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Preparation and Characterization of Polycrystalline Alumina with Small Grain Size

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Abstract

Fine Al_2O_3 powder prepared by the ammonium alum method was encapsulated in a stainless steel mold with inner diameter, outer diameter and height of 10, 22 and 30 mm, respectively. The mold containing Al_2O_3 was preheated at 1200 or 1300°C for about 8 min and then rapidly press-forged under a uniaxial compressive load. The mean Al_2O_3 particle size slightly increased from 0·15 μm in the raw powder to 0·2–0·3 μm during the preheating process and conserved this size after the forging process which led to a dense polycrystalline body. The polycrystalline Al_2O_3 in the hot-forged status did not show a satisfactory hardness value, mainly because of some stored residual stress around the grain boundaries. This interpretation is supported by the results of annealing experiments by which the hardness of the hot-forged material after holding at a relatively low temperature (1000–1200°C) for 24 h, was found to increase up to an excellent value of about 23 GPa.

Feinkörniges Al_2O_3-Pulver, hergestellt mit Hilfe der Ammoniak-Alum-Methode, wurde in einer Edelstahlform mit einem Innen- und Außendurchmesser von 10 bzw. 22 mm und einer Höhe von 30 mm eingeschlossen. Die das Al_2O_3 enthaltende Form wurde für etwa 8 Minuten auf 1200 oder 1300°C erhitzt und dann schnell unter einer einachsigen Last preßgeschmiedet. Die mittlere Al_2O_3-Teilchengröße nahm leicht von 0·15 μm im Ausgangspulver auf 0·2–0·3 μm während des Erhitzens zu, und behielt diese Größe auch nach dem Schmieden bei. Dies ergab eine dichte, polykristalline Masse. Das polykristalline Al_2O_3 besaß im heißgeschmiedeten Zustand keine zufriedenstellende Härte, hauptsächlich aufgrund der restlichen Spannungen an den Korngrenzen. Diese Interpretation wird durch Anlaßexperimente gestützt, bei denen das heißgeschmiedete Material für 24 Stunden bei relativ niedrigen Temperaturen (1000–1200°C) angelassen wurde. Der Härtewert stieg dabei auf etwa 23 GPa an.

Une poudre fine d'alumine, préparée par la méthode de l'alun d'aluminium est encapsulée dans un moule en acier inoxydable dont les diamètres interne, externe et la hauteur valent respectivement 10, 22 et 30 mm. Après un court traitement thermique à 1200 ou 1300°C (environ 8 min), le moule contenant l'Al_2O_3 est rapidement forgé par compression uniaxiale. Au cours du traitement de préchauffage, la taille moyenne des particules d'alumine s'accroît légèrement (0·15 μm à 0·2–0·3 μm) mais ne se modifie pas après le forgeage qui permet l'obtention d'un matériau dense polycristallin. La dureté de cette alumine polycristalline est insatisfaisante principalement à cause de contraintes résiduelles présentes au niveau des joints de grains. Cette interprétation est basée sur les résultats des expériences des traitements de recuit montrant que la dureté de ces échantillons forgés à chaud et traités à relativement faible température (1000–1200°C) durant 24 h s'accroît pour atteindre une excellente valeur de 23 GPa.

1 Introduction

The development of ceramic materials with superior properties necessarily requires the concurrent improvement of each technological step of their processing such as powder control, forming and sintering. Recently, the technology for producing

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controlled ceramic powders has been significantly improved and processes such as mechanical grinding (breakdown process) have become gradually replaced by new synthesis techniques (buildup process) by which fine and easily sinterable ceramic powders can be obtained. Despite this remarkable progress in the powder-synthesis technology, however, problems related to a poor degree of homogeneity in the ceramic bodies still persist due to the formation of coarse and hard agglomerates of powder during successive handling and/or forming. In other words, it appears clear that new processes for forming and sintering of ceramics should also be developed in order to allow the full exploitation of the new and highly reactive ceramic powders. One common problem with the sintering of ceramics resides in difficult densification as a consequence of undesired premature grain-growth during the first stage of sintering. In order to resolve this problem and fabricate highly dense ceramic sintered bodies with fine microstructures, new high-pressure forming of ultrafine powders[1,2] and successive sintering processes[3] have been recently developed. In addition, for the same purpose, a cyclic cold-isostatic-pressing (CIP) forming process has been proposed and is now under development.[4,5]

