Ceramics International 29 (2003) 707–712

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The effect of starting powder on the microstructure development of alumina–aluminum titanate composites

Sang-Yeup Park[a,b,*], Sug-Woo Jung[b], Yung-Bin Chung[a]

[a]*Department of Ceramics Engineering, Kangnung National University, Kangnung, Kangwondo 210-702, South Korea*
[b]*Technology Innovation Center for Fine Ceramics, Kangnung National University, Kangnung, Kangwondo 210-702, South Korea*

Received 12 May 2002; received in revised form 30 May 2002; accepted 12 September 2002

Abstract

The effect of starting powder on Al_2TiO_5 morphology and grain growth of Al_2O_3 was investigated in alumina–aluminum titanate composites using Al_2O_3, TiO_2 and calcined Al_2TiO_5 as starting powders. Depending on the composition of starting powders, various Al_2TiO_5 morphologies, such as rod-like, polyhedron-like, and irregular shape were observed. When Al_2O_3 and TiO_2 were used as starting powder, the rod-like shape and the irregular shape of Al_2TiO_5 were observed. In the addition of calcined Al_2TiO_5 as starting powder, however, the polyhedron-like shape and the irregular shape of Al_2TiO_5 were observed. When the starting powder was consisted of Al_2O_3 and TiO_2, alumina-aluminum titanate composites provided more narrow size distribution and smaller average size of Al_2O_3 grains compared to those consisting of Al_2O_3 and Al_2TiO_5.

Keywords: A. Grain growth; B. Composites; D. Al_2O_3; D. Al_2TiO_5; Morphology

1. Introduction

Aluminum titanate, Al_2TiO_5, is known to be a promising candidate material for the application fields of refractory and engine components because of its low thermal expansion, excellent thermal shock resistance, and low thermal conductivity [1]. In general, aluminum titanate can be formed by the solid-state reaction between Al_2O_3 and TiO_2 above the eutectoid temperature 1280 °C. Because aluminum titanate can be dissociated to alumina and rutile in the temperature range 750–1280 °C, however, the stabilizers such as Fe_2O_3, MgO or SiO_2 are needed to overcome such dissociation [2–5].

In alumina-based composites, much attention has been focused on the improvement of fracture toughness in alumina either by the addition of second phase or by the microstructure designs such as duplex [6] or duplex-bimodal [7], heterogeneous [8–10], and layer structures [11–13]. The addition of Al_2TiO_5 to Al_2O_3 improves the fracture toughness of alumina due to the enhancement of the local residual stress induced by the difference of thermal expansion coefficient between Al_2O_3 and Al_2TiO_5 [7,14]. Considering the toughening mechanisms in alumina-based composites materials, it is important to control the microstructure of matrix as well as the morphology of second-phase [15]. However, the morphology control of Al_2TiO_5 and its effect on grain growth of Al_2O_3 matrix have not been investigated yet in alumina–aluminum titanate composites [1,14,16–20].

The present work is aimed at the investigating of the effect of starting powders on morphology of Al_2TiO_5 and grain growth behavior of Al_2O_3. Also, the shape formation process of Al_2TiO_5 grain was discussed in terms of coalescence behavior via pore trapping process.

2. Experimental

Samples were prepared from commercial α-Al_2O_3 (~0.3 μm average size, ~99.999% purity, AKP-50, Sumitomo Chemicals, Japan) and TiO_2 (~0.5 μm average size, ~99.9% purity, Sigma-Aldrich, USA) powders. Al_2TiO_5 powder (~5.1 μm average size) was prepared from the calcination of equimolar mixtures of Al_2O_3 and TiO_2 at 1300 °C for 3 h in air. The compositions of the

* Corresponding author. Tel.: +82-33-640-2363; fax: +82-33-640-2244.

E-mail address: sypark@knusun.kangnung.ac.kr (S.-Y. Park).

