

Chemical inhomogeneity in commercial alumina powders and its effect on abnormal grain growth during sintering

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Abstract

Chemical inhomogeneity in four commercial alumina powders and its effect on the abnormal grain growth (AGG) during sintering have been investigated. Classification and chemical analyses revealed that relatively small portions of coarse particles in all the powders contained a significantly higher concentration of impurities than their corresponding large portions of fine particles. Hot pressing showed that AGG occurred for all the coarse portions whereas there was no significant indication of AGG for the fine portions. AGG also occurred for all unclassified powders during sintering at the interfaces of bilayer specimens fabricated by repeated centrifugal casting, which could also be attributed to the coarse particles mass-segregated during centrifugal casting. Results of this investigation indicate that coarse particles in commercial purity alumina powder generally contain high concentration of impurities and thus can cause AGG during sintering. Particle aggregates were attributed to the high concentration of impurities in the coarse portions.

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1. Introduction

In sintering of alumina, it is sometimes observed that a few selected grains grow abnormally large. This abnormal grain growth (AGG) is deleterious for densification during sintering and the mechanical properties of sintered body. Thus, many investigations have been made to understand and control AGG.^{1–10} It is now well known that the presence of impurities, notably Si and Ca, plays a key role.^{3–6,8} It is also well recognized that the addition of a small amount (250–2000 ppm) of MgO effectively suppresses AGG.^{9–10} However, there has been no clear answer to the question of why only a few selected grains grow abnormally.

Handwerker et al.⁴ showed that microstructural regions where AGG occurred contained a higher concentration of impurities than the regions where normal grain growth (NGG) occurred. This may suggest that the reason why only a few selected grains grow abnormally is related to the inhomogeneous distribution of impurities in the microstructure. However, it has not been understood yet what causes the inhomogeneous distribution of impurities in the microstructure.

Recently, we reported an extensive AGG at the interface of a bilayer specimen fabricated by repeated centrifugal casting.¹¹ Systematic experiments indicated that particle aggregates segregated at the interface during centrifugal casting were responsible for the AGG.¹¹ More recently, by classification and chemical analysis, we demonstrated that a relatively small portion of coarse particles (that included aggregates) in a particular commercial powder indeed contained a higher concentration of impurities than the remaining fine

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portion.¹² It was also demonstrated that the coarse portion exhibited AGG during hot pressing while the corresponding fine portion did not.¹² These results strongly suggest that particle aggregates in starting powder be responsible for the inhomogeneous distribution of the impurities in the microstructure and thus for the AGG of only a few selected grains.

Today most commercial alumina powders with typical concentration of impurities are produced from bauxite by similar processes based on the Bayer process. Particle aggregates are usually present in these powders. Therefore, the above-mentioned role of the particle aggregates on AGG is generally expected in most commercial alumina powders. The purpose of this investigation is, therefore, to test the generality of the role of particle aggregates on AGG, using four different commercial powders. As in the previous investigation,¹² we extracted a relatively small portion of coarse particles that include aggregates from each powder by classification. Chemical analyses were made on the coarse portions and remaining fine portions. Microstructures of specimens hot pressed from the coarse and fine portions were then compared for each powder. Microstructural evolution during sintering of a bilayer specimen fabricated from each powder by repeated centrifugal casting was also examined with focuses given to the interfaces.

2. Experimental procedure

Four Bayer-processed commercial alumina powders were received from three manufacturers, Alcoa Industrial Chemicals Division, USA, Reynolds Metals Company, USA, and Sumitomo Chemicals, Japan. Three powders were doped with MgO and one was an undoped powder. Each powder is designated in this paper as 'P-0', 'P-400', 'P-1000' and 'P-1100' [with numbers the nominal contents of doped MgO (ppm)]. According to the manufacturer, powder 'P-1000' was produced by doping MgO into powder 'P-0'.

