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Effects of High Concentrations of Liquid Phase and Magnesia on the Grain Growth of Alumina

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Abstract: Grain growth phenomenon of alumina in the presence of various quantities of liquid phase and magnesia was investigated at 1600°C, and the data were regressed by a statistical approach. The statistical result indicated that liquid phase, compared with magnesia, was a major factor in determining the grain growth mechanism of alumina. The alumina phase developed into faceted grains when the liquid phase was so abundant as to penetrate all the grain boundaries and junctions of alumina, whether with the doping of magnesia or not. This observation implied that magnesia, when co-existing with a large quantity of liquid phase, did not effectively reduce the degree of anisotropy in interfacial energy of alumina. Nevertheless, when its concentration was high enough to result in the precipitation of $MgAl_2O_4$, it avoided the evolution of elongated alumina grains by pinning the fast moving boundaries. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

It is generally believed that the presence of small quantities of impurities, notably of CaO and SiO_2, plays a decisive role in triggering the abnormal grain growth of alumina in final stage sintering.[1–5] The critical concentrations of SiO_2 and CaO for triggering abnormal grain growth are about 300 and 30 ppm, respectively, approximately equivalent to their solubility limits in alumina.[1] These impurities promote grain growth of alumina during sintering as they form liquid films in grain boundaries and junctions. As a result of abnormal grain growth, elongated grains having high aspect ratios in two dimensional microstructure evolve. These elongated grains are constituted by two long parallel basal planes {0001} of alumina and two short curved boundaries.[3,4,6] The low energy facets, to which the liquid phase preferentially segregates, have lower grain boundary mobilities than the unwetted planes.

Inhomogeneous distribution of the liquid phase both microscopically and macroscopically in the alumina matrix is responsible for triggering the abnormal grain growth of alumina.[2,3] For example, for a clean-room processed ultra-high purity alumina having a total impurity content less than 50 ppm[2,3] or a normally processed alumina having a total impurity content less than 300 ppm,[5] abnormal grain growth occurred only locally in regions where the liquid phase existed. Hence, it was proposed that there might exist an upper limit of liquid phase, above which the grain boundaries of alumina could be totally covered by the liquid phase and abnormal grain growth could be prevented.[1,7] Experimental results had shown that addition of 1 wt% liquid phase forming additive (anorthite, $CaO.Al_2O_3.2SiO_2$) effectively reduced

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*To whom correspondence should be addressed. Fax: 886-27376460; e-mail: stlin@mail.ntust.edu.tw the grain growth rate of a high purity alumina.[5] However, for an alumina containing 15 vol% liquid phase, abnormal grain growth still occurred, leading to abundance of elongated grains in the microstructure.[8]

Magnesia[3,5,6,9–14] is an unique dopant for alumina, as it enhances the densification rate and yet reduces the grain growth rate of alumina. The classical models regarding the role of magnesia on the sintering of alumina focused mostly on the relationship between magnesia and alumina, without taking into consideration the existence of a small quantity of liquid phase in the system. Consequently, different mechanisms had been proposed as the origins of inhibiting abnormal grain growth, including solid solution of magnesia into alumina grains,[15] segregation of magnesia to grain boundaries,[10,12,16] and precipitation of a second phase such as $MgAl_2O_4$ in grain boundaries.[11,17,18] With the discovery of liquid films in the grain boundaries of alumina, several new concepts had been proposed. For example, it was proposed that magnesia acted as a scavenger that drew the impurity ions making up the liquid phase into alumina grains.[2,6] On the other hand, it was suggested that magnesia promoted uniform wetting of liquid phase on alumina such that the degree of non-uniform grain growth was minimised.[19] It was also proposed that the mobility of the fast moving grain boundaries wetted by the liquid phase was reduced by magnesia.[3] Another report asserted that magnesia resulted in partial crystallisation or increased viscosity of the liquid phase, which in turns blocked the transport of ions.[14]

The effect of magnesia on the sintering of alumina investigated so far mostly used high or ultra-high purity alumina powders, with a magnesia doping concentration less than 0.1 wt%. The roles of magnesia were proposed based on micro-examination of a few grains or grain boundaries, which might have caused uncertainties in analysis. In this study, high concentrations of liquid phase forming additives, SiO_2 and CaO, were intentionally added to a high purity alumina powder, and magnesia was doped to a concentration as high as 10 wt%. The experiments were carried out for extended sintering such that they provided the limiting cases for determining the role of magnesia on the grain growth of alumina containing liquid phase.

2 EXPERIMENTAL

A commercial grade 99.8% pure α-alumina powder (AES-11, Sumitomo Chemical, Japan) was used as the starting powder. The principal impurities of this powder were MgO (0.1%), SiO_2 (0.06%), Na_2O (0.04%), and Fe_2O_3 (0.01%), among which MgO was added as the intentional dopant. The mean particle size and crystal size of this powder were 0.5 and 0.3 μm, respectively. Alumina powder having a purity of 95 or 92% in weight was prepared by incorporating CaO and SiO_2, with equal weight ratio, into the as-received powder. These 99.8, 95, and 92% pure alumina powders were then doped with 0.1,1, or 10 wt% magnesia. Powders having different compositions were prepared in separate batch, by mixing the as-received powder with a high purity (99.9%) SiO_2 powder (0.2 μm) in the aqueous solution of $CaCl_2$ and $Mg(NO_3)_2$. The slurries were stirred, dried at 200°C for 2 h, and then ball-milled to crush the powder agglomerates.