0272-8842/03/$30.00
doi:10.1016/S0272-8842(02)00221-3

starting powder are listed in Table 1. T(5), T(10), and T(20) mean the samples using TiO_2 as starting powder, resulting in the composition of Al_2O_3–$05Al_2TiO_5$ (wt.%), Al_2O_3–$10Al_2TiO_5$, and Al_2O_3–$20Al_2TiO_5$, respectively. AT(5), AT(10), and AT(20) mean the samples using calcined Al_2TiO_5 as starting powder, resulting in the composition of Al_2O_3–$5Al_2TiO_5$, Al_2O_3–$10Al_2TiO_5$, and Al_2O_3–$20Al_2TiO_5$, respectively.

The proportioned powders were mixed by wet-milling in a teflon jar using Si_3N_4 balls as milling media for 3 h. The slurries were dried and then sieved to ~200 mesh. The powders were isostatically pressed under ~200 MPa, and then sintered at 1600 °C for 1 h in air. The sintered samples were polished to a 1 μm finish and thermally etched at 1450 °C for 20 min in air. Average grain size and grain size distribution were determined by measuring each grain using image analyzer (Omnimet Advantage, Buehler, USA). About 400 grains were measured for each sample.

Table 1
The compositions of starting powder used for alumina–aluminum titanate composites

Sample	Compositions (wt.%)	Starting powders
T(5)	Al_2O_3–$5Al_2TiO_5$	Al_2O_3, TiO_2
T(10)	Al_2O_3–$10Al_2TiO_5$	Al_2O_3, TiO_2
T(20)	Al_2O_3–$20Al_2TiO_5$	Al_2O_3, TiO_2
AT(5)	Al_2O_3–$5Al_2TiO_5$	Al_2O_3, Al_2TiO_5
AT(10)	Al_2O_3–$10Al_2TiO_5$	Al_2O_3, Al_2TiO_5
AT(20)	Al_2O_3–$20Al_2TiO_5$	Al_2O_3, Al_2TiO_5

3. Results and discussion

Fig. 1 shows the SEM micrographs of (a) T(5), (b) T(10), and (c) T(20) samples sintered at 1600 °C for 1 h in air using Al_2O_3, TiO_2 as starting powder. Darker grains are Al_2O_3 and lighter grains are Al_2TiO_5. The grain shape of Al_2TiO_5 shows an irregular in T(5) and T(20) samples of Fig. 1(a) and (c), whereas a rod-like shape in T(10) sample of Fig. 1(b). The rod-like shape of Al_2TiO_5 indicated by the arrow in Fig. 1(b) exhibited the aspect ratio up to ~21. As an interesting result, the Al_2TiO_5 particles with rod-like shape were observed and the Al_2TiO_5 particles were located at the junction of Al_2O_3 grains with trapped pores. Fig. 2 shows the SEM micrographs of (a) AT(5), (b) AT(10), and (c) AT(20) samples sintered at 1600 °C for 1 h in air using calcined Al_2TiO_5 as starting powder. Compared to T-series samples, Al_2TiO_5 particles in AT-series samples showed irregular or polyhedron-like shapes without showing any rod-like shape. Similar to the T-series samples, Al_2TiO_5 particles were located at the junction of Al_2O_3 grains with trapped pores.

Fig. 3 shows the SEM micrographs of (a) T(20), (b) T(10), and (c) AT(5) samples showing Al_2TiO_5 particles of irregular, rod-like, and polyhedron-like shapes, respectively. Regardless of shapes, the Al_2TiO_5 particles were composed of single or poly-grains. A possible explanation might be that Al_2TiO_5 poly-grains were coalescenced into a single grain, and pores were trapped into the Al_2TiO_5 grain during the coalescence process. From the careful observation of Al_2TiO_5 grains, trapped pores were disappeared during the successive coarsening of Al_2TiO_5. Taruta et al. showed that Al_2TiO_5 particles formed by the reaction between Al_2O_3 and TiO_2 at the junction of Al_2O_3 grains [21]. When the Al