Extraction of coarse portions from powders was conducted by centrifugal classification, as described in the previous investigation.¹² Dispersed aqueous slurries (PH~4) containing 13 vol.% fraction alumina were centrifuged at the acceleration of 300 g in a cylindrical mold rotating around its axis. Coarse portions were taken by collecting the cake that was built up on the mold wall in a relatively brief centrifuge time. A constant centrifuge time was selected for all powders such that about 10% of the particles in the slurries were taken as coarse portions. Fine portions were taken by collecting particles remaining in the supernatants. To ensure that fine portions do not contain aggregates, centrifuging was continued, in this case, until approximately 50% of the particles formed cake. Generally, to get rid of excessive water, the supernatants were centrifuged again

in a new mold until all particles were cast on the mold wall, and the resultant cakes were collected and dried. But, in some cases, the supernatants were dried as they contained excessive water. Particle size distributions of powder portions were analyzed by a laser scattering technique. Chemistry analyses were conducted by inductively coupled plasma (ICP)-atomic emission spectroscopy (AES).

Coarse and fine powder portions were hot-pressed at 1650 °C for 2 h under vacuum in a graphite mold lined with graphite foil. Heating rate was 15 °C/min and cooling was done by turning-off the electric powder to the furnace. Bilayer specimens were fabricated from unclassified powders by repeated centrifugal casting as in the previous investigation.¹¹ The bilayer specimens were sintered at 1650 °C for 0.5–6 h. Heating rate was again 15 °C/min. Hot pressed and sintered bilayer specimens were cut, ground, polished with diamond pastes 15, 6 and 1 μm successively, and thermally etched at 1550 °C for 10 min. Microstructures were observed with optical or scanning electron microscopy.

3. Results and discussion

3.1. Characteristics of coarse and fine powder portions

3.1.1. Particle size and morphology

Fig. 1 presents the particle size distributions of various coarse and fine portions. Particle sizes of all fine portions ranged from 0.2 to 2.5 μm, as shown in Fig. 1(a). Mean particle size was 0.6 μm for powder 'P-1100' and 0.5 μm for all other powders. Coarse portions had broader particle size distributions as shown in Fig. 1(b). They contained particles larger than 2.5 μm, which were not contained in the fine portions, as much as approximately 10% for powders 'P-0', 'P-1000' and 'P-1100' and 25% for powder 'P-400', respectively. Mean particle size was 0.8, 1.1, 0.9 and 0.7 μm for powders 'P-0', 'P-400', 'P-1000' and 'P-1100', respectively.

In order to compare the particle morphologies of the coarse and fine portions, the microstructures of the outer and inner surfaces of a centrifugally cast tubular green body obtained from unclassified powder 'P-1100' are presented in Fig. 2. Though the outer and inner surfaces correspond to the extremes of the coarse and fine portions, respectively, the general difference between the particle morphologies of the two portions may be noted. The outer surface was characterized by a porous microstructure consisting mainly of particle aggregates that were mass-segregated during centrifugal casting, as shown in Fig. 2(A). By contrast, the inner surface was characterized by a dense microstructure consisting only of fine primary particles as shown in Fig. 2(B). Essentially the same microstructures were observed for all other powders. These results, together