These powders respectively were uniaxially pressed into disks under a pressure of 40 MPa. These specimens were sintered in air at 1600°C for an isothermal holding time of 1, 12, or 24 h. The sintered specimens were then ground to a depth of approximately 0.5 mm prior to X-ray diffraction (XRD) analysis, which was carried out under an accelerating voltage of 50 keV and a current of 100 mA. The specimens were subsequently polished with diamond pastes and thermally etched at 1450°C for 2 h. Scanning electron microscope (SEM) was utilised to examine the grain morphology of the etched surface. Cumulative distributions of intercept length of alumina grains were determined based on more than 400 intercept lengths, which were measured by lineal analysis (Cambridge Quantimet 520) of the SEM micrographs.

3 RESULTS AND DISCUSSION

3.1 Microstructural evolution

Figure 1 shows the development of microstructure with the extending of isothermal holding time at 1600°C for the undoped 99.8% pure alumina. It is noted that there already had 0.1 wt% magnesia as an intentional dopant in the as-received alumina powder. Though the alumina crystals grew from a mean of 0.3 μm in the powder state to about 8 μm after sintering for 24 h, evolution of elongated grains having high aspect ratios did not occur. Thus, 0.1 wt% magnesia effectively inhibited the abnormal grain growth of the high purity alumina. Figure 2 shows the microstructures of undoped and magnesia-doped 95% pure alumina, sintered at 1600°C for 1 h. Abnormal grain growth resulting in elongated grains took place with the existence of a large quantity of liquid phase, even doped with additional 0.1 wt% magnesia. Such an occurrence

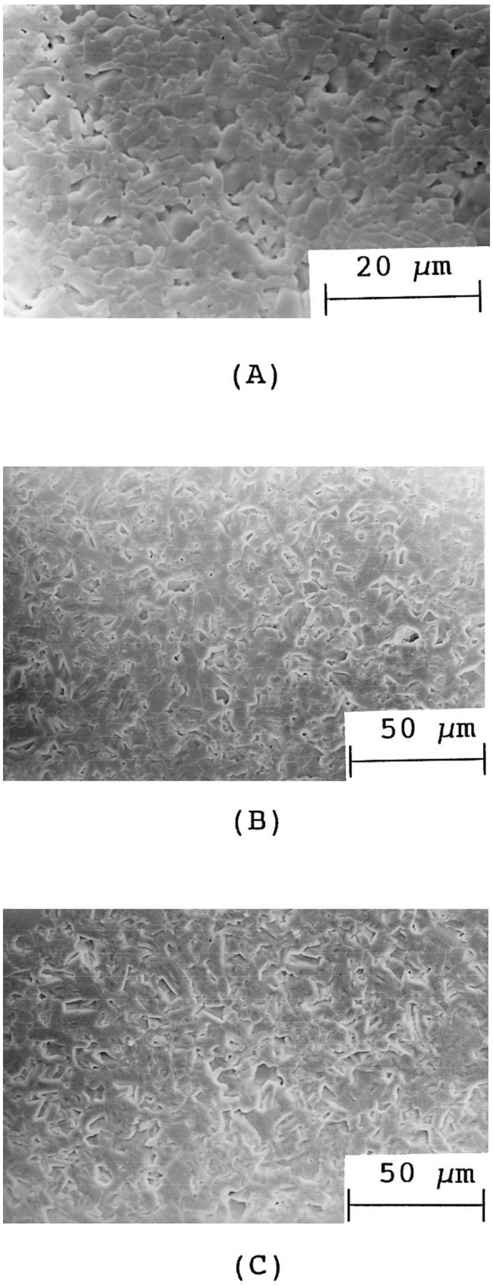

Fig. 1. Microstructures of undoped 99.8% pure alumina sintered at 1600°C for (A) 1 h, (B) 12 h, and (C) 24 h.

was effectively avoided with higher doping concentrations of magnesia, such as 1 and 10 wt%. Thus, the significance of liquid phase in triggering the growth of elongated alumina grains can be easily observed by comparing the microstructure of 99.8% pure alumina sintered at 1600°C for 24 h (Fig. 1(C)) and that of 95% pure alumina sintered at 1600°C for 1 h (Fig. 2(A)).

Figure 3 compares the microstructures of 95 and 92% pure alumina, doped with either 1 or 10 wt% magnesia, and sintered at 1600°C for 12 h. It is reminded that doping 1 wt% magnesia effectively avoided the evolution of elongated grains of 95% pure alumina for an isothermal holding time of 1 h, as shown in Fig. 2(C). However, doping of 1 wt% magnesia was insufficient to inhibit the abnormal grain growth of 92 or 95% pure alumina for a prolonged isothermal holding, and a higher magnesia doping concentration, such as 10 wt%, was required. Consequently, large elongated grains could hardly been found in Fig. 3(B) and (D). Figure 4 compares the microstructures of 92% pure alumina doped with either 1 or 10 wt% magnesia, sintered at 1600°C for 24 h. These conditions posed an extreme case of examining the abnormal grain growth in this study. Based on this comparison, it can be concluded that a magnesia doping concentration as high as 10 wt% could effectively avoid the abnormal grain growth of alumina that contained a large quantity of liquid phase during sintering.