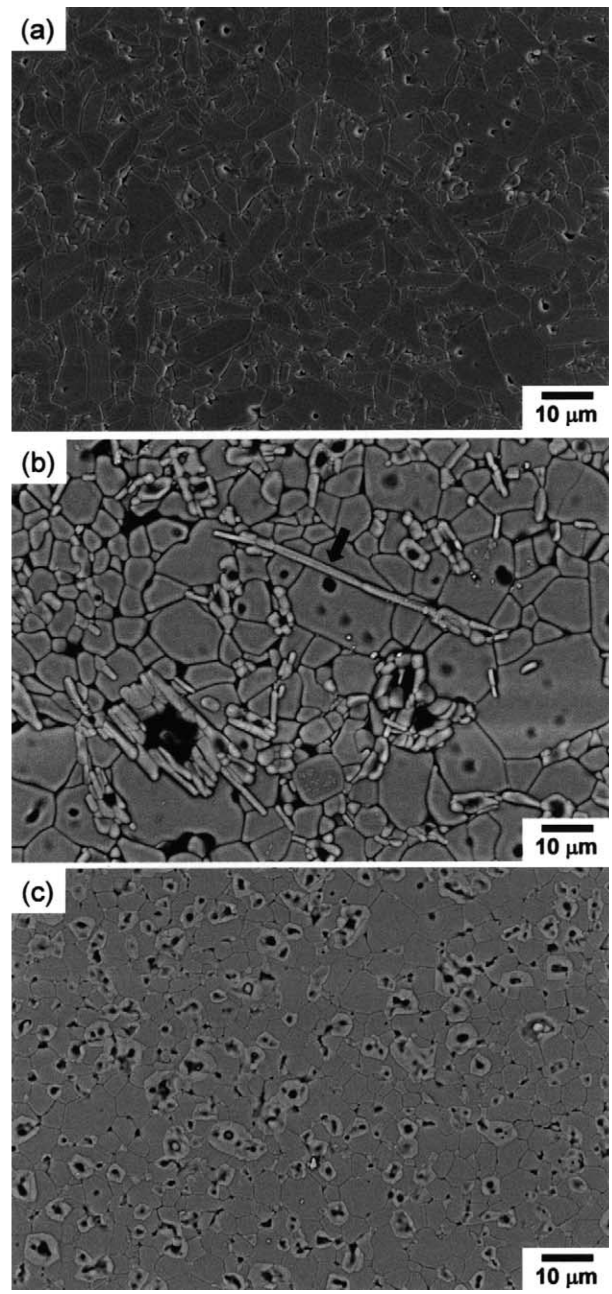

Fig. 1. SEM micrographs of (a) T(5), (b) T(10), and (c) T(20) samples sintered at 1600 °C for 1 h in air using TiO_2 as a starting powder. The arrow in (b) shows a rod-like Al_2TiO_5 precipitate of which aspect ratio is up to ~21.