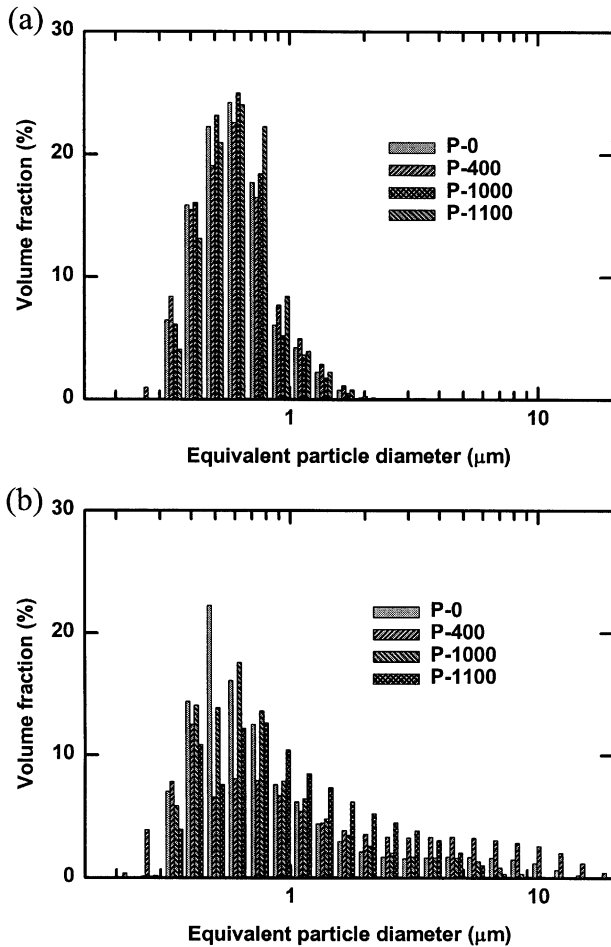


Fig. 1. Particle size distributions of (a) fine portions and (b) coarse portions of various commercial alumina powders.

with the particle size distributions shown in Fig. 1, indicate that all the coarse portions contained an appreciable amount of particle aggregates whereas their corresponding fine portions did not.

3.1.2. Chemistry

Chemical analyses of the coarse and fine portions of each powder are presented in Table 1. The fine portions

Table 1
Chemical analyses of coarse and fine portions (unit: ppm)

Powder	Portion	Si	Ca	Na	Fe	Mg
P-0	Coarse	400	40	170	45	130
	Fine	140	30	60	40	7
P-400	Coarse	220	90	120	100	100
	Fine	110	55	90	65	85
P-1000	Coarse	410	40	140	55	190
	Fine	180	40	50	45	160
P-1100	Coarse	290	110	130	140	335
	Fine	115	70	80	115	385

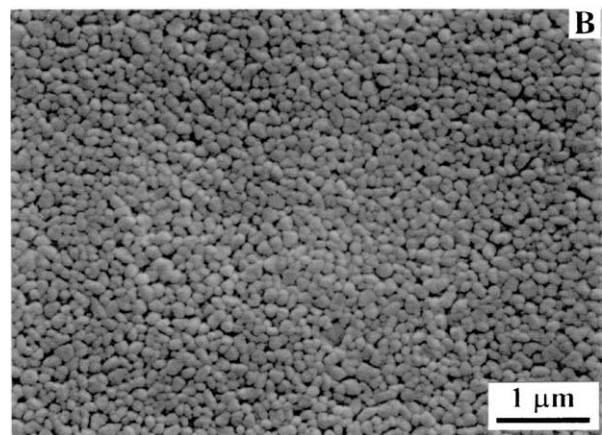
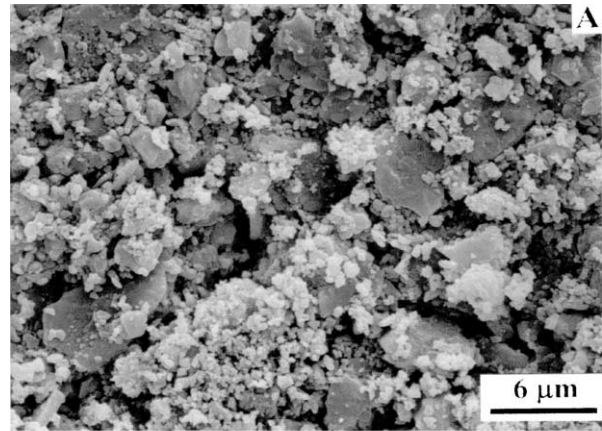


Fig. 2. Microstructures of centrifugally cast green tube. (A) Outer surface and (B) inner surface.

were those prepared by drying supernatants after removing excessive water. Several points can be noted. First, all coarse portions contained significantly higher concentrations of impurities than their corresponding fine portions. By contrast, Mg contents between the two portions were relatively comparable for all powders except powder 'P-0'. Second, Mg content was appreciable in the coarse portion of powder 'P-0', whereas it was negligible in the corresponding fine portion. Appreciable amount of Mg in the coarse portion of the undoped powder 'P-0' is somewhat surprising. However, it should be noted that Mg could have been brought into the coarse portion during powder processing as an impurity in the same manner as other impurities did. Third, the difference between the Mg contents in the coarse portions of powder 'P-1000' and powder 'P-0' was relatively small. Considering that powder 'P-1000' had been produced by doping MgO into powder 'P-0', this indicated that a large fraction of Mg in the coarse portion of powder 'P-1000' was not from doping but introduced during powder processing as impurity. This, in turn, indicated that doped MgO was mainly

placed on fine particles rather than coarse particles during doping process.

