Fabrication of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Micro/Nano-Composite Prepared by High Energy Ball Milling

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An Al_2O_3 -5 vol% ZrO_2 micro/nano-composite was successfully fabricated by sintering the high-energy ball milled mixture of commercial Al_2O_3 powder and zirconium alkoxide. The composite could be sintered to a nearly full density at 1450°C in the ambient atmosphere. The microstructure consisted of the fine dispersions of ZrO_2 particles, both intra-granular type of ~ 50 nm and inter-granular type of ~ 0.2 μm , and Al_2O_3 matrix grains of ~ 0.6 μm . The role of high energy ball milling in the present nano-composite formation was primarily the refinement of the Al_2O_3 grains and the introduction of strains in them.

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1. Introduction

Since Niihara *et al.*¹⁻³⁾ reported that the incorporation of nanometer-sized dispersoid into ceramic matrix could significantly improve mechanical properties, there has been a growing interest in ceramic-matrix nano-composites. For example, Al_2O_3 based nano-composites with 5 vol% particles of non-oxide such as SiC, Si_3N_4 and TiC showed a 2 to 3 times higher fracture strength and 1.5 times higher fracture toughness than those of monolithic Al_2O_3 . However, because of the relatively poor sinterability of the mixed powder, hot pressing or HIPing at a temperature above 1600°C is required. They also required a controlled atmosphere to avoid the oxidation of the non-oxide particles. Therefore the incorporation of oxide particles seems to be favorable for Al_2O_3 matrix, since the compact can be sintered in the ambient atmosphere. The material is also expected to have better sinterability, because oxide ceramics generally have higher sinterability than non-oxide ceramics.

ZrO_2 -toughened Al_2O_3 (ZTA), in which ZrO_2 exists as the dispersed second phase, has attracted much interest because of its enhanced strength and fracture toughness.⁴⁾ In the composites, however, the sizes of ZrO_2 particles are relatively large and they are predominantly dispersed between Al_2O_3 grains. The conventional ball mill mixing of commercial powders does not seem to embed nano-size particles into the matrix grains. To fabricate an intra-granular nano-composite, there seem to be two conditions to be met. One is starting with fine-particles especially for the dispersoid, and the other is the homogeneous mixing of both powders. Commercially available Al_2O_3 powder (0.2 μm) appears to be sufficiently fine for the matrix. However, the particle size of commercial zirconia seems to be too large for the dispersoid unless the particles are further refined by some means before ball mill mixing.

High energy ball milling (HE ball milling) is known to induce a significant phenomenon called mechanical alloying (MA), which is often used to prepare solid solutions, amorphous and nano-crystalline particles.⁵⁻⁸⁾ Even though the effect of MA is not known for $\text{Al}_2\text{O}_3/\text{ZrO}_2$ system, a refinement

of Al_2O_3 powder and the formation of a homogeneous mixture are expected.

The purpose of the present study is to fabricate $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nano-composite using HE ball-mill and zirconium alkoxide along with commercial Al_2O_3 powder as matrix. The mechanism of nano-composite formation was also investigated.

2. Experimental Procedure

Commercial α - Al_2O_3 powder (TM-DAR, Taimei Chemical Co., Japan) with an average grain size of 200 nm was used as matrix. Zirconium n-butoxide ($\text{Zr}(\text{O}-n\text{C}_4\text{H}_9)_4$, Hokko Chemicals Co., Japan) was used as the starting material for the dispersoid. Zirconium n-butoxide with 5 vol% ZrO_2 in final $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite was deposited on Al_2O_3 powder as follows. Al_2O_3 powder was poured into a dilute solution of zirconium butoxide in ethanol. The suspension was severely agitated by ultrasonic homogenizer and stirred while heating at 50°C. Dilute water solution in ethanol was also prepared and heated to 50°C. The solution was poured into the previously prepared mixture of powder/alkoxide suspension and allowed the hydration of the alkoxide. After stirring for several hours, the slurry was washed and dried in a rotary evaporator. The powder was calcined at 700°C for 2 h and then HE ball-milled by a planetary ball mill (Fritsch, Model P6). High purity Al_2O_3 balls of 5mm diameter in an Al_2O_3 jar of volume 250 ml are used in HE ball milling. A batch of 15 g powder was milled with 70 g of Al_2O_3 balls for 1 to 4 h with a rotating speed of 500 rpm. To improve the sinterability, the HE ball milled powder was further milled in ethanol for 24 h using a conventional ball mill with the addition of 0–0.5 mass% MgO. The conventional ball milling was conducted in a polyethylene pot (600 ml) with Al_2O_3 balls. The milled powder mixtures were uniaxially pressed and then CIPed at 200 MPa. The compacts were sintered at a temperature between 1450 and 1550°C for 2 h.