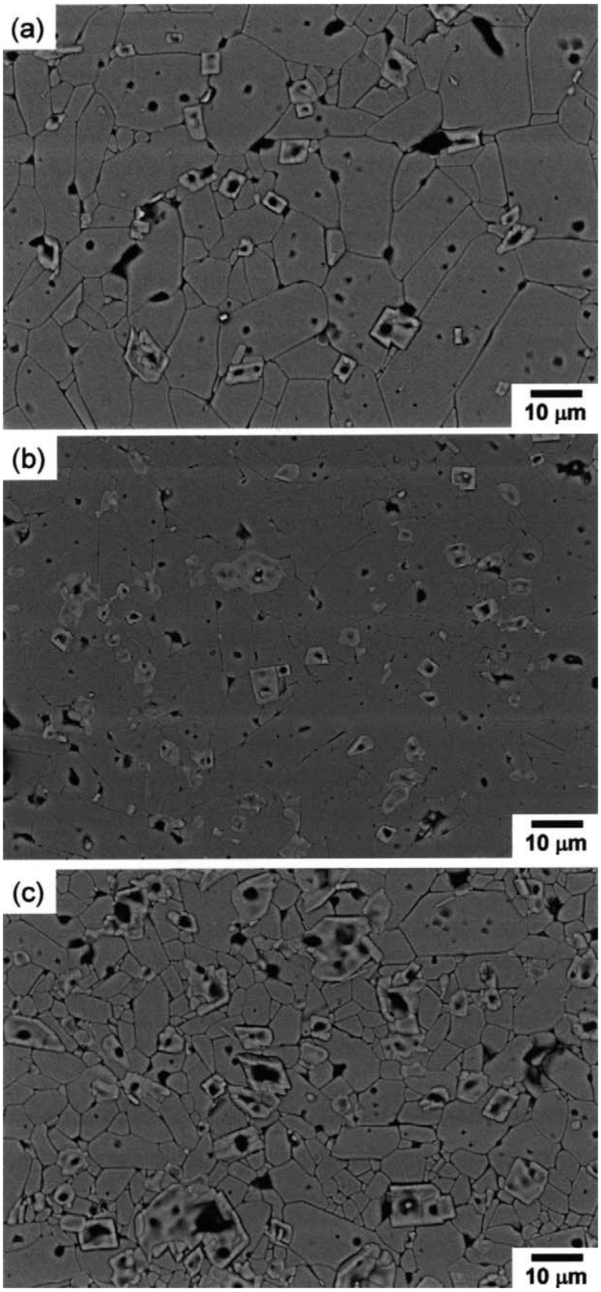

Fig. 2. SEM micrographs of (a) AT(5), (b) AT(10), and (c) AT(20) samples sintered at 1600 °C for 1 h in air using calcined Al_2TiO_5 as a starting powder.

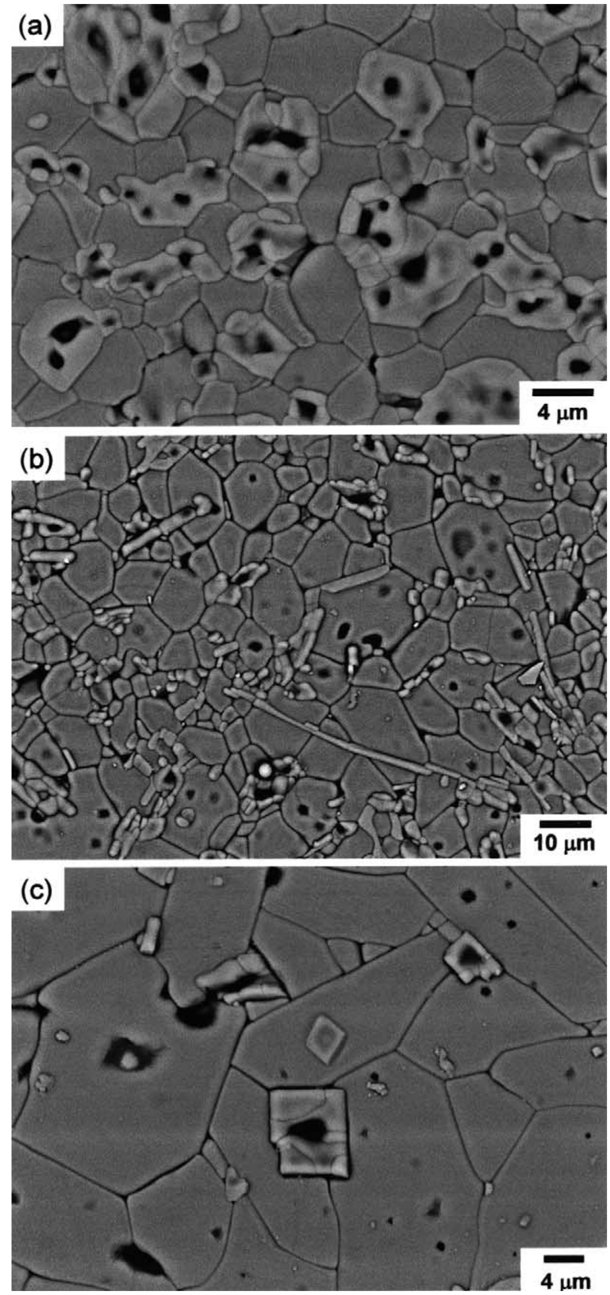

Fig. 3. SEM micrographs of (a) T(20), (b) T(10), and (c) AT(5) samples showing Al_2TiO_5 particles of irregular, rod-like, and polyhedron-like shapes, respectively.

ions were supplied easily for the growth, Al_2TiO_5 particle might be nucleated on the Al_2O_3 grains. Once the small size of Al_2TiO_5 particles grow and contact with each other, a large Al_2TiO_5 poly-grain forms at the junction of Al_2O_3 grains.