In the present research, a simple and useful sintering technique for preparing fine ceramic sintered bodies has been developed.[6-10] This consists of a uniaxial press-forging process in a metallic mold, the pressure being applied after short time heating up to moderate temperatures. When fine and highly reactive raw powders are used, this technique allows the occurrence of a quick densification/sintering process. This method, whose procedure may seem similar to traditional hot-pressing (HP), has the two following important peculiarities: (1) the ceramic powder is kept at high temperature only for a short time, (2) both the metallic mold and the ceramic specimen are subjected to shear deformation in the plane perpendicular to uniaxial pressing. These two concurrent circumstances permit the breakage of coarse and hard powder agglomerates and a consistent densification before appreciable grain-growth can occur.

Table 1. Impurity contents and some physical properties of the starting Al_2O_3 powder

Process	Ammonium alum method
Crystal type	α-Alumina
Purity	99·99%
Average particle size	≒0·15 μm
BET surface area	14 m^2/g
Impurities	Si; 15 ppm
	Na; 8 ppm
	K; 3 ppm
	Mg; 2 ppm
	Ca; 3 ppm
	Fe; 8 ppm

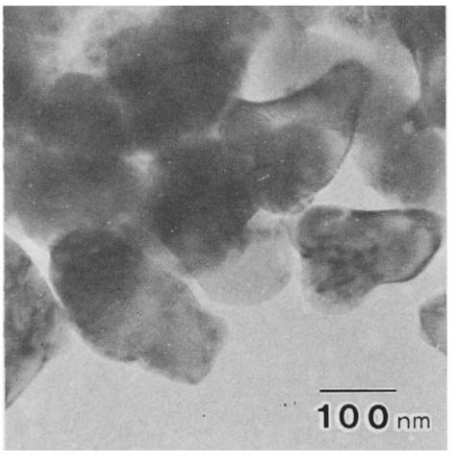

Fig. 1. TEM photograph of the Al_2O_3 starting powder.

The present method will be referred to as hot-forge sintering in the following paragraphs.

Based on previous studies of hot-forge sintering,[6-10] it has been recognized that the main densification mechanism varies for different materials. For example, the presence of a liquid phase at the contact point of the grains is very important in processing high-temperature superconducting oxide powders.[6,7] On the other hand, dislocation glide and the presence of a noncrystalline phase are determinant factors in the densification process of highly pure superfine MgO powder.[8,9] It has also been shown that the plastic behavior of a ductile metal phase plays a prevalent role in the densification of ceramic/metal composites.[10]

In this paper, we report about the densification behavior during hot-forging of an Al_2O_3 fine powder which can be considered as a typical example of a high-melting-point oxide ceramic whose densification behavior is only slightly influenced by the presence of a liquid or noncrystalline phase.

2 Experimental

Highly pure (99·99%) and fine (average grain-size 0·15 μm) Al_2O_3 powder* prepared by ammonium alum method was purchased and used in the present investigation. Table 1 shows the results of impurity analyses and some physical properties of this Al_2O_3 raw powder. The raw powder was also observed by transmission electron microscopy (TEM). As seen in Fig. 1, the particles were approximately round and smooth, and their size distribution appeared relatively uniform.

A cylindrical stainless steel mold (shown in Fig. 2) with inner diameter, outer diameter and height of 10, 22 and 30 mm, respectively, was filled with the

*TM-DAR, Taimei Kagaku Kogyo Ltd, Japan.

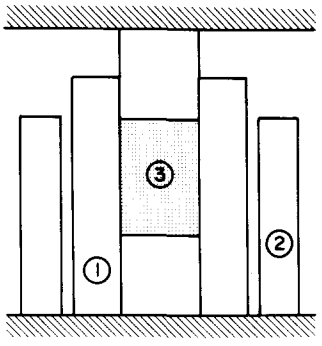

Fig. 2. Stainless steel mold with compression ring for hot-forge processing: (1) SUS 304 mold; (2) compression ring; (3) Al_2O_3 powder.