Figure 5 shows the effect of magnesia on the phase evolution of 95 and 92% pure alumina powders sintered at 1600°C for 1 h. It can be observed that, in addition to the diffraction peaks of α-alumina, several additional peaks associated with $MgA1_2O_4$ spinel phase evolve with doping of 10 wt% magnesia. Though several other binary and ternary compounds can possibly form for the ternary Al_2O_3–MgO–SiO_2 system,[20] the $MgAl_2O_4$ spinel phase was the predominant phase in the sintered specimens. Such an observation is analogous to the finding of isolated $MgAl_2O_4$ precipitates along the grain boundaries for alumina containing less than 200 ppm of impurities, which was doped with 2400 ppm magnesia and sintered at 1650°C.[21]

Based on previous observations, it is clear that the doping concentration of magnesia should be high enough to result in the precipitation of $MgAl_2O_4$, in order to avoid the evolution of elongated grains for alumina having a low purity and experiencing a prolong sintering. There exist liquidus lines lower than 1600°C for the ternary alumina–magnesia–silica system, whose compositions are located in the domain composed of approximately less than 50 wt% magnesia.[20] Thus, by forming a liquid phase composed of magnesia, calcia, alumina, and silica, the liquid phase forming additives (calcia and silica) behaved as a scavenger for magnesia and reduced the effect of magnesia on the grain growth of alumina. For example, magnesia effectively reduced the grain growth rate constant of alumina by a factor of about 50 for an ultra-high purity powder,[22] but by a factor of about 5 for the same powder containing a small quantity of liquid phase forming impurities.[23] Consequently, to inhibit the abnormal grain growth of alumina having a low purity, the doping concentration of magnesia should be maintained high enough to compensate its dissolution into the

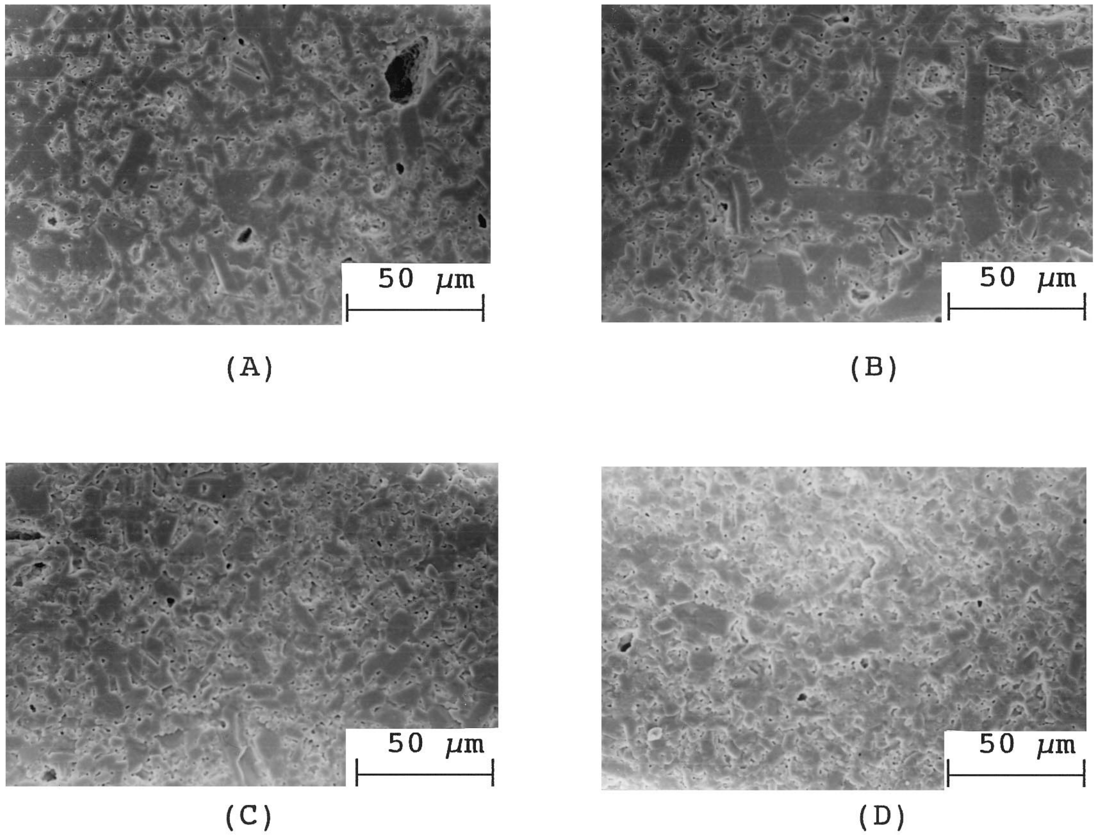

Fig. 2. Microstructures of 95% pure alumina sintered at 1600°C for 1 h, with the doping of (A) 0 wt%, (B) 0.1 wt%, (C) 1 wt%, and (D) 10 wt% magnesia.