When the Al_2TiO_5 particles grow faster until pore closure occurs, pore remains at the inside of Al_2TiO_5 poly-grain. Depending on the pore size after pore closure, a small pore disappears and a large pore will remain at the inside of Al_2TiO_5 poly-grain. During the successive coarsening of Al_2TiO_5, the large pore shrinks and then the pore moves into the center region of Al_2TiO_5 poly-grain. Such mechanism of pore shrinkage is somewhat different compared to normal grain growth; i.e. when the pores were located at the inside of grain, such pores could not be eliminated even if high external pressure was applied.

The precipitate shapes are closely related with the interface coherency between precipitate and matrix [22]. When the precipitate is especially located on grain

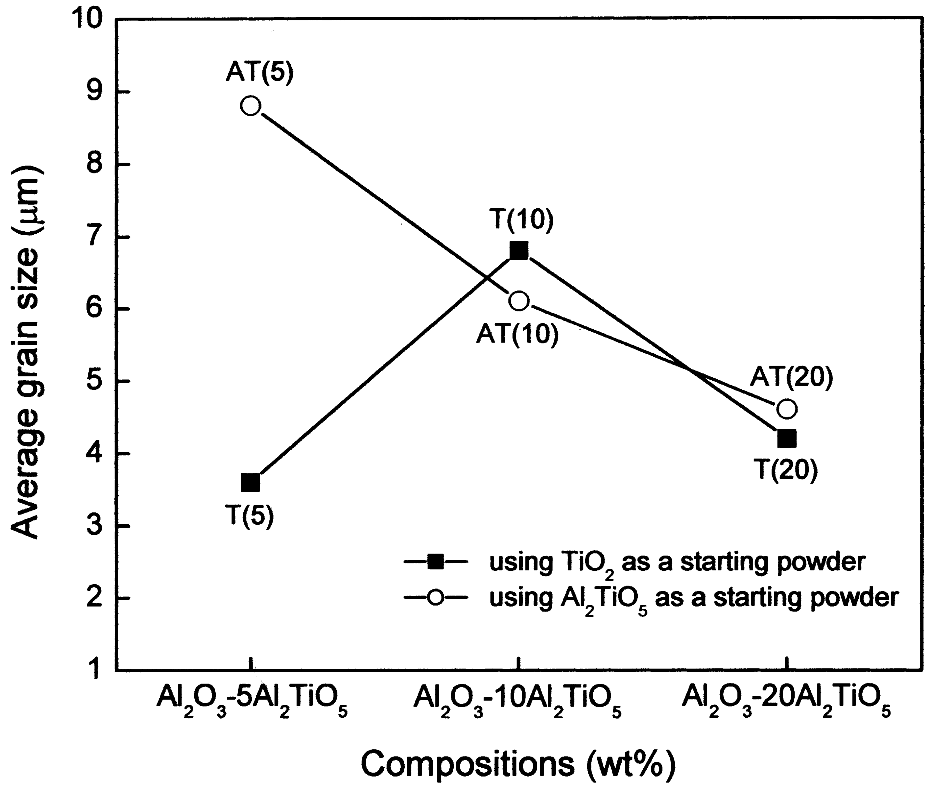

Fig. 4. Variation of average grain size of Al_2O_3 in T-series and AT-series samples. T(5) sample shows the smallest Al_2O_3 grain size.

