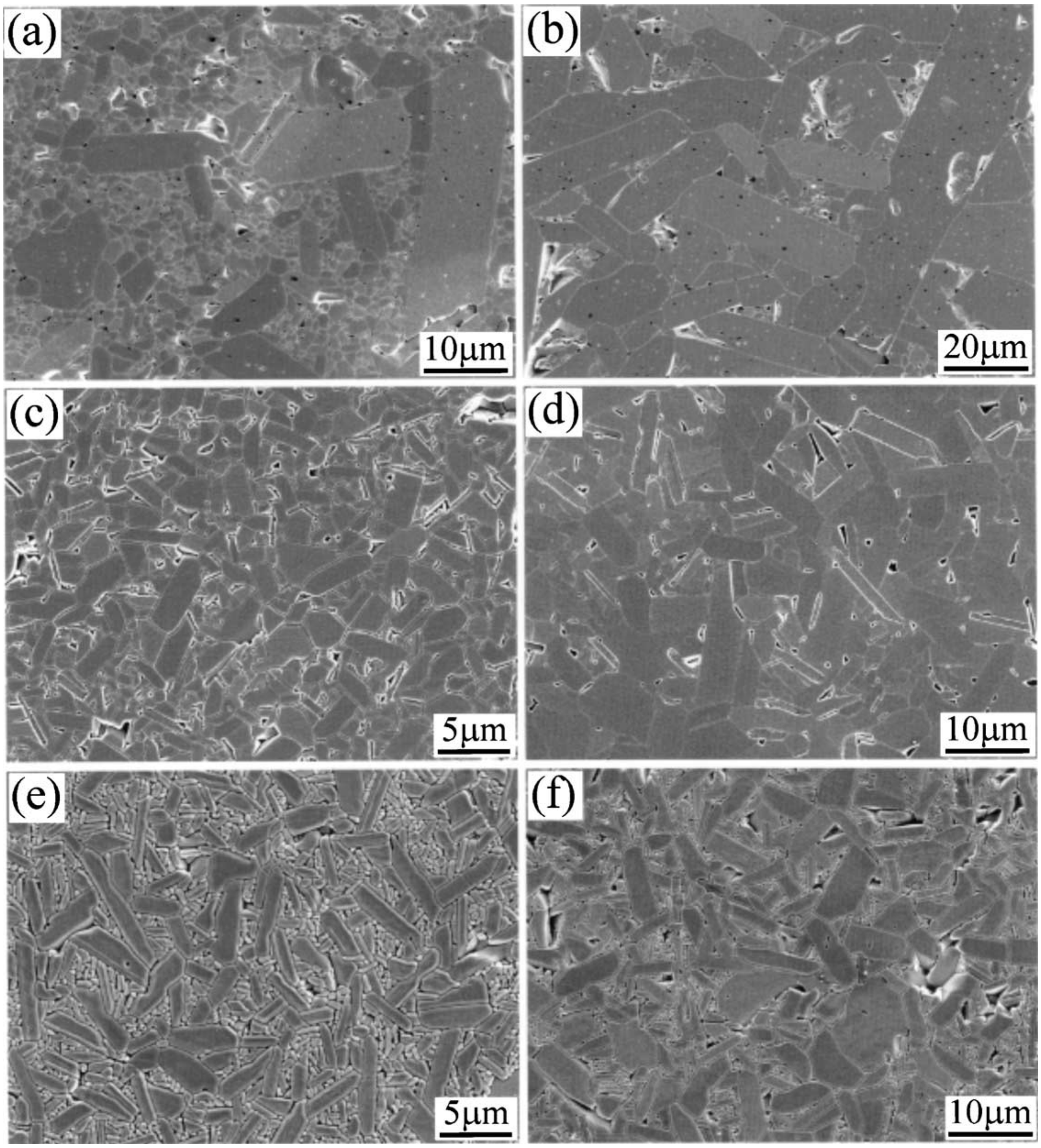

Fig. 4. Scanning electron micrographs of polished and thermally etched surfaces of (a) low soda alumina sintered at 1550 °C and (b) 1600 °C, pressure less sintered seeded low temperature calcined powder at (c) 1500 °C and (d) 1600 °C, hot pressed low temperature calcined powder at (e) 1430 °C and (f) 1480 °C.