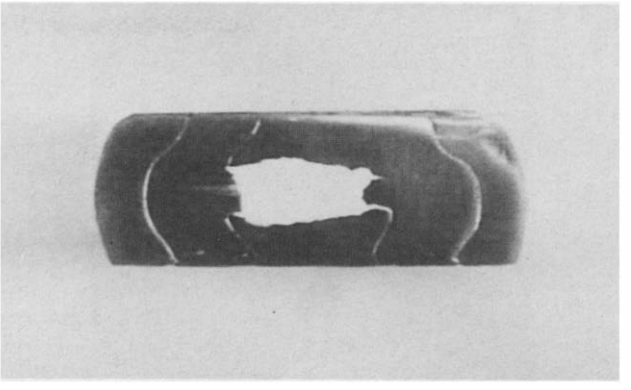

Fig. 3. Cross-section photograph of the assembled Al_2O_3 specimen, metallic mold and external ring (inner to outer side).

Al_2O_3 powder (about 3 g) and a preforming pressure cycle under 98 MPa was conducted. The mold containing the powder compact was first introduced in an electric furnace present at a fixed temperature (termed the preheating temperature hereafter) and then kept at the temperature for 5–8 min until thermal equilibrium was achieved. The achievement of the equilibrium temperature inside the mold within the above holding time was previously checked by introducing a thermocouple inside the mold itself together with the Al_2O_3 powder. Then, the hot mold containing Al_2O_3 was removed by tongs from the furnace, promptly set in the uniaxial press apparatus and immediately subjected to the high-pressure cycle. In all the present experiments, the descent speed of the pressing ram was fixed at 15 mm/s.

In the present study, it was necessary to heat the Al_2O_3 powder inside the metal mold to 1200–1300°C in order to promote the sintering process. As a consequence of this high temperature, the yield stress of the metallic mold (SUS 304) obviously decreased and, because of the occurrence of plastic deformation in the mold, the effect of the applied pressure on the internal Al_2O_3 compact was also found to diminish. In order to obviate this technological problem, an external metallic ring (also made with SUS 304) but not subjected to the preheating cycle and acting as support was added to the press apparatus (cf. Fig. 2). Figure 3 shows the cross-section of the metal mold after a hot-forging cycle conducted in the presence of the external metallic ring. Differently from super-conducting ceramics[6,7] or MgO,[8,9] during the hot-forge sintering of Al_2O_3 powder, anomalous deformation and/or cracking of the internal ceramic specimen frequently occurred. We report here the results of microstructural SEM and TEM observations, and hardness measurements (Vickers indentation with a load of 49 N) performed on the pieces of the Al_2O_3 sintered body some few millimeters in size which remained unfractured.

3 Results and Discussion

3.1 Dependence of the Al_2O_3 average grain size and hardness on the hot-forging process conditions

Average grain size and Vickers hardness values of the hot-forged Al_2O_3 body are listed in Table 2 for various process conditions. Preheating temperatures were selected at 1200 or 1300°C because, according to the above quoted references, it was thought that in this temperature range enough densification could be achieved without significant grain growth.

An important find was that the deformation ratio of the metallic mold (defined as the ratio of the height difference before and after hot-forging to the height before hot-forging) should not exceed the range 30–60%. Actually, rather than influencing the

Table 2. Microstructural and hardness characteristics of Al_2O_3 for various hot-forging conditions

No.	*Preheating temp. (°C)*	*Max. load (MPa)*	*Type of compression ring*[a]	*Deformation ratio (%)*	*Grain size (μm)*	*Vickers hardness (GPa)*
1	1 200	80	—	30	0·19	7·6
2	1 200	282	A	30	0·19	8·0
3	1 200	392	A	50	0·20	12·4
4	1 200	414	B	40	0·19	15·7
5	1 200	467	A	60	0·19	18·2
6	1 200	520	B	50	0·19	19·1
7	1 300	40	—	30	0·30	15·3
8	1 300	282	A	30	0·30	15·5

[a] —, no ring; A, 35–25 × 25[h] mm; B, 30–25 × 25[h] mm.