boundary, it is necessary to consider the types of interface between two different grain orientations. The minimization of interfacial energy leads to planar (semi-) coherent interfaces and smoothly curved incoherent interfaces although the interfacial tensions and torques must be balanced at the intersection between the precipitate and the matrix [22]. Al_2TiO_5 precipitates are located at the junction of Al_2O_3 grains and form interfaces with more than three differently oriented grains. Even though the situation is more complex comparing with a precipitate on grain boundaries, the entire shape of the Al_2TiO_5 precipitate will, therefore, become irregular shape, such as T(5) and T(20) samples showing in Fig. 1, because their interfaces can be mixed with planar and smoothly curved interfaces. On the other hand, in the case of partially coherent precipitates which have (semi-) coherent and incoherent interfaces at the same time, the incoherent interface grows faster than the (semi-) coherent one because of higher interfacial energy [22]. It is feasible that Al_2TiO_5 precipitates become partially coherent as the amount of Al_2TiO_5 increase, in respect to that the interface of a precipitate varies from (semi-) coherent to incoherent as the precipitates grow [22]. Therefore, we suppose that Al_2TiO_5 precipitates became rod-like shape such as the T(10) sample in Fig. 1(b) because of partially coherent interface.

In the addition of Al_2TiO_5 particles as starting powder in AT-series, the Al_2TiO_5 particles wouldn't react with Al_2O_3 grains, but only coalescence with each other at the junction of Al_2O_3 grains during sintering. If the polygonization of Al_2TiO_5 particles, of which crystal structure is end-centered orthorhombic [2], proceeds with sintering before the complete besiegement of Al_2O_3 grains, it is possible that Al_2TiO_5 particles will have polyhedron-like shapes such as the AT-series samples shown in Fig. 2.

Fig. 4 shows the variation of average grain size of Al_2O_3 in T-series and AT-series samples. T(5) and T(20) samples, except for T(10) sample, have smaller average grain sizes of Al_2O_3 than AT-series samples. In addition, the average grain sizes of Al_2O_3 in AT-series samples decreases with increasing the Al_2TiO_5 content, whereas the average grain sizes of Al_2O_3 in T-series samples increase with increasing the Al_2TiO_5 content. Fig. 5 shows the grain size distribution of Al_2O_3 in six samples, as shown in Fig. 4. T-series samples exhibited more narrow size distribution and small grain size compared to those of AT-series samples. This grain growth behavior of Al_2O_3 in AT-series indicates that Al_2TiO_5 particles act as an inhibitor for grain growth. In contrast, the unique behavior of Al_2O_3 in T(10) sample, resulting in accelerating the grain growth of some of Al_2O_3, is supposed to the rapid growth of rod-like Al_2TiO_5 precipitates due to the local increase of Al ions.