Table 2 presents the chemical analyses of fine portions for powders ‘P-400’ and ‘P-1000’, which were prepared by drying supernatants as it contained excessive water. It is interesting to note that the contents of all impurities and Mg were significantly higher than those in the same fine portions prepared by drying the supernatants after removing excessive water (Table 1). This indicates that all the elements dissolved to some extent into acidic water. When the supernatant containing excessive water was dried, elements that had been dissolved in water could remain in dried powder portion enriching their concentration. By contrast, when the excessive water was removed, no dissolved elements could remain in the powder portion resulting in significantly lower concentrations.

3.2. Microstructure observations

The microstructures of specimens hot pressed from various coarse and fine portions are presented in Figs. 3 and 4. Fine portions are those prepared by drying supernatants after removing excessive water. A previous investigation¹² showed that the difference between the

Table 2

Chemical analyses of fine portions prepared by drying supernatants as they contained excessive water (unit: ppm)

Powder	Si	Ca	Na	Fe	Mg
P-400	155	300	940	70	330
P-1000	250	85	180	50	390

grain growth behaviors in the coarse and fine portions of powder ‘P-1000’ was generally maintained during hot pressing. Thus, in the present investigation, the microstructures of specimens after hot pressing only for 2 h were observed. The microstructures for the coarse portions of powders ‘P-0’, ‘P-400’ and ‘P-1000’ are characterized by distinctively extensive AGG as shown in Fig. 3(A)–(C), respectively. Abnormal grains between fine matrix grains appeared to grow as large as 60–70 μm long and 20–40 μm wide as shown in Fig. 3(A)–(C). For the fine portions of the same powders, however, such extensive AGG as in Fig. 3 was not observed, as shown in Fig. 4(A)–(C). Grains were significantly more uniform in size, with all grains apparently less than 10 μm for both powders ‘P-0’ [Fig. 4(A)] and ‘P-400’ [Fig. 4(B)], and 5 μm for powder ‘P-1000’ [Fig. 4(C)].