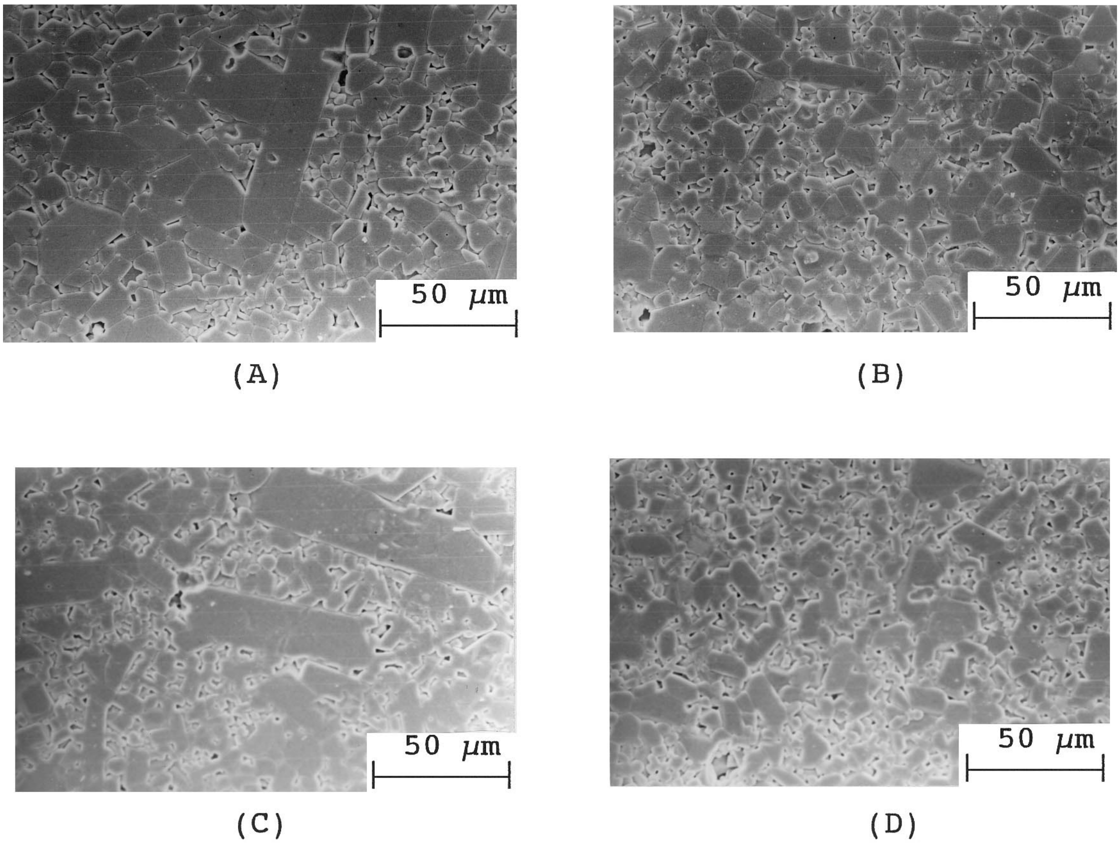

Fig. 3. Microstructures of 95% pure alumina doped with (A) 1 wt% and (B) 10 wt% magnesia, and 92% pure alumina doped with (C) 1 wt% and (D) 10 wt% magnesia, sintered at 1600°C for 12 h.

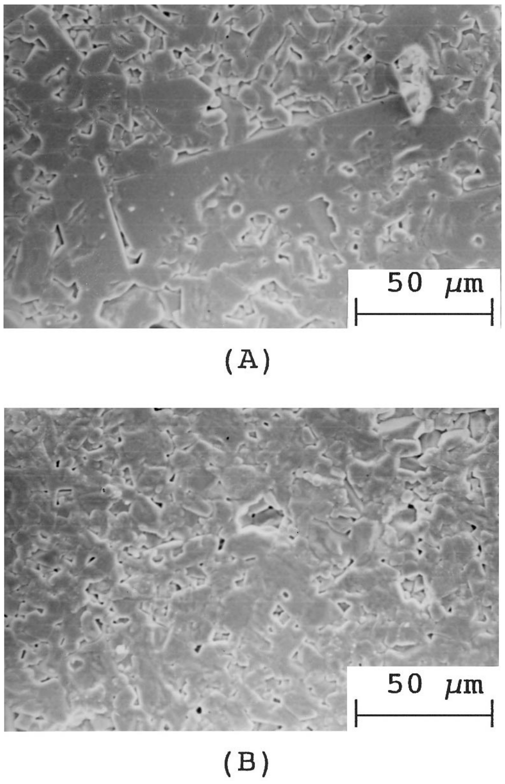

Fig. 4. Microstructures of 92% pure alumina doped with (A) 1 wt% and (B) 10 wt% magnesia, sintered at 1600°C for 24 h.

liquid phase. In comparison, similar observations regarding the counteracting effect of liquid phase and magnesia were observed elsewhere, but with lower concentrations of liquid phase and magnesia.[2,21] However, it was suggested that magnesia inhibited the abnormal grain growth of alumina by enhancing the dissolution of silica into the alumina grains.

3.2 Statistical analysis of intercept length of grains

The variation of intercept length distribution of alumina grains with the experimental variables is analyzed using a log-normal distribution model. This distribution model is described mathematically by a modified form of the Gaussian probability function.[24]

$$F(X) = \int_0^X P(X)\mathrm{d}X = \int_0^X (2\pi\sigma)^{-1/2} \exp\left[\frac{(X - X_o)^2}{2\sigma^2}\right] \mathrm{d}X \quad (1)$$

where X is the natural logarithm of intercept length ($X = \ln(L)$), X_o is the median value of X, $P(X)$ is the probability of observing X, $F(X)$ is the cumulative probability expressed in terms of the