These large amount of small anisotropic grains impinge with each other during growth, so that it is very difficult for then to grow to a large size. In consequence, the microstructures consisting of small anisotropic grains are attributed to low temperature densification due to the normal purity fine powder made by low temperature calcination of the Bayer aluminum hydroxide.

Mechanical properties of conventionally sintered and hot pressed seeded low temperature calcined powder made in this study are summarized in Fig. 5. The figure shows the relationship between bending strength and fracture toughness of the samples sintered at various temperatures, together with mechanical properties of sintered commercial high purity and low soda powder.[11] The samples sintered at low temperature show high bending strength and low fracture toughness. Inversely, high temperature sintered samples show low bending strength and high fracture toughness. This relation is a "trade off" relationship and it can be seen in sintered bodies produced from all the different raw materials. However, the data of sintered low temperature calcined powder shifts toward higher bending strength and higher fracture toughness. In the sample sintered at intermediate temperature around 1550 °C, both high bending strength of 500 MPa and high fracture toughness more than 5 MPa $m^{1/2}$ are obtained. Moreover, much higher mechanical properties of 600MPa bending strength and 6 MPa $m^{1/2}$ fracture toughness can be

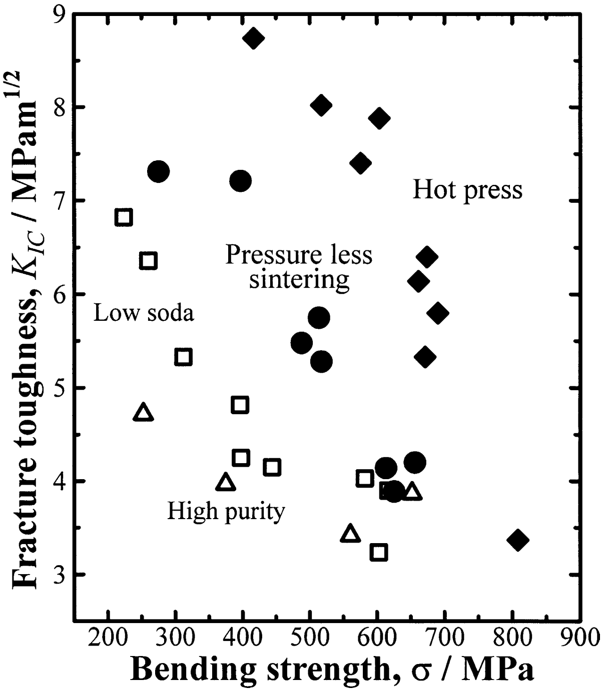

Fig. 5. Relationship between bending strength and fracture toughness of high purity, low soda and seeded low temperature calcined powder sintered at various temperatures.

achieved in the sample hot pressed at 1430 °C. The toughening mechanism in sintered alumina is the grain-bridging mechanism.[18,19] This effect is much more effective in microstructures containing rod-like or plate-like anisotropic grains than it is for equiaxed grains.[20] It is considered that the microstructure consisting of uniform small anisotropic grains increased the bridging effect, and high fracture toughness could be obtained without large bending strength decline.

4. Conclusions

The effect of seeding a low cost Bayer aluminum hydroxide on the α-alumina transition temperature, powder characteristics and properties of sintered bodies was investigated. Addition of a small amount of ball mill wear powder as α-alumina seed into aluminum hydroxide drastically lowered the α-alumina transition temperature. The particle size of low temperature transformed seeded powder was smaller than non-seeded powder. Although the purity of the powder was not high, the powder could be sintered at lower temperature. The microstructure of sintered low temperature calcined powder was composed of uniform small anisotropic grains, and showed high bending strength and high fracture toughness.

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