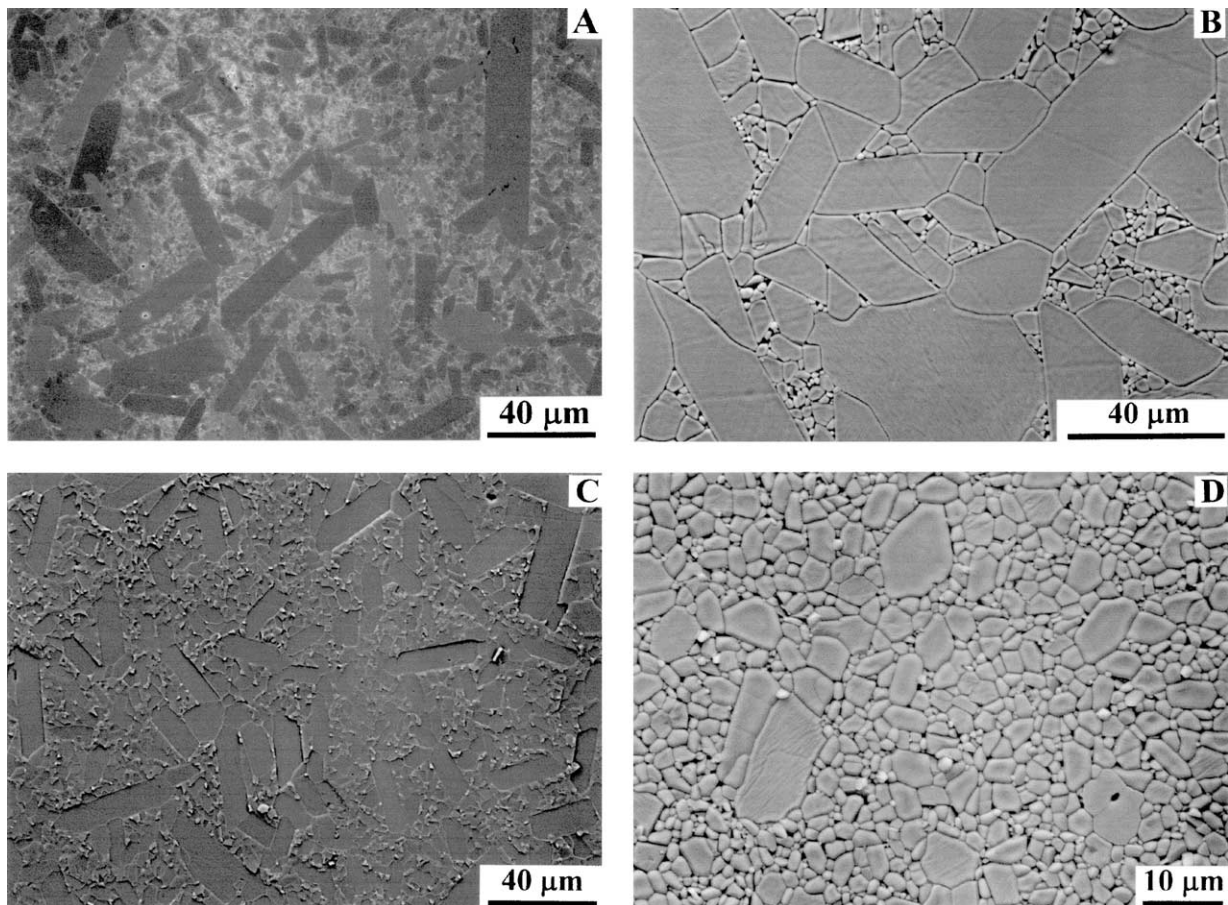


Fig. 3. Microstructures of specimens for coarse portions of powders (A) ‘P-0’, (B) ‘P-400’, (C) ‘P-1000’ and (D) ‘P-1100’, after hot pressing for 2 h.