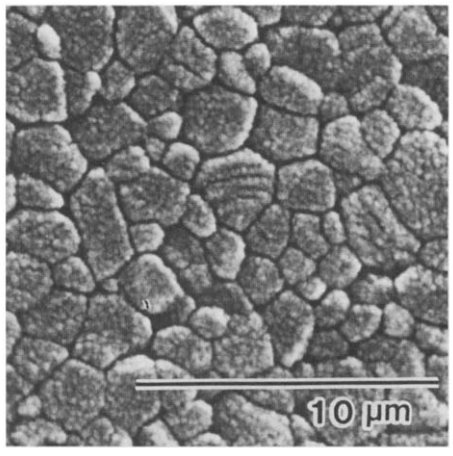

Fig. 4. Polished and thermal etched surface of hot-forged Al_2O_3 specimen (Specimen No. 5 in Table 2).

densification process, increasing deformation ratios were found to promote specimen cracking. This trend, which is found only in Al_2O_3 ceramics, could not be completely explained on the basis of the present experiments. The microstructure of the hot-forged Al_2O_3 specimen is shown in Fig. 4 after thermal etching of a polished surface. In Table 2, the average grain size as determined by intercept method on the polished and etched surfaces of various specimens are also shown. As seen, the Al_2O_3 average grain size slightly increased from 0·2 to 0·3 μm with increasing preheating temperature from 1200 to 1300°C. Furthermore, when the external supporting ring was used, due to the marked increase of the effect of pressure, a Vickers hardness value close to 19 GPa was measured.

It is known that the hardness of ceramic materials depends upon their density, the amount of impurities and the grain size. For example in sintered Al_2O_3 ceramics, although a value as high as 27 GPa has been exceptionally reported[11] for long-holding-time sintering at high temperature due to the presence of large grains, the hardness value of hot-pressed materials is generally measured in the range 19–22 GPa.[12–14] The hardness value measured in the present hot-forged material was very close to that reported in the previous literature. This represents a very promising result considering that the entire hot-forge processing of Al_2O_3 required only a few minutes of preheating cycle and 2 or 3 s of compression forging time. However, during removing of the Al_2O_3 sintered body from the metallic mold after hot-forging, the specimen was often chipped or fractured as a consequence of the high residual strains which generally remain stored in rapidly sintered ceramics.[8] In order to avoid this undesirable phenomenon, we examined the effect of a relatively long-term annealing process (24 h) at 1000–1200°C on typical hot-forged Al_2O_3 materials (specimens 2–6 as listed in Table 2). The selected range of annealing temperatures was thought to give a negligible grain-growth effect on the specimens. The results of the annealing experiments are listed in Table 3 in terms of average grain size and Vickers hardness. The grain size remained almost unchanged during annealing, but a marked increase in hardness was found. The hardness value measured in the present hot-forged/annealed materials was very close to the highest value previously reported for sintered Al_2O_3.[11–14]

Table 3. Microstructural and hardness characteristics of the hot-forged Al_2O_3 (Specimens No. 2 and 6 in Table 2) after annealing at various temperatures

No.	*Annealing temperature (°C)*[a]	*Grain size (μm)*	*Vickers hardness (GPa)*
2-1	1 000	0·19	8·8
2-2	1 100	0·19	20·0
2-3	1 200	0·21	21·6
6-1	1 100	0·19	23·2
6-2	1 200	0·23	23·0

[a] Annealing time: 24 h.

3.2 Microstructural characteristics of hot-forged bodies

According to the conclusions reached in the previous section, it is possible to densify Al_2O_3 by the hot-forge process avoiding almost completely the phenomenon of grain growth from the original size of the raw powder. In this section, the evolution during hot-forging of the Al_2O_3 microstructure is examined by SEM and TEM observation. The grain size of the starting Al_2O_3 powder was found to be homogeneously distributed around an average value of 0·15 μm (cf. Fig. 1). In Fig. 5, the fracture surface of the Al_2O_3 specimen hot-forged with a preheating temperature of 1200°C (corresponding to specimen No. 3 in Table 2), is shown as observed by SEM. At this stage of processing, the grain size distribution was found to be still homogeneous but the average grain size slightly increased. In order to

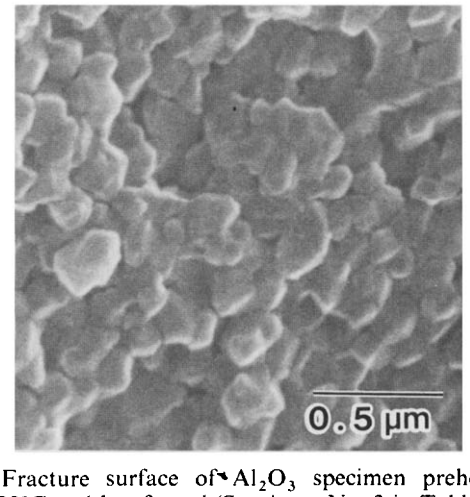

Fig. 5. Fracture surface of Al_2O_3 specimen preheated at 1200°C and hot-forged (Specimen No. 3 in Table 2).

