Microstructure Development during Sintering in Polycrystalline $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ Spinel

Edoardo PROVERBIO, Masaki YASUOKA*, Kiyoshi HIRAO* and Shuzo KANZAKI*

ICMMPM Department, University of Rome "La Sapienza", via Eudossiana, 18-00184, Rome, Italy

*Ceramic Science Department, Government Industrial Research Institute, Nagoya, 1, Hirate-cho, Kita-ku, Nagoya-shi 462

多結晶 $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ スピネルの焼結過程での微構造変化

Edoardo Proverbio・安岡正喜*・平尾喜代司*・神崎修三*

ICMMPM Department, University of Rome "La Sapienza", via Eudossiana, 18-00184, Rome, Italy

*名古屋工業技術試験所, 462 名古屋市北区平手町 1

[Received June 15, 1992; Accepted October 15, 1992]

Fine Al-rich spinel $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ powder was synthesized by hydrolysis of mixed alkoxides. High sinterability of powder allowed to obtain relative density higher than 95% at temperature as low as 1300°C by pressureless sintering in air. Samples sintered at temperature of 1100–1500°C had quite heterogeneous microstructure owing to precipitation of large corundum particles (<1400°C) and discontinuous grain growth of spinel matrix (>1400°C). However, homogeneous microstructure with fine grains could be obtained by a two step sintering process in which spinel grain growth at high temperature was inhibited by corundum particles momentarily retained above solvus temperature. Precipitation behavior during sintering was compared with that during annealing, and the precipitation mechanism was discussed.

Key-words: Al-rich spinel, Powder synthesis, Sintering, Microstructure, Precipitation

1. Introduction

Spinel forms wide range solid solution with alumina at high temperature. Precipitation of corundum can readily occur in $\text{MgO} \cdot \text{Al}_2\text{O}_3$ – Al_2O_3 system at temperatures lower than equilibrium temperature since the composition range over which spinel solid solution phase is stable changes with temperature. However, a solid solution of a given composition can be easily retained at room temperature by quenching from temperature higher than solvus temperature. Studies have been widely conducted to understand the precipitation mechanism on Al-rich spinel.^{1)–5)} Saalfeld and Jagodzinski^{1),2)} showed that precipitation occurs by the following three stages: (I) formation of monoclinic metastable pre-precipitate phase, resembling to Guiner–Preston (G.P.) zones in metals, (II) formation of a monoclinic intermediate phase of composition $\text{MgAl}_{26}\text{O}_{40}$ and (III) final precipitation of $\alpha\text{-Al}_2\text{O}_3$. Different composition and crystal forms have been reported on the intermediate phase, however, it is generally accepted that precipitation of corundum from Al-rich single crystal spinel occurs by way of the formation of intermedi-

ate phases. On the other hand, in case of polycrystalline spinel a discrepancy on the presence of a metastable pre-precipitate phase remained.^{6),7)}

Although many studies concerning sintering of stoichiometric spinel have also been carried out,^{8)–10)} little is known about sinterability and microstructure development of Al-rich spinel.¹¹⁾ Since Al-rich spinel is unstable at lower temperature, its sintering behavior is considered to be influenced by the characteristics of starting powders as well as sintering conditions. In preparing polycrystalline Al-rich spinel ceramic two routes can be followed: a) starting from a mixture of aluminum and magnesium oxides and sintering at a temperature higher than solvus temperature for that composition, b) starting from Al-rich spinel powder. In the former case sintering at high temperature and for longer time is required, otherwise a low homogeneous product will be obtained. Consequently, it would be difficult to control grain growth microstructure. In the latter case the following methods are available to synthesize starting powder: solid–solid reaction, coprecipitation or salt mixture decomposition. These methods still have a disadvantage in that high calcination temperature is necessary to obtain single phase powder, and hence result in poor sinterability. Using new techniques such as vapor-phase oxidation technique¹²⁾ or alkoxide method¹³⁾ it is theoretically possible to prepare non-stoichiometric spinel powder at low temperature and with nanometric particle size.