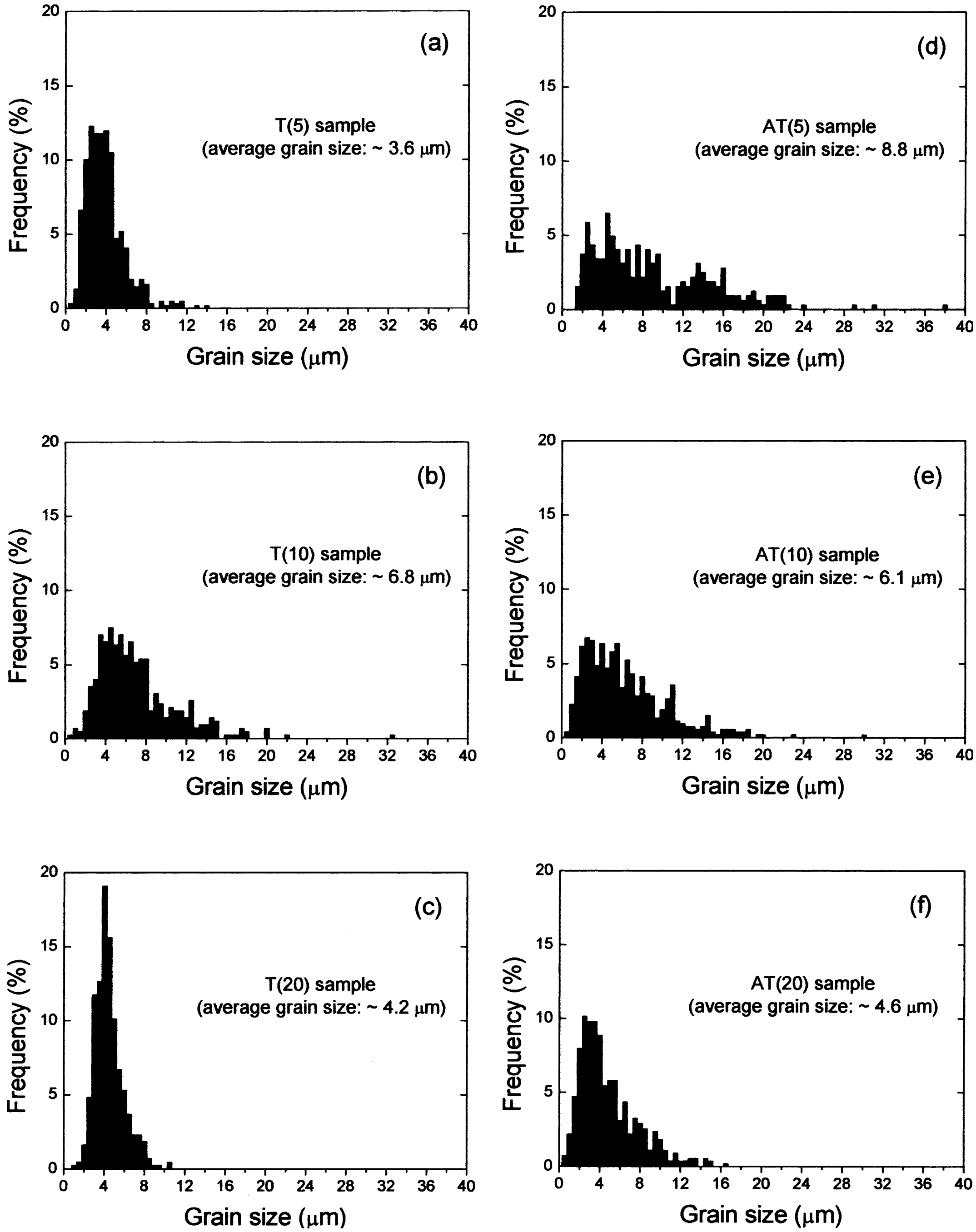

Fig. 5. Grain size distributions of Al_2O_3 matrix of T-series and AT-series samples in Fig. 4. T(20) sample shows the most narrow size distribution of Al_2O_3 grains.

4. Conclusions

In this study, the effect of starting powders on the Al_2TiO_5 morphology and the grain growth behavior of Al_2O_3 was investigated in alumina-aluminum titanate composites. When Al_2O_3 and TiO_2 were used as starting powders, the rod-like shape of Al_2TiO_5 was changed into the irregular shape with increasing the Al_2TiO_5 content. When Al_2O_3 and calcined Al_2TiO_5 were used as starting powders, the polyhedron-like shape of Al_2TiO_5 was changed into the irregular shape with increasing the Al_2TiO_5 content. The trapped pores inside of Al_2TiO_5 grain were explained by the coalescence behavior of small Al_2TiO_5 particles. Based on the grain growth behavior of Al_2O_3, when we are aiming at more narrow size distribution and smaller average size of Al_2O_3 grains in alumina-aluminum titanate composites, it would be more helpful to use Al_2O_3 and TiO_2 as starting powder than those using Al_2O_3 and Al_2TiO_5.

References

[1] I.M. Low, Synthesis and properties of in situ layered and graded aluminum titanate/alumina composites, Mater. Res. Bull. 33 (10) (1998) 1475–1482.

[2] H.A.J. Thomas, R. Stevens, Aluminium titanate—a literature review. Part 1: microcracking phenomena, Trans. Br. Ceram. Soc. 88 (1989) 144–151.

[3] E. Kato, K. Daimon, J. Takahashi, Decomposition temperature of β-Al_2TiO_5, J. Am. Ceram. Soc. 63 (5-6) (1980) 355–356.