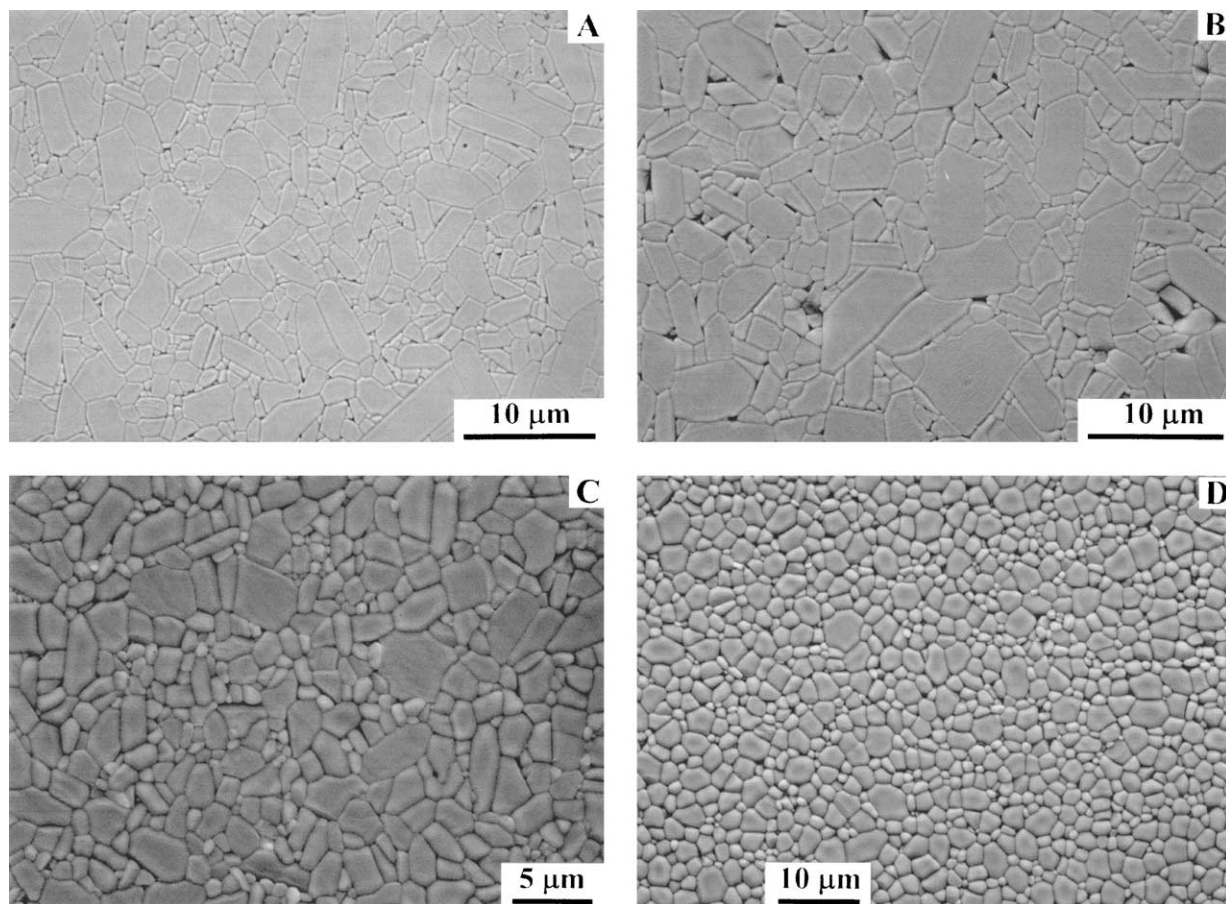


Fig. 4. Microstructures of specimens for the fine portions of powders (A) 'P-0', (B) 'P-400', (C) 'P-1000' and (D) 'P-1100', after hot pressing 2 h.

For the coarse portion of powder 'P-1100', such distinctive AGG was not observed [Fig. 3(D)]. However, some grains in this specimen were still quite a lot larger than the other matrix grains. By contrast, grains in the specimen for the fine portion were more uniform in size [Fig. 4(D)].

Bae and Baik⁹ demonstrated that the minimum content of MgO required for the prevention of AGG increases with the increase of Ca content. This suggests that AGG may or may not occur as a result of the competition between the concentrations of impurities and MgO. Our chemical analyses showed that the coarse portions of all powders contained significantly more impurities than their corresponding fine portions. By contrast, the results showed that the contents of MgO in the two portions (for powders 'P-400', 'P-1000' and 'P-1100') were comparable or its difference was relatively small (for powder 'P-0') (Table 1). Therefore, the AGG in coarse portions [Fig. 3(A)] is attributable to the high concentration of impurities.

The high concentration of impurities in coarse portions can be attributed to particle aggregates. It has been well recognized that the disintegration of aggregates into primary particles by conventional ball milling or ultrasonic treatment is difficult. This suggests that

primary particles in aggregates are relatively strongly bonded together. It is possible that primary particles bond together with impurities acting as bond materials. Thus, aggregates may contain a higher concentration of impurities than primary particles.

Fig. 5 presents the microstructural evolution during sintering of bilayer specimen of powder 'P-400'. The microstructural evolution is again characterized by the occurrence of extensive AGG. The AGG apparently initiated at the interface [Fig. 5(A)] and then grew into the first layer [Fig. 5(B) and (C)] upon further sintering. Relatively small abnormal grains were also nucleated in the first layer ahead of the interface-initiated large abnormal grains, as seen in Fig. 5(B), but they were eventually consumed by the large abnormal grains upon prolonged sintering [Fig. 5(C)]. The large abnormal grains grew into the first layer as deep as 800 μm after sintering for 1 h and 1300 μm after sintering for 2 h. The AGG at the interface of bilayer specimens also occurred for all other powders as shown in Fig. 6.