In the present paper a mixture of Al-iso-propoxide and Mg-ethoxide was hydrolyzed to synthesize homogeneous $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ spinel powder. Sinterability, variation of crystalline phases and microstructure development of the powder were examined. Exsolution and/or redissolution process of corundum during sintering and annealing were also studied.

2. Experimental procedures

2.1 Powder preparation

Aluminum iso-propoxide [$\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$] (Wako Pure Chemical Ind., Ltd.) was dissolved in toluene, then a solution of Mg-ethoxide [$\text{Mg}(\text{OC}_2\text{H}_5)_2$]

OEt)₂] (Hokko Chemical Ind., Ltd.) in toluene was added in the proper proportion to obtain MgO·1.5Al₂O₃ spinel as a final product. The mixture was allowed to homogenize at 60°C for one hour while stirring. Distilled water was then added to hydrolyze metal alkoxides. Two different amounts of water, 3 and 10 times (powder B3 and B10, respectively) the stoichiometric amount required for the following reactions, were examined:

where R is the organic radical.

After refluxing at 60°C for two hours, 15 wt% of surfactant (Reodoru SP-S10, Kao Corporation) against the calculated total amount of metal hydroxide was added to separate excess water in the further step. Ultrasonic agitation was performed to improve homogeneity. Water was then removed at the azeotropic point of the mixture (about 85°C). When boiling point of toluene was reached (112°C), the mixture was filtered, then rinsed with fresh hot toluene and filtered again. The obtained cake was vacuum dried at 150°C, followed by crushing and screening to pass a #100 mesh sieve and was finally calcined at 900°C for one hour. After calcination, spinel powder was planetary ball milled in methanol for 30 min, dried, screened to pass a #100 mesh sieve and calcined again at 700°C for 30 min to remove all residual organic compounds.

Phase identification during calcination (carried out for one hour at temperature of 500°–1300°C) was made by X-ray diffraction (XRD) using a Cu K α radiation filtered by graphite monochromator. Specific surface area of the powder was measured by BET method.

2.2 Sintering and microstructure observation

Spinel powder was formed in a 20 mm diameter die at 10 MPa, followed by cold isostatic pressing at 200 MPa. Sintering was carried out in air. Samples were placed on a MgO·1.5Al₂O₃ spinel powder bed in a closed alumina crucible. Heating rate was 10°C/min up to 900°C, 2°C/min up to 1300°C to avoid formation of cracks due to high shrinkage rate in this temperature range, and finally 10°C/min up to 1500°C. To understand densification phenomena and grain growth several samples were fired for six hours at different temperature starting from 900°C up to 1500°C. On these samples density, porosity and grain morphology were detected. Obtained data (Figs. 3 to 5) suggested to use a two steps sintering method to evidence the influence of heat treatment on physical properties of full densified samples as discussed afterwards. So at first, a densification at low temperature (1050°, 1100° or 1300°C) for six hours, and secondly, a final densification and grain growth at 1500°C for four hours (samples named E105, E110 and E130, respectively) was used. A set of samples was also directly sintered at 1500°C for six hours without intermediate steps (A150). Density and

porosity measurements were carried out by Archimedes' method using distilled water. Phase identification was examined by XRD, and spinel lattice parameter was calculated using Si as internal standard and high 2 θ reflections of spinel (110–150 degrees) by Cohen least squares method. Microstructure was observed by scanning electron microscope (SEM) on polished and thermally etched surface. Grain size distribution of samples was measured by the linear intercept method.

2.3 Heat treatment

Sintered A150 samples were ground and polished with <1 μm diamond paste. Heat treatment was carried out in air in a closed platinum crucible at 1200°C for various times (from 0.5 to 90 h). Sample was heated at a rate of 10°C/min and allowed to cool in the furnace. After annealing, samples were ground and polished again to remove at least a 0.5 mm surface layer and then chemically etched with phosphoric acid at 185 $\pm$ 5°C for 8 min.

3. Results

3.1 Powder characteristics

X-ray diffraction patterns of the calcined B10 and B3 powders are shown in Figs. 1 and 2, respectively. Both powders already had broad spinel reflection at 500°C calcination. The B10 powder showed a trace of MgO peak (not indicated in the figure). However, MgO phase disappeared at higher calcination temperature and only spinel phase was present after a treatment at 900°C. Corundum reflections began to appear with the increase of temperature.