[4] L. Zhien, Z. Qingmin, Y. Jianjun, The effects of additives on the properties and structure of hot-pressed aluminum titanate ceramics, J. Mater. Sci. 31 (1996) 90–94.

[5] T.S. Liu, D.S. Perera, Long-term thermal stability and mechanical properties of aluminium titanate at 1000–1200 °C, J. Mater. Sci. 33 (1998) 995–1001.

[6] M.P. Harmer, H.M. Chan, G.A. Miller, Unique opportunities for microstructural engineering with duplex and laminar ceramic composites, J. Am. Ceram. Soc. 75 (7) (1992) 1715–1728.

[7] N.P. Padture, S.J. Bennison, H.M. Chan, Flaw-tolerance and crack-resistance properties of alumina–aluminum titanate composites with tailored microstructures, J. Am. Ceram. Soc. 76 (9) (1993) 2312–2320.

[8] P.L. Chen, I.W. Chen, In-situ alumina/aluminate platelet composites, J. Am. Ceram. Soc. 75 (9) (1992) 2610–2612.

[9] J. Wang, C.B. Ponton, P.M. Marquis, Silver-toughened alumina ceramics, Br. Ceram. Trans. 92 (2) (1993) 67–74.

[10] L. An, H.M. Chan, R-curve behavior of in-situ-toughened Al_2O_3:$CaAl_{12}O_{19}$ ceramic composites, J. Am. Ceram. Soc. 79 (12) (1996) 3142–3148.

[11] C.J. Russo, M.P. Harmer, H.M. Chan, G.A. Miller, Design of a laminated ceramic composite for improved strength and toughness, J. Am. Ceram. Soc. 75 (12) (1992) 3396–3400.

[12] P.E.D. Morgan, D.B. Marshall, Ceramic composites of monazite and alumina, J. Am. Ceram. Soc. 78 (6) (1995) 1553–1563.

[13] L. An, H.M. Chan, N.P. Padture, B.R. Lawn, Damage-resistant alumina-based layer composites, J. Mater. Res. 11 (1) (1996) 204–210.

[14] J.F. Bartolomé, J. Requena, J.S. Moya, M. Li, F. Guiu, Cyclic fatigue crack growth resistance of Al_2O_3–Al_2TiO_5 composites, Acta Mater. 44 (4) (1996) 1361–1370.

[15] B.R. Lawn, Fracture of Brittle Solids, Cambridge University Press, 1996, pp. 72–85, 202–206.

[16] S.C. Lee, P.G. Wahlbeck, Chemical kinetics and mechanism for the formation reaction of Al_2TiO_5 from alumina and titania, High Temp. Sci. 21 (2) (1986) 27–40.

[17] B. Freudenberg, A. Mocellin, Aluminum titanate formation by solid-state reaction of fine Al_2O_3 and TiO_2 powders, J. Am. Ceram. Soc. 70 (1) (1987) 33–38.

[18] B. Freudenberg, A. Mocellin, Aluminum titanate formation by solid-state reaction of coarse Al_2O_3 and TiO_2 powders, J. Am. Ceram. Soc. 71 (1) (1988) 22–28.

[19] D.P.H. Hasselman, K.Y. Donaldson, E.M. Anderson, T.A. Johnson, Effect of thermal history on the thermal diffusivity and thermal expansion of an alumina–aluminum titanate composite, J. Am. Ceram. Soc. 76 (9) (1993) 2180–2184.

[20] L.A. Stanciu, J.R. Groza, Effect of high heating rates on microstructure of alumina and aluminum titanate ceramics, Microscopy and Microanalysis 7 (2) (2001) 414–415.

[21] S. Taruta, Y. Itou, N. Takusagawa, K. Okada, N. Otsuka, Influence of aluminum titanate formation on sintering of bimodal size-distributed alumina powder mixtures, J. Am. Ceram. Soc. 80 (3) (1997) 551–556.

[22] D.A. Porter, K.E. Eastering, Phase Transformations in Metals and Alloys, Van Nostrand Reinhold Company, New York, 1981, pp. 142–161.