The AGG at the interface of the bilayer specimen is also attributable to particle aggregates.¹¹ Because of differential settling between large particles and fine particles during centrifugal casting, the interface of bilayer specimens is composed of a porous micro-

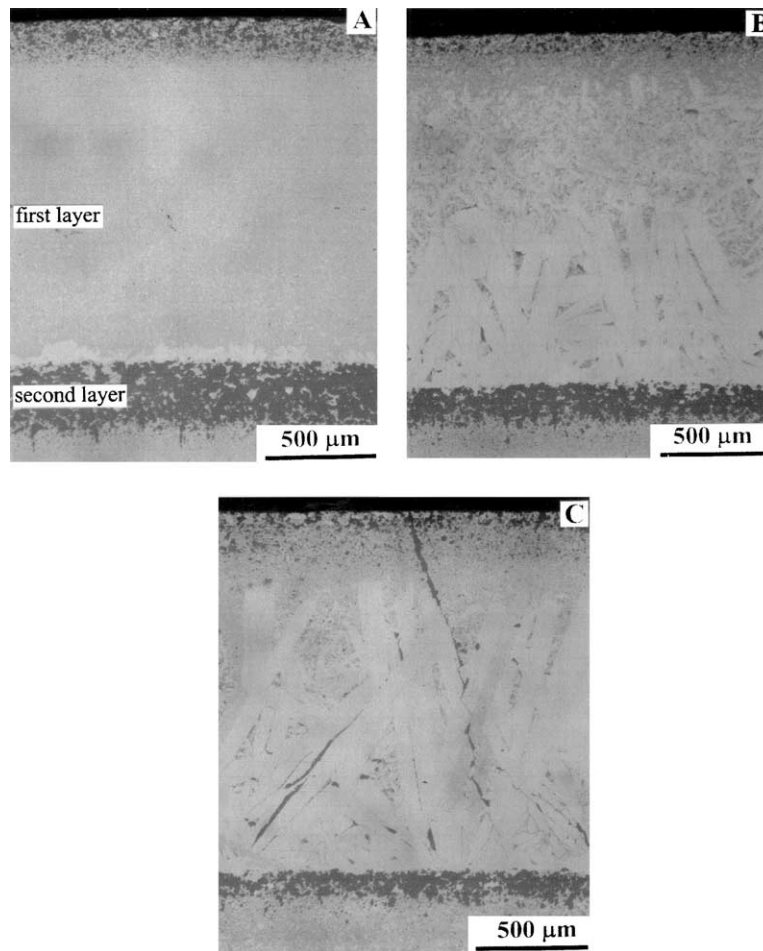


Fig. 5. Microstructures of bilayer specimens fabricated by repeated centrifugal casting from powder 'P-400' after sintering for (A) 30 min, (B) 1 h and (C) 2 h.

structure consisting of aggregates toward the second layer [Fig. 1(A)] and a dense microstructure consisting of fine primary particles toward the first layer [Fig. 1(B)]. The aggregates in the second layer, which contain a high concentration of impurities, supply impurities to the first layer, giving rise to the observed extensive AGG at the interface. The AGG at the interface for all powders again indicates the generality of the role of aggregates.

It might be noted in Figs. 3, 5 and 6 that the extent of AGG during both hot pressing of coarse portions and sintering of bilayer specimens was different for different powders. Apparently, the AGG seemed to be most extensive for powder 'P-400' and least extensive for powder 'P-1100', as may be noted in Figs. 3, 5 and 6. The difference in the extents of AGG among powders might be related to their different contents of impurity and MgO. Unfortunately, however, we could not make any correlation between the difference with impurity or MgO contents, because an individual contribution of each impurity element was not known.

It is worth pointing out that impurities dissolve in acidic water. Chemical analyses showed that the concentration

of impurities in fine portions prepared by drying supernatants after removing excessive water was significantly less than that in the fine portions prepared by drying supernatants as it contained excessive water. This is an evidence of the dissolution of impurities in acidic water medium. The dissolution of impurities implies that impurities in alumina powders can be reduced by washing them with acidic water. The reduction of impurities by washing would result in the improvement of the microstructure.