On the contrary, B3 powder showed appreciable asymmetry on the spinel peaks at 900°C. This asymmetry increased with temperature owing to the presence of a concomitant metastable phase, proba-

Fig. 1. X-ray diffraction patterns of powder B10 calcined at different temperatures. S=spinel, C=corundum.

Fig. 2. X-ray diffraction patterns of powder B3 calcined at different temperatures.

S=spinel, C=corundum, P=periclase, M=Mg-Al-O metastable phase.¹⁴⁾

bly $\text{Mg-Al-O}^{14)}$ (see twinned peaks at 1200°C). Detectable phases at 1300°C were spinel, corundum and periclase.

Particle size of both powders calcined at 500°C, calculated from BET specific surface area, was about 4–4.5 nm. This value increased at about 8 nm after calcination at 900°C.

3.2 Densification, phase evolution and microstructure development during sintering

Since the powder B10 was superior than the B3 in compositional homogeneity, only the B10 powder was used for sintering studies. The variation of relative density and porosity with temperature are shown in Fig. 3. Relative density (RD) of about 97% at 1300°C indicates high sinterability of the powder. The maximum RD (98.5%) was obtained at 1500°C. Open porosity gradually decreased with increasing temperature and disappeared at 1200°C; while closed porosity increased temporarily at 1200°C, where momentary cessation of densification was also observed, then decreased with temperature.

Figure 4 shows change of spinel lattice parameter and volume fraction of corundum with sintering temperature. Amount of $\alpha\text{-Al}_2\text{O}_3$ in the samples was estimated by using the Viertel and Seifert equation as reported by Panda and Raj.⁷⁾

$$n = (0.86109 - a_0) / (3a_0 - 2.37195)$$

where n is the molar composition ratio in $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ crystal and a_0 is the spinel lattice parameter. Known the n value it is possible to calculate the weight fraction of $\alpha\text{-Al}_2\text{O}_3$ (W_α).

$$W_\alpha = (1.5 - n) / (R + 1.5)$$

where R is the ratio of the molecular weights of MgO and Al_2O_3 , =0.395291. The volume fraction of α -

Fig. 3. Relative density (closed circles), open porosity (open squares) and closed porosity (closed squares) during sintering after 6 h at each temperature.

Fig. 4. Spinel lattice parameter (closed circles) and $\alpha\text{-Al}_2\text{O}_3$ volume fraction (open circles) during sintering after 6 h at each temperature.

Al_2O_3 (V_α) is given by

$$V_\alpha = (W_\alpha / \rho) [W_\alpha / \rho + (1 - W_\alpha) / \rho_s] \\ = 1 / (1.1106 / W_\alpha - 0.1106)$$

where $\rho = 3.987 \text{ g/cm}^3$ is the density of corundum and ρ_s the density of spinel which has been assumed constant and equal to 3.59 g/cm^3 . The theoretical density of spinels $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and $\text{MgO} \cdot 2\text{Al}_2\text{O}_3$ for example, are respectively 3.58 and 3.612 g/cm^3 , thus taking ρ_s as 3.59 g/cm^3 will involve a very small error in the estimates of volume fractions.

Corundum phase was not detected by XRD at temperatures lower than 1100°C but the molar composition ratio n determined by spinel lattice parameter corresponded to about 1.18. Spinel lattice parameter increased with increasing temperature up to 1100°C due to corundum exsolution from spinel lattice (at this temperature Al-rich spinel is not a stable phase, Fig. 5) and then gradually decreased at higher temperatures. At 1500°C only spinel phase was detected by XRD and the corresponding n calculated from lattice parameter was 1.5. Its parameter was also in agreement with data on $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ reported by others.^{16)–18)}

Microstructure development during sintering is shown in Fig. 6. The microstructure was remarkably affected by the presence and the morphology of corundum. Although the calcined powder was com-