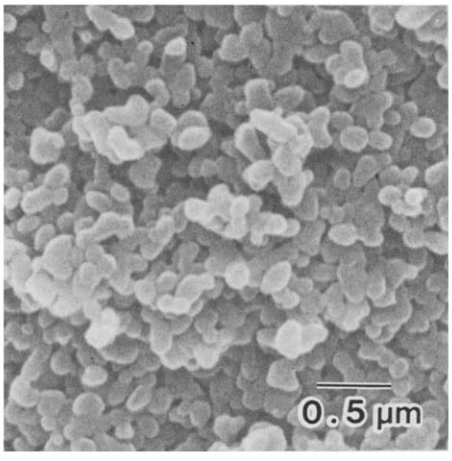

Fig. 6. Fracture surface of Al_2O_3 powder compact after 8 min preheating at 1200°C.

recognize whether such grain growth has occurred during hot-forging or, before this process, during preheating of the specimen, SEM observation of the specimen preheated at 1200°C for 8 min was carried out after removing it from the metallic mold. The result of this experiment is shown in Fig. 6. The specimen was found to be not sintered and its condition did not allow hardness measurements. The average grain size measured from Fig. 6 was about 0·2 μm. These circumstances prove that densification occurred almost completely in the few-second process of hot-forging while the grain size reached after the preheating stage was almost unchanged. Apart from the similar average grain size, however, the microstructures after preheating and after the preheating/hot-forging process (respectively shown in Fig. 6 and Fig. 5), show significant morphological differences. The most significant difference which could be observed by SEM is that, in the former specimens, the grains were round while in the latter a polyhedral shape implying a developed boundary between grains was clearly observed. This observation suggests that the deformation process under compression plays an important role in promoting both densification and bonding between grains.

Figure 7 shows the fracture surface of the hot-forged specimen preheated at 1200°C and annealed for 24 h at 1200°C which corresponds to No. 6-2 as listed in Table 3. This specimen was one showing a high hardness value. Beside a slight increase in grain size and in the flatness of the fracture surface compared with the as forged specimen, however, no further information could be obtained by observation at the SEM scale.

In the present report, then, we attempted to clarify the densification mechanisms by high-resolution TEM observation of the Al_2O_3 starting powder, and of the hot-forged and hot-forged/annealed bodies.

A TEM image of the starting powder with the respective result of electron-diffraction analysis are shown in Fig. 8. Despite the very fine size of the present raw Al_2O_3, the observed grains always showed a completely crystalline structure. It should be noted that the field of the electron beam in the present experiment was larger than the average grain size. This fact made it very difficult to obtain regular diffraction patterns during the analysis of the raw powder. However, the halo-pattern which is characteristic of glassy structures and frequently found in very fine powders, was never detected among the many analyses performed. A further, although indirect, confirmation of the crystalline nature of the present Al_2O_3 powder could be obtained by X-ray diffraction analysis. By comparing the raw powder and the same powder after 2 h annealing at 1300°C, the peak intensity of the two X-ray patterns did not

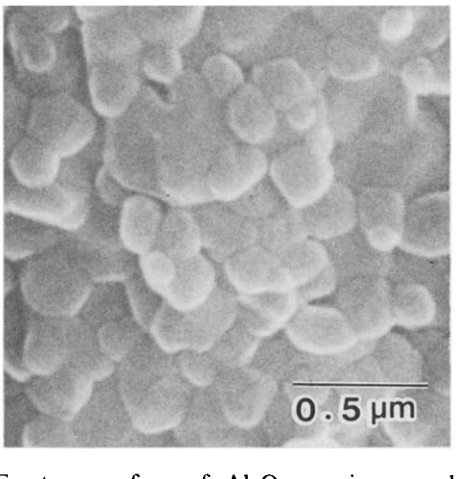

Fig. 7. Fracture surface of Al_2O_3 specimen preheated at 1300°C, hot-forged and annealed at 1200°C for 24 h (Specimen No. 6-2 in Table 3).