The results of the present investigation may have an important implication in understanding and controlling AGG in alumina. In sintering of commercial purity alumina containing a typical concentration of impurities, all grains do not grow abnormally but only a few selected grains do. Results by Handwerker et al.⁴ suggested that this is attributable to the inhomogeneous distribution of impurities in the microstructure. Our results imply further that the inhomogeneous distribution of impurities may be closely related to particle aggregates. Therefore, removing aggregates in starting powders may reduce AGG. Washing powders with acidic water can also reduce AGG.

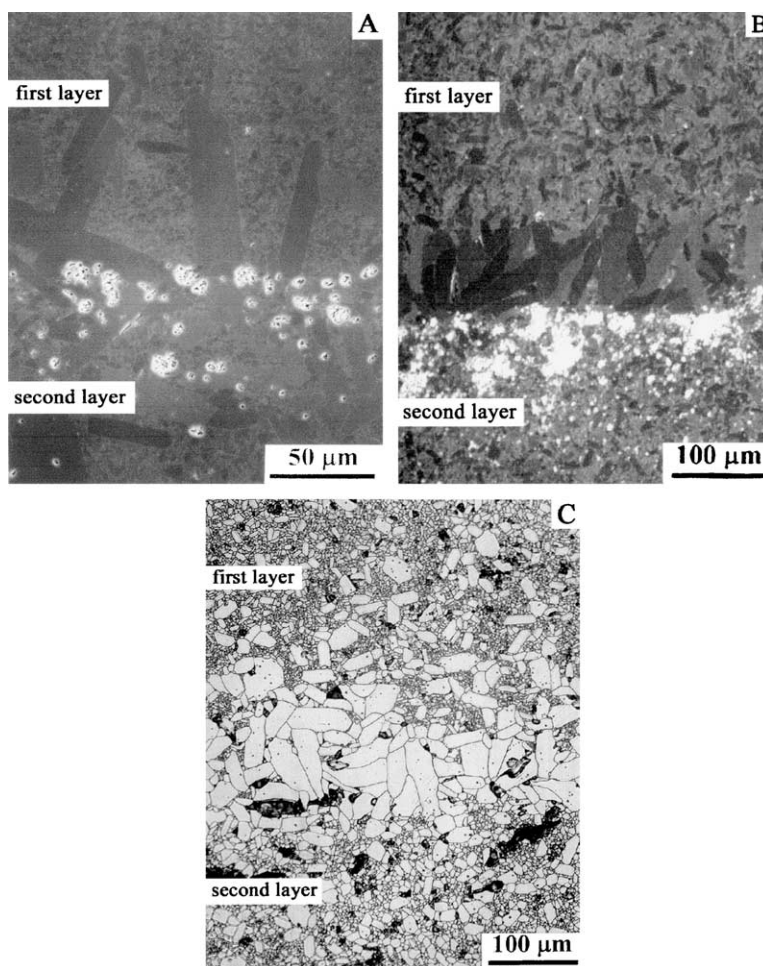


Fig. 6. Microstructures of bilayer specimens (A) for powder 'P-0' after sintering for 1 h, (B) for powder 'P-1000' after sintering for 1 h and (C) for powder 'P-1100' after sintering for 2 h.

4. Summary and conclusion

Chemical inhomogeneity in four commercial alumina powders and its effect on AGG during sintering have been investigated. Classification and chemical analyses showed that relatively small portions of coarse particles in all the powders contain a significantly higher concentration of impurities than their corresponding fine portions. The high concentration of impurities in coarse portions was attributed to particle aggregates contained in them. Hot pressing demonstrated that AGG generally occurred in coarse portions whereas there was no significant indication of AGG in fine portions. During sintering of bilayer specimens that were fabricated by repeated centrifugal casting, extensive AGG also occurred for all powders at their interface, which was also attributable to particle aggregates. Therefore, it can be concluded that particle aggregates in commercial alumina powders generally contain a high concentration of impurities and thus causes AGG during sintering.

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