Fig. 5. Phase diagram of system $\text{MgO} \cdot \text{Al}_2\text{O}_3 - \text{Al}_2\text{O}_3$.¹⁵⁾

posed of only spinel, when the sample was sintered at 1000°C large corundum particles of about 0.8 μm were observed within spinel matrix with grain size smaller than 0.1 μm (as confirmed by diffraction patterns obtained using transmission electron microscopy (TEM) not reported here). Most of precipitated corundum particles were linked to form clusters. The clusters coalesced to form larger particles by further heating, and some pores were trapped or originated in the corundum particles (Fig. 6b). Well developed corundum grains with a size of about 2 μm were observed at 1200°C. Many intergranular pores were detectable. At 1300°C spinel grain size slightly increased and corundum particles showed quite rounded shape and internal pores were coalesced (Fig. 6d). Noticeable grain growth was observed at 1500°C.

Figure 7 shows microstructure of samples obtained by two steps sintering schedule (samples E105, E110 and E130). The final microstructure was significantly affected by the temperature of first soaking stage. Grain size distribution of these samples and A150 sample are shown in Fig. 8. Samples

Fig. 6. Microstructure development during sintering. (a) after 6 h at 1100°C, (b) 1150°C, (c) 1200°C, (d) 1300°C, (e) 1400°C and (f) 1500°C. Thermally etched samples.

Fig. 7. Different microstructure obtained by changing heating schedule. (a) Sample E105: 6 h at 1050°C and 4 h at 1500°C, (b) sample E110: 6 h at 1100°C and 4 h at 1500°C, (c) sample E130: 6 h at 1300°C and 4 h at 1500°C. Thermally etched samples.

Fig. 8. Grain size distribution of samples A150, E105, E110 and E130.

E105 and E110 showed a bimodal grain size distribution. In spite of the heterogeneous microstructure (the end of first stage of stepwise heating) as shown in Fig. 6d, sample E130 showed rather uniform microstructure with average grain size of only $0.69 \mu\text{m}$. On the other hand, sample A150 sintered directly at 1500°C showed a broad grain size distribution with average grain size of $1.05 \mu\text{m}$ (Fig. 6f).

3.3 Precipitation behavior during heat treatment

Annealing of the sample A150 was performed at 1200°C . Appreciable precipitation of Al_2O_3 was confirmed by XRD after 4-h annealing. The amount of precipitated Al_2O_3 increased notably with annealing time and almost all excess corundum exsolved after 48 h. Change of grain size with annealing time and microstructure of annealed samples are shown in Figs. 9 and 10, respectively. Remarkable grain growth of corundum with grain size ranging from 10 to $20 \mu\text{m}$ was observed after 6-h annealing. Grain boundaries were considerably irregular and many small particles (probably spinel) were engulfed in the bulk crystal (Fig. 10a). With increasing annealing time, corundum grew rapidly and became more

Fig. 9. $\alpha\text{-Al}_2\text{O}_3$ grain size vs. time during annealing at 1200°C compared with Eq. (1).

regular in shape (Fig. 10b). Large voids were observed around corundum particles. After 48 h average grain size of the corundum was around $60 \mu\text{m}$ and some grains joined each other (Fig. 10c).

4. Discussion

Fine $\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3$ spinel powder was obtained by alkoxide method, as confirmed by XRD and spinel lattice parameter value. However, as predicted from the phase diagram of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ – Al_2O_3 system (Fig. 5), the spinel powder underwent decomposition to form corundum and spinel ($\text{MgO} \cdot n\text{Al}_2\text{O}_3$, $1 < n < 1.5$) when heated below solvus temperature ($< 1400^\circ\text{C}$) and the precipitated corundum re-solved in spinel at higher temperature ($> 1400^\circ\text{C}$).

The decomposition reaction during sintering could affect densification behavior. Precipitation of corundum is accompanied by generation of voids, as was confirmed by SEM observation (see Fig. 6), since density of precipitated corundum is higher than that of spinel matrix. These voids are responsible for the momentary cessation of densification in the temperature range about 1100° and 1300°C shown in Fig. 3.

Morphology of the sintered body at first sintering step was also remarkably influenced by the precipitation of corundum. The grain size of precipitated corundum particles was much larger than that of spinel matrix. These are in analogy with the microstructure observed during annealing of the sample A150 below the solvus temperature (1200°C) as shown in Fig. 10.