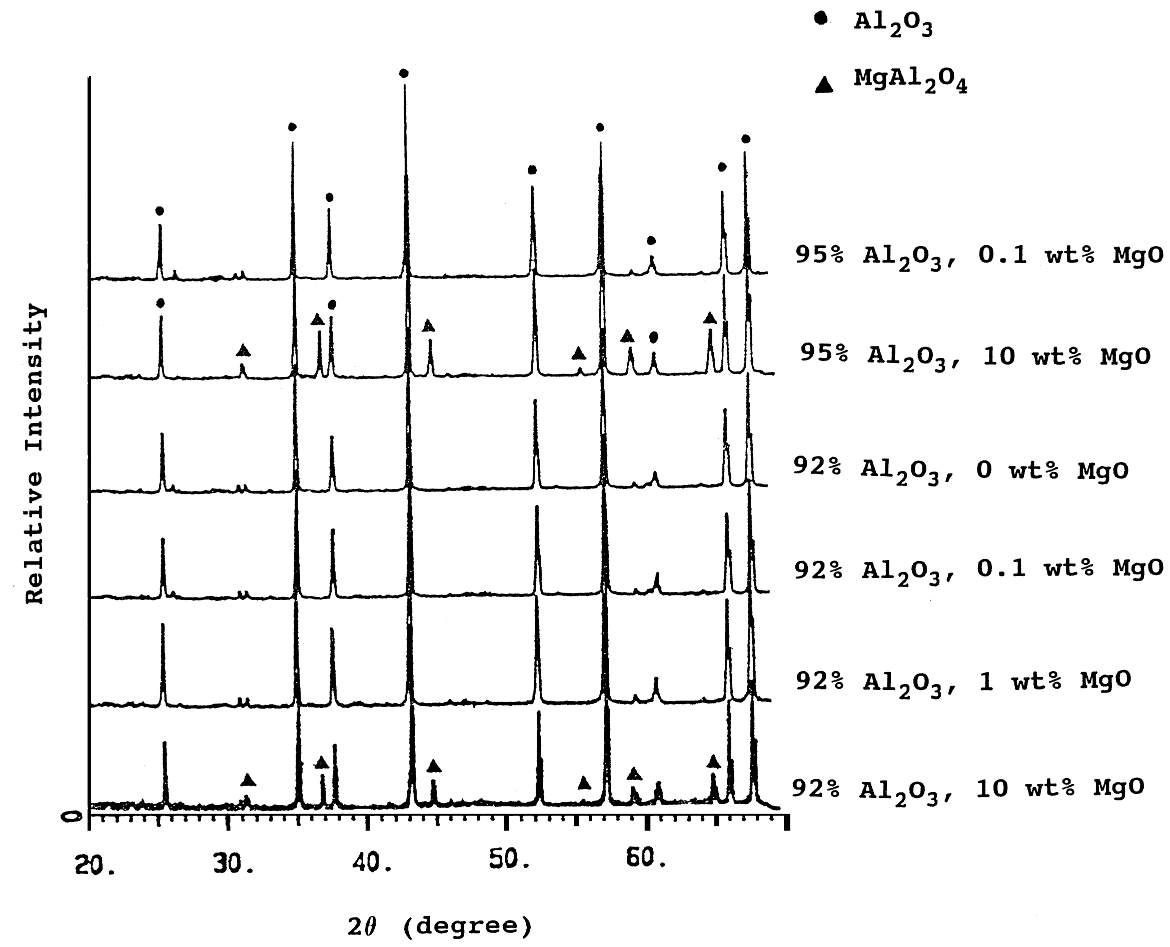

Fig. 5. Doping concentration of magnesia on the phase evolution of 95 and 92% pure alumina sintered at 1600°C for 1 h.

integral of $P(X)$ over the interval from 0 to X, and σ is the standard deviation of the distribution on a logarithmic scale. The cumulative distribution function, $F(X)$, when plotted against the logarithm of intercept length, gives a non-linear curve and possesses difficulty for analysis. Consequently, a log–normal distribution model is created by replacing the percentage points of the cumulative distribution using their equivalent values of deviation. This approach gives an expression of the cumulative distribution function by a linear fitting, which in turn can be represented by just two parameters, the median value and slope. The median value is used for the evaluation of median intercept length, while the slope is for the judgement of the relative distribution width of the intercept length. Additionally, the slope of the linear fitting and can be correlated with the standard deviation of the distribution by:

$$\frac{1}{S} = \sigma = \ln\left(\frac{L_{84}}{L_{50}}\right) = \ln\left(\frac{L_{50}}{L_{16}}\right) \qquad (2)$$