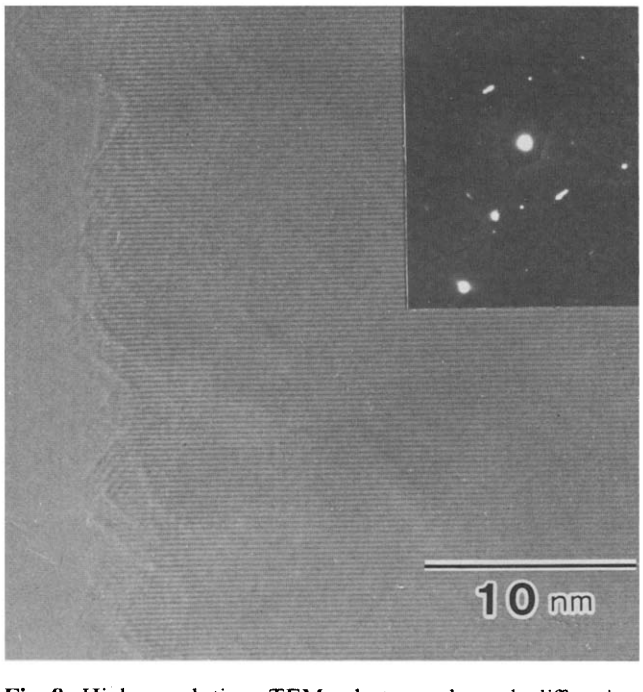

Fig. 8. High resolution TEM photograph and diffraction pattern of starting Al_2O_3 powder.

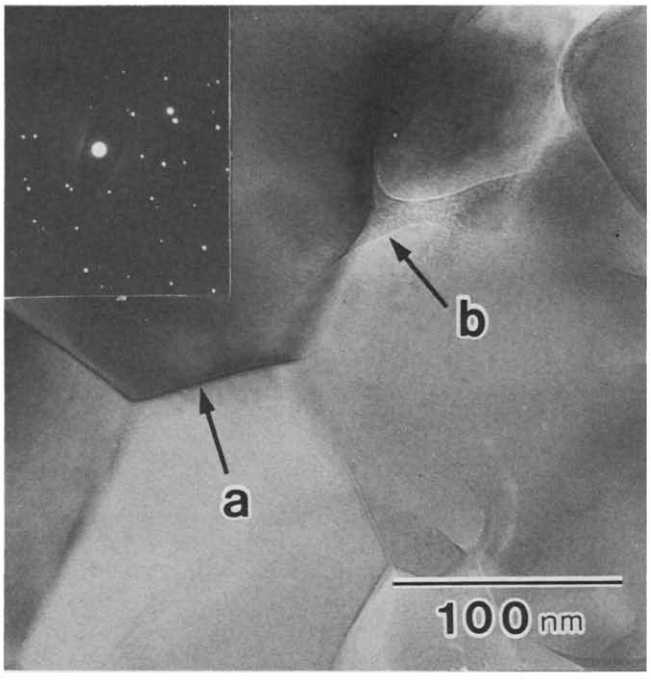

Fig. 9. TEM photograph and diffraction pattern of hot-forged Al_2O_3 specimen (Specimen No. 6 in Table 2). Zone well bonded (a) and zone still remaining non bonded (b) are clearly visible in the grain boundary.

show any detectable difference or, in other words, no trace of additional crystallization was found.

Figure 9 represents a TEM image of the Al_2O_3 specimen after hot-forging (No. 6 in Table 2). This specimen showed small grain size (comparable with that of the reheated only specimen) and it appeared dense. A more detailed examination, however, revealed both portions in which the grain boundary was well bonded [portion (a) in Fig. 9] as well as portions still disconnected as in the starting powder [portion (b) in Fig. 9]. Electron-diffraction analysis performed in the neighborhood of portion (b) is also shown in Fig. 9. Also in this specimen which was obtained by hot-forging only a crystalline structure of Al_2O_3 was systematically detected. A typical TEM image of the grain boundary in the hot-forged specimen is shown in Fig. 10 at the triple junction of