Fig. 10. SEM images of $\alpha\text{-Al}_2\text{O}_3$ precipitates (larger grains) after: (a) 6 h at 1200°C , (b) 12 h and (c) 48 h. Chemically etched samples.

Panda and Raj investigated kinetics of precipitation of $\alpha\text{-Al}_2\text{O}_3$ in $\text{MgO}\cdot 2\text{Al}_2\text{O}_3$ spinel solid solution.⁷⁾ They suggested that: (1) $\text{MgO}\cdot 2\text{Al}_2\text{O}_3$ spinel transformed directly to $\alpha\text{-Al}_2\text{O}_3$ and spinel; (2) the grain growth of the precipitates occurred by a nucleation-growth process and a grain growth rate dG/dt at 1550°C was given by the following equation:

$$dG/dt = 5.4 \times 10^{-3} \ln(X/X_s) \text{ } (\mu\text{m/s}) \quad (1)$$

with

$$1 \leq X/X_s \leq 1.2$$

where X is the concentration of alumina in the spinel phase and X_s is the concentration at the equilibrium when no more corundum exsolves. From Eq. (1), dG/dt at $X/X_s = 1.2$, namely in the first precipitation stages, is $0.98 \times 10^{-3} \mu\text{m/s}$ and this value was plotted in Fig. 9. It is found that our data are approximately in agreement with their result at the early stage of precipitation. Therefore, the rapid grain growth of corundum during sintering and annealing is considered to occur by a nucleation-growth process. This fact reflects compositional homogeneity of raw spinel powder prepared by the alkoxide method.

However, concerning the initiation of precipitation, Kanzaki et al. in a previous work⁶⁾ on $\text{MgO}\cdot 1.22\text{Al}_2\text{O}_3$ and $\text{MgO}\cdot 1.5\text{Al}_2\text{O}_3$ polycrystalline spinel, showed that pre-precipitated metastable phase occurred (G.P. zones) after short annealing time at relatively low temperature ($1100^\circ\text{--}1500^\circ\text{C}$) by TEM observation. The metastable Mg-Al-O phase detected in the B3 powder (Fig. 2) also supported this hypothesis.

To summarize the above discussion it would be possible to describe microstructure development of $\text{MgO}\cdot 1.5\text{Al}_2\text{O}_3$ spinel derived from the alkoxide route during sintering as outlined in the schemes shown in Fig. 11. Fine corundum particles are precipitated by way of intermediate phases in a fine grained spinel matrix (Fig. 11a). Corundum particles grow by coarsening effect and/or nucleation-growth process and are gradually joined with each other to form larger particles (Figs. 11b-d). In this

coalescing process voids generated by corundum formation are trapped in larger corundum particles (Fig. 11c). With the increase in temperature grain growth of spinel occurs. However, due to the increase of solubility in spinel alumina grain growth stops and gradually incorporates into spinel grain to form bimodal grain size distribution (Figs. 11e-f).

Grain size of precipitated corundum tended to increase with increasing sintering temperature (Figs. 6a-e). Some possible explanations are as follows: (1) transfer path of constituent atoms for grain growth is restricted at lower temperature because of lower compaction; (2) at higher temperature the amount of corundum particle initially precipitated is less than that of lower temperature owing to low supersaturation; (3) coarsening effect is enhanced with increasing temperature.

Moreover, the microstructure of the final sintered body was exceedingly influenced by this first sintering condition. That is, microstructure of E105, E110 and A150 samples were highly heterogeneous because of discontinuous grain growth (see Figs. 6 and 7). On the contrary, E130 sample shows finer and uniform microstructure regardless of its remarkably heterogeneous microstructure at first sintering step (see Figs. 6d and 7c). It is considered that these differences in the final microstructure are attributable to the presence and the size of corundum grains after first sintering step. Smaller corundum grains easily re-dissolve in spinel matrix at 1500°C because only spinel phase is stable at that temperature. However, larger corundum grains momentarily remain even at 1500°C . The remaining corundum could inhibit spinel grain growth and form more homogeneous microstructure. Consequently, it is revealed that the final microstructure of Al-rich spinel prepared by alkoxide method can be controlled by a two step sintering process.