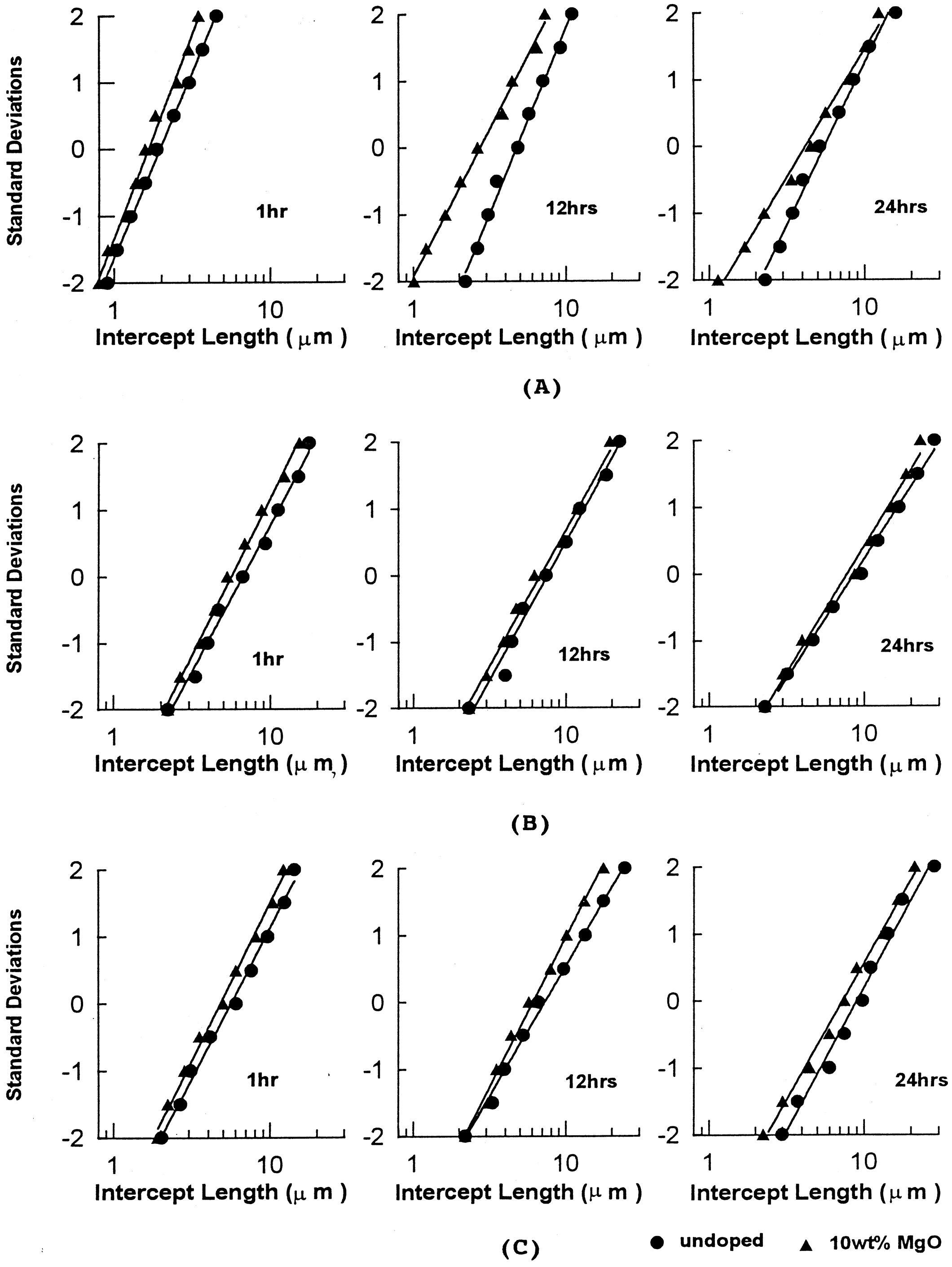

Fig. 6. Log–normal plots of intercept length distribution of alumina grains as a variation of the experimental factors investigated. Purity of alumina powder: (A) 99.8%, (B) 95%, (C) 92%.

where S is the slope in the log–normal plot, L_n is the intercept length for a cumulative population of n%. Percentage points of 84, 50, and 16% equals to deviation values of 1.0, 0, and −1.0, respectively. Distribution function expressed on population basis can be correlated with that expressed on volume basis with such an approach easily, because their slopes are the same while their median values differ by a number that is determined by the slope.

Figure 6 shows the log–normal plots of intercept length distribution as a variation of the experimental factors investigated in this study. It is the general trend of these plots that the distribution width of the intercept length increases with the incorporation of liquid phase forming additives and extending the isothermal holding time, whereas there is no strong trend showing the effect of magnesia on the distribution width of intercept length. The standard deviations for these curves vary between 0.68 and 0.37, which are equivalent to the variation of L_{84}/L_{50} between 1.97 and 1.45. Thus, the distribution widths of the intercept length distribution shown in Fig. 6 do not differ significantly from each other.

The median intercept length is defined as the intercept length value for a cumulative population of 50%, or a deviation of zero. Figure 7 shows the variation of the median intercept length with isothermal holding time in a log–log scale. The median intercept length, when multiplied by 1.5, is generally considered as the median grain size.[25] Therefore, the increase of median intercept length with isothermal holding time can be expressed by an empirical law of the form [26]

$$L^n = L_o^n + kt \tag{3}$$

where k is a grain growth rate constant, and n is a grain size exponent whose value depends on grain growth kinetics. Theoretical treatment of the grain growth kinetics, for both solid state sintering and liquid phase sintering, predicts that n varies between 2 and 3.[26] Grain growth of high purity alumina with or without magnesia doping obeys this kinetic law.[22,23]Nevertheless, n varies between 1.7 and 10 for most experimental correlations.[27] Table 1 shows the values of grain size exponent calculated from. Fig. 7 Doping of magnesia did not resulted in a dramatic variation of the grain size exponents, whereas addition of liquid phase forming additives did cause substantial change of grain size exponent from approximately 3.3 to 8. Consequently, the liquid phase forming additives clearly altered the sintering mechanism of alumina from solid state sintering into liquid phase sintering, which was not affected by the precipitation of a high concentration of $MgAl_2O_4$.