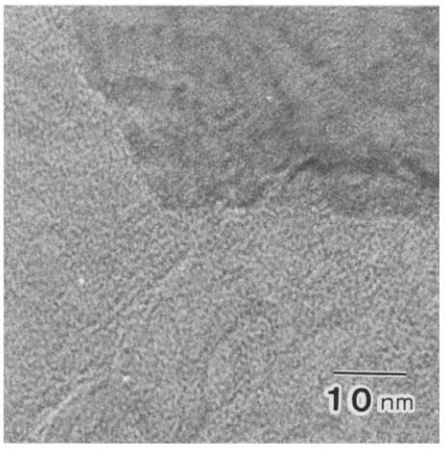

Fig. 10. Corrugated grain boundary observed in hot-forged Al_2O_3 specimen (same specimen as Fig. 9).

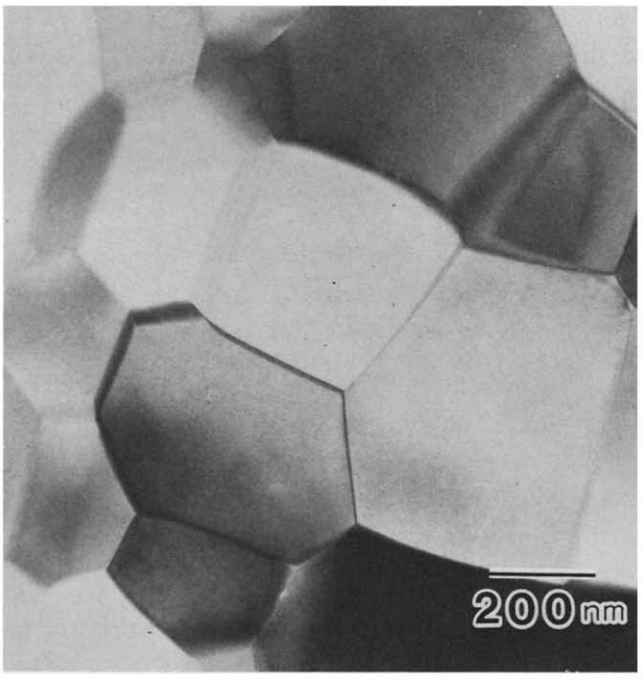

Fig. 11. TEM photograph of hot-forged Al_2O_3 specimen after annealing (Specimen No. 6-1 in Table 3).

the Al_2O_3 grains. The grain boundary appears very similar to that normally observed in Al_2O_3 sintered by other conventional methods but the presence of a visible curvature and of small corrugations may suggest that an incompletely stable thermodynamic status is reached in this specimen.

The result of TEM observation performed on the specimen hot-forged and successively annealed for 24 h at 1100°C (No. 6-1 in Table 3) is shown in Fig. 11. In this specimen, a homogeneous polycrystalline microstructure constituted by partially grown Al_2O_3 grains was developed. Furthermore, a clean and well bonded interface was observed throughout the TEM specimen (Fig. 12). In other words, it is recognized that, while the hot-forge method can be generally considered as a powerful method for densifying high-melting-point ceramic powders in a few seconds, in the case of Al_2O_3, a successive

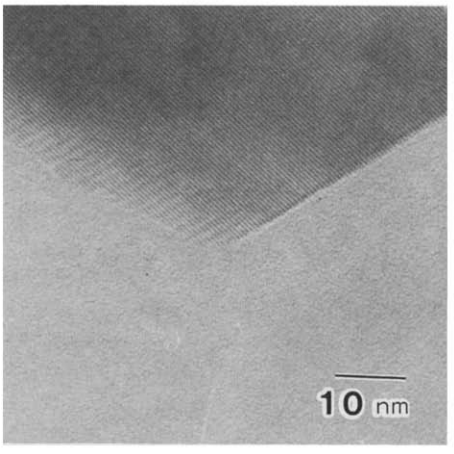

Fig. 12. TEM photograph of the grain boundary in annealed Al_2O_3 specimen (same specimen as Fig. 11).

annealing treatment for a relatively long time at moderate temperatures, is necessary to obtain an homogeneous and stable microstructure.