5. Conclusions

Fine $\text{MgO}\cdot 1.5\text{Al}_2\text{O}_3$ spinel powder was synthesized by hydrolysis of mixed alkoxides followed by calcination at 900°C . Densification behavior, phase evolution, and microstructure development during sintering were investigated. The results are summarized as follows:

(1) Synthesized powder had high sinterability to densify over 95% relative density at a temperature as low as 1300°C .

(2) Decomposition reaction occurred to form corundum during sintering at temperatures of $1100^\circ\text{--}1400^\circ\text{C}$. Precipitation of corundum was accompanied by generation of voids, which caused a momentarily cessation of densification in the temperature range of $1100^\circ\text{--}1300^\circ\text{C}$.

(3) The grain size of precipitated corundum particles was much larger than spinel matrix, which was in analogy with the case when a sintered sample composed of single phase ($\text{MgO}\cdot 1.5\text{Al}_2\text{O}_3$) spinel was an-

Fig. 11. Schematic illustration of $\alpha\text{-Al}_2\text{O}_3$ precipitation sequence and grain growth during sintering. Temperature increases from (a) to (f). White areas=spinel; shadowed areas=corundum; closed circles=pores.

nealed below the solvus temperature. In both cases, the rapid grain growth of corundum was considered to occur by a nucleation-growth process.

(4) Microstructure of sintered specimens were quite heterogeneous because of the precipitation of large corundum particles ($<1400^\circ\text{C}$) and discontinuous grain growth of spinel matrix ($>1400^\circ\text{C}$). However, homogeneous microstructure with fine grains could be obtained by first sintering at 1300°C and second sintering at 1500°C in which spinel grain growth was inhibited by the presence of corundum particles.

References

- 1) H. Saalfeld and H. Jagodzinski, *Z. Kristallogr., Kristallogeometrie, Kristallphys., Kristallchem.*, **109**, 87–109 (1957).
- 2) H. Jagodzinski, *ibid.*, **109**, 388–409 (1957).
- 3) M. H. Lewis, *Phil. Mag.*, **20**, 985–98 (1969).
- 4) M. Doukhan, J. C. Doukhan and B. E. Scaig, *Mater. Res. Bull.*, **11**, 125–34 (1976).
- 5) W. T. Donlon, T. E. Mitchel and A. H. Heuer, *J. Mater. Sci.*, **17**, 1389–97 (1982).
- 6) S. Kanzaki, K. Hamano, Z. Nakagawa and K. Saito, *Yogyo-Kyokai-Shi*, **88**, 59–65 (1980).
- 7) P. C. Panda and R. Raj, *J. Am. Ceram. Soc.*, **69**, 365–73 (1986).
- 8) J. T. Bailey and R. Russell, *Trans. Brit. Ceram. Soc.*, **68**, 159–64 (1969).
- 9) R. J. Bratton, *Am. Ceram. Soc. Bull.*, **48**, 1069–75 (1969).
- 10) R. J. Bratton, *J. Am. Ceram. Soc.*, **54**, 141–43 (1971).
- 11) P. Hing, *J. Mater. Sci.*, **11**, 1919–26 (1976).
- 12) K. Itatani, H. Sakai, F. S. Howell, A. Kishioka and M. Kinoshita, *Brit. Ceram. Trans. J.*, **88**, 13–16 (1989).
- 13) M. Sugiura and D. Kamigaito, *Yogyo-Kyokai-Shi*, **92**, 605–11 (1984).
- 14) Powder Diffraction Files: Cards n. 10–238, 10–238a, Joint Com. Powd. Diff. Stnd., Philadelphia (1980).
- 15) E. F. Osborn, *J. Am. Ceram. Soc.*, **36**, 147–51 (1953).
- 16) K. Shirasuka and G. Yamaguchi, *Yogyo-Kyokai-Shi*, **82**, 650–53 (1974).
- 17) A. Navrotsky, D. A. Wechsler, K. Geisinger and F. Seifert, *J. Am. Ceram. Soc.*, **69**, 418–22 (1986).
- 18) Y. M. Chiang and W. D. Kingery, *J. Am. Ceram. Soc.*, **72**, 271–77 (1989).