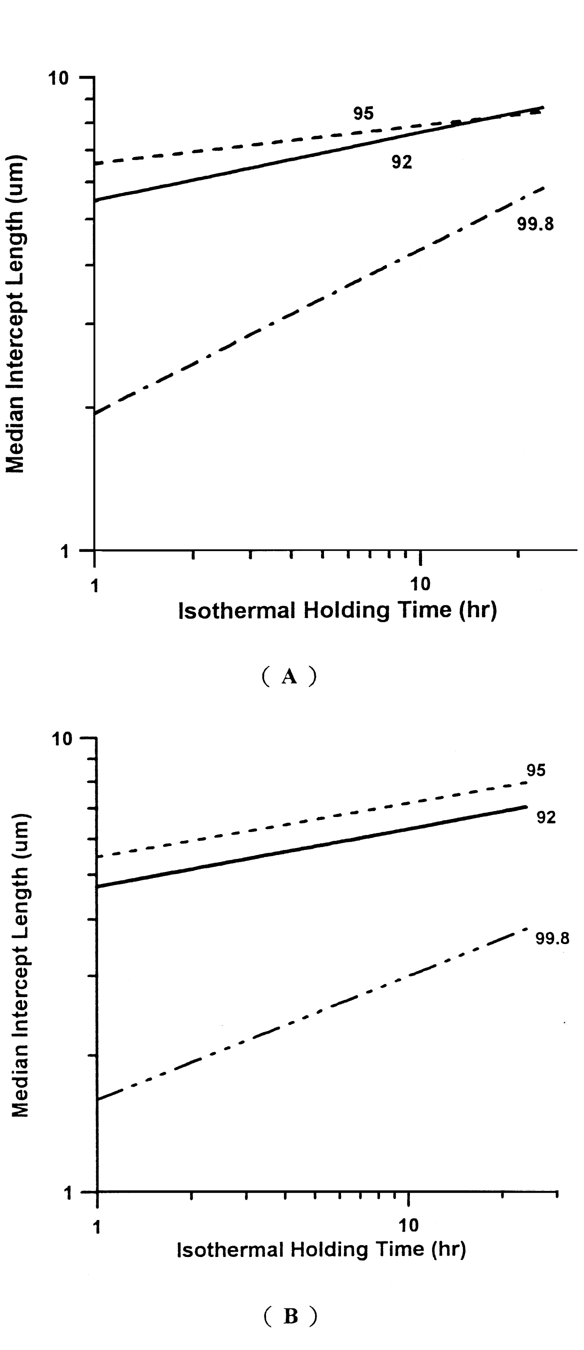

Fig. 7. Log–log plots of median intercept length vs isothermal holding time at 1600°C for alumina having different purities and with the doping of (A) 0 wt%, or (B) 10 wt% magnesia.

Table 1. Grain growth exponent (n) for alumina powders that have different quantities of liquid phase forming additives and magnesia doping

Purity of alumina powder (wt%)	99.8		95		92	
Magnesia doping concentration (wt%)	0	10	0	10	0	10
Grain growth exponent (n)	2.9	3.7	8.8	7.2	8.2	8.1

As the average interfacial energy between liquid phase and alumina is about one half the average grain boundary energy of alumina,[28] the alumina grains are expected to be covered by the liquid phase should it is so abundant as to penetrate all the grain boundaries and junctions. In fact, 5 wt% of liquid phase forming additives (calcia and silica) in alumina could have developed about 8 wt%, or 12 vol% of calcia aluminosilicate liquid phase during sintering.[4] According to the suggestion that abnormal grain growth of alumina was induced by the microscopically inhomogeneous distribution of liquid phase in the grain boundaries of alumina,[2,4] such a high quantity of liquid phase was sufficient to distribute homogeneously in all the grain boundaries and junctions of alumina. The uniform distribution of liquid phase could possibly avoid non-uniform grain boundary mobilities. Nevertheless, abnormal grain growth leading to the formation of elongated grains still took place when the undoped 95 and 92% pure powders were exposed to prolonged isothermal holdings. Such a phenomenon was the result of non-uniform grain boundary mobilities caused by the anisotropy in interfacial energy.[9,29] With the precipitation of $MgAl_2O_4$ by doping a high concentration of magnesia, elongated alumina grains could hardly been found whereas faceted alumina grains predominated in the microstructure. This observation implied that the precipitation of $MgAl_2O_4$ did not significantly alter the degree of anisotropy in interfacial energy of alumina, contrary to the implication presented elsewhere.[9] Instead, the $MgAl_2O_4$ precipitates reduced the mobilities of the fast moving boundaries (high index planes) by a second phase drag mechanism.

4 CONCLUSION

Statistical analysis of the distribution width of the intercept lengths of alumina grains indicated that liquid phase, compared with magnesia, was the principal factor affecting the grain growth mechanism of alumina. The liquid phase easily triggered the development of elongated alumina grains. The effect of magnesia on the intercept length distribution of alumina grains was insignificant statistically, when the liquid phase was so abundant as to penetrate all the grain boundaries and junctions of alumina. However, as the doping concentration of magnesia was sufficiently high to cause precipitation of $MgAl_2O_4$, the evolution of elongated alumina grains, but not the equiaxed prismitic alumina grains, was retarded. This observation implied that the degree of interfacial energy anisotropy of alumina was not altered dramatically by the precipitation of $MgAl_2O_4$. Instead, the non-uniform grain boundary mobilities that caused the development of elongated alumina grains was moderated as the $MgAl_2O_4$ precipitates pinned the fast moving grain boundaries.