4 Summary

Dense Al_2O_3 ceramics with fine grain size were densified by the hot-forging of highly pure (99·99%) submicron-size (average 0·15 μm) Al_2O_3 starting powder. Although no sintering aid was added, a high degree of densification was achieved and no significant grain growth occurred when preheating and hot-forging at 1200°C. A detailed microstructural characterization by SEM and TEM revealed that a successive annealing cycle carried out at 1000–1200°C for 24 h on the hot-forged specimen made the microstructure more homogeneous and stable. Because of the relatively low value selected for the annealing temperature, the Al_2O_3 grains did not grow significantly beyond the size found in the as-forged specimen and a final grain size of about 0·2 μm was found. The hardness values measured in the annealed specimens were comparable with the high values usually found in Al_2O_3-based materials. Further studies and mechanical characterization will be necessary for a full understanding of both the densification mechanisms and the actual applicability of the present hot-forged Al_2O_3.

It is essential to note that, in the present processing, the temperature needed for densifying the Al_2O_3 powder was about 200°C lower than that usually found for other conventional sintering techniques, the required time was also very short (only a few seconds). Although several problems remain such as cracking or the presence of residual strains in the as-forged body or a perhaps not negligible degree of grain growth during the preheating of larger size specimens (obviously requiring a longer time for a homogeneous preheating), hot-forging sintering appears to be a very interesting technique for densifying highly refractory ceramics with small grain size.

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References

1. Karch, J., Barringer, R. & Gleiter, H., Ceramic ductile at low temperature. *Nature*, **330** (1987) 556–8.
2. Abe, S., Aoki, S., Kanzaki, S. & Tabata, H., Structural homogeneity of CIP formed powder compact (Part 3). *J. Ceram. Soc. Jpn*, **97** (1989) 432–8.
3. Kamiya, H., Suzuki, H., Kato, D. & Jimbo, G., Densification of alkoxide-derived fine silica powder compact by ultra-high-pressure cold isostatic pressing. *J. Am. Ceram. Soc.*, **76** (1993) 54–64.
4. Matsuo, Y., Nishimura, T., Jinbo, K., Yasuda, K. & Kimura, S., Forming of alumina powder by cyclic CIP. In *Proc. MRS '88*, **5** (1989) 151–7.
5. Matsuo, Y., Nishimura, T., Yasuda, K., Jinbo, K. & Kimura, S., Forming of silicon carbide powder by cyclic CIP. *J. Ceram. Soc. Jpn*, **99** (1991) 187–90.
6. Nishida, T., Shimano, S. & Urabe, K., Microstructure of Bi-superconducting ceramics prepared by hot-extrusion processing. *J. Jpn Soc. Powder & Powder Metallu.*, **38** (1991) 1089–93.
7. Nishida, T., Shimano, S. & Urabe, K., Microstructure of Bi-superconducting ceramics prepared by hot-forge processing. *J. Jpn Soc. Powder & Powder Metallu.*, **39** (1992) 397–400.
8. Nishida, T., Shiono, T., Fujioka, H. & Nishikawa, T., MgO and MgO–SiC whisker composite ceramics prepared by hot-forge processing. *J. Soc. Mater. Sci. Jpn*, **38** (1989) 1241–6.
9. Nishida, T., Fujioka, H., Adachi, K. & Urabe, K., Microstructure and mechanical properties of polycrystalline MgO prepared by hot-forge processing. *J. Soc. Mater. Sci. Jpn*, **41** (1992) 855–60.
10. Nishida, T., Shiono, T., Fujioka, H. & Nishikawa, T., Preparation of functionally gradient composite of MgO–Stainless steel by hot-forge processing. *J. Soc. Mater. Sci. Jpn*, **39** (1990) 292–7.
11. Jorgensen, P. J. & Westbrook, J. H., Role of solute segregation at grain boundaries during final stage sintering of alumina. *J. Am. Ceram. Soc.*, **47** (1964) 332–8.
12. Bradt, R. C., Cr_2O_3 solid solution hardening of Al_2O_3. *J. Am. Ceram. Soc.*, **50** (1967) 54–5.
13. Rankin, D. T., Stiglich, J. J., Petrak, D. R. & Ruh, R., Hot-processing and mechanical properties of Al_2O_3 with an Mo-dispersed phase. *J. Am. Ceram. Soc.*, **54** (1971) 277–81.
14. *Ceramic Source*, Vol. 1. The American Ceramic Society, OH, 1985, p. 325.