REFERENCES

1. BAE, S. I. & BAIK, S., Determination of critical concentrations of silica and/or calcia for abnormal grain growth in alumina. *J. Am Ceram. Soc.*, **76** (1993) 1065–1067.
2. HANDWERKER, C. A., MORRIS, P. A. & COBLE, R. L., Effects of chemical inhomogeneities on grain growth and microstructure in Al_2O_3. *J. Am. Ceram. Soc.*, **72** (1989) 130–136.
3. BATEMAN, C. A., BENNISON, S. J. & HARMER, M. P., Mechanism for the role of magnesia in the sintering of alumina containing small amounts of a liquid phase. *J. Am. Ceram. Soc.*, **72** (1989) 1241–1244.
4. HANSEN, S. C. & PHILLIPHS, D. S., Grain boundary microstructures in a liquid-phase sintered alumina σ-Al_2O_3. *Phil. Mag. A*, **47** (1983) 209–234.
5. KAYSSER, W. A., SPRISSLER M. HANDWERKER, C. A. & BLENDELL, J. E., Effects of a liquid phase on the morphology of grain growth in alumina. *J. Am. Ceram. Soc.*, **70** (1987) 339–343.
6. HARMER, M. P., Use of solid-solution additives in ceramic processing. In *Structures and Properties of MgO and Al_2O_3 Ceramics*, ed. W. D. Kingery. American Ceramic Society, Columbus, OH, 1984, pp. 679–696.
7. KOLAR, D., Discontinuous grain growth in multiphase ceramics. In *Sintering of Advanced Ceramics*, Ceramic Transactions, Vol. 7, ed. C. A. Handwerker, J. E. Blendell & W. A. Kaysser. American Ceramic Society, Westerville, OH, 1990, pp. 529–545.
8. HODGE, J. D., The effect of particle size distribution on liquid phase sintering in alumina. In *Sintering of Advanced Ceramics,* Ceramic Transactions, Vol. 7, ed. C. A. Handwerker, J. E. Blendell & W. A. Kaysser. American Ceramic Society, Westerville, OH, 1990, pp. 415–435.
9. IKEGAMI, T. & KOTANI, K., Some roles of MgO and TiO_2 in densification of a sinterable alumina. *J. Am. Ceram. Soc.*, **70** (1987) 885–890.
10. ZHAO, J. & HARMER, M. P., Sintering of ultra-high-purity alumina doped simultaneously with MgO and FeO. *J. Am. Ceram. Soc.*, **70** (1987) 860–866.
11. JOHNSON, W. C. & STEIN, D. F., Additive and impurities distributions at grain boundaries in sintered alumina. *J. Am. Ceram. Soc.*, **58** (1975) 485–488.
12. TAYLOR, R. I., COAD, J. P. & BROOK, R. J., Grain boundary segregation in Al_2O_3. *J. Am. Ceram. Soc.*, **57** (1974) 539–540.
13. MARAIS, H. L. & FINE, M. E., Grain-boundary segregation in MgO-doped Al_2O_3. *J. Am. Ceram. Soc.*, **55** (1972) 568–570.
14. BENNISON, S. J. & HARMER, M. P., A history of the role of MgO in the sintering of ψ-Al_2O_3, In *Sintering Of Advanced Ceramics*, Ceramic Transactions, Vol. 7, ed. C. A. Handwerker, J. E. Blendell & W. A. Kaysser, American Ceramic Society, Westerville, OH, 1990 pp. 13–49.
15. PEELEN, J. G. J., Influence of MgO on the evolution of the microstructure of alumina. *Mater. Sci. Res.*, **10** (1975) 443–54.

16. MARCUS, H. L. & FINE, M. E., Grain boundary segregation in MgO-doped Al_2O_3. *J. Am. Ceram. Soc.*, **55** (1972) 568–70.
17. BENNISON, S. J. & HARMER, M. P., Grain growth and cavity formation in MgO-doped Al_2O_3. In *Character of Grain Boundaries*, Advances in Ceramics, Vol. 6, ed. M. F. Yan & A. H. Heuer. American Ceramic Society, Columbus, OH, 1983, pp. 171–183.
18. MOCELLIN, A. & KINGERY, W. D., Microstructural changes during heat treatment of sintered alumina. *J. Am. Ceram. Soc.*, **56** (1973) 309–314.
19. SPRISSLER, M. , KAYSSER, W. A., HUPPMAN, W. J. & PETZOW, G., Influence of MgO on liquid phase sintering and solid phase sintering of Al_2O_3. *Sci. Ceram.*, **10** (1980) 321–26.
20. KINGERRY, W. D., BOWEN, H. K. & UHLMANN, D. R., *Introduction to Ceramics*, 2nd edn. John Wiley & Sons, New York, 1976, p . 307.
21. MORRIS, P. A. & COBLE, R. L., Grain boundary structures in high-purity Al_2O_3 bicrystals grown from the melt, In *Defect Properties and Processing of High-Technology Nonmetallic Materials*, Vol. 60, ed. Y. Chen. Materials Research Society, Pittsburgh, PA, 1986, pp. 281–289.
22. BENNISON, S. J. & HARMER, M. P., Grain-growth kinetics for alumina in the absence of a liquid phase. *J. Am. Ceram. Soc.*, **68** (1985) C22.
23. BENNISON, S. J. & HARMER, M. P., Effect of MgO solute on the kinetics of grain growth in Al_2O_3. *J. Am. Ceram. Soc.*, **66** (1983) C90.
24. GERMAN R. M., *Powder Metallurgy Science*, 2nd edn. Metal Powder Industries Federation, Princeton, NJ, 1994, pp. 57–61.
25. KWON, O. H. & , MESSING, G. L., Kinetic analysis of solution-precipitation during liquid-phase sintering of alumina. *J. Am. Ceram. Soc.*, **73** (1990) 275–281.
26. GERMAN, R. M., *Sintering Theory and Practice*. John Wiley & Sons, New York, 1996, pp. 163–164, 293–296.
27. DOREMUS, R. H., *Rates of Phase Transformations*. Academic Press, London, 1985, pp. 149–151.
28. FLAITZ, P. L. & PASK, J. A., Penetration of polycrystalline alumina by glass at high temperatures. *J. Am. Ceram. Soc.*, **70** (1987) 449–455.
29. TASKER, P. W., Surfaces of magnesia and alumina. In *Structures and Properties of MgO and Al_2O_3 Ceramics*, ed. W. D. Kingery. American Ceramic Society, Columbus, OH, 1984, pp. 176–189.