Phase identification of the specimens was performed by X-ray diffraction analysis (XRD) with $\text{CuK}\alpha$ radiation. The volume fraction of m- ZrO_2 with respect to the total ZrO_2 (here after referred to as the relative content of m- ZrO_2) was

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determined from the integrated peak intensities of $(\bar{1}11)_m$, $(111)_m$ and $(111)_t$ peaks.⁹⁾ The lattice parameters of the α - Al_2O_3 in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites were measured by XRD and compared with the raw Al_2O_3 powder. Crystallite size and lattice strain were also estimated from the peak broadening.¹⁰⁾ The densities of sintered specimens were measured by Archimedes method, where the theoretical densities of α - Al_2O_3 , t- ZrO_2 and m- ZrO_2 were used as 3990, 6080 and 5840 kg/m^3 , respectively.^{11–13)}

Microstructures were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The average grain size of both Al_2O_3 and ZrO_2 particles was measured separately by the linear intercept method on SEM micrographs.¹⁴⁾ The particle size distribution of intra-/inter-granular ZrO_2 particles was measured from SEM micrographs of at least 450 grains for each sample.

3. Results

Figure 1 shows the microstructure of Al_2O_3 -5 vol% ZrO_2 composite prepared from Al_2O_3 powders and Zr alkoxide mixed in the conventional ball mill and sintered at 1500°C for 2 h. Although relatively small ZrO_2 particles were uniformly dispersed, they were predominantly located along the grain boundaries and at triple points of Al_2O_3 grains. Thus, simply adding fine ZrO_2 powders through Zr alkoxide was not sufficient to bring about an intra-granular nano-composite.

Figure 2 shows the variation of the relative density with HE ball milling time for the specimens sintered at 1550°C for 2 h. The density of the composite significantly decreased with increasing HE ball milling time. However, when the HE ball milled powders were further treated with a conventional ball mill, the density was partly recovered (Fig. 3). Further densification was obtained by doping a small amount of MgO. The density of the sintered pellet was also plotted in Fig. 3 against the amount of MgO dopant for both 1 h and 2 h HE ball milled powders. Maximum density of the sintered pellet was achieved at 0.2 mass% of MgO dopant for both 1 h and 2 h HE ball milled powders. Based on these results, the procedure where HE ball milling for 1 h followed by conventional ball milling with the addition of 0.2 mass% MgO was adopted

as the optimum powder preparation.

Figure 4 shows the relative density of the composite against the sintering temperature. The composite attained a density above 99% when sintered at a temperature between 1450 and 1550°C, which is considerably lower than those required for Al_2O_3 /non-oxide nano-composites.²⁾ ZrO_2 particles could be either tetragonal (t- ZrO_2) or monoclinic phase (m- ZrO_2). The relative content of the m- ZrO_2 is plotted also in Fig. 4, where a monotonic increase of the m-phase is observed with increasing sintering temperature.

The microstructure of the specimen sintered at 1550°C is

Fig. 2 The variation of the relative density with the time of HE ball milling for Al_2O_3 -5 vol% ZrO_2 composite sintered at 1550°C for 2 h.

Fig. 3 The relative densities of Al_2O_3 -5 vol% ZrO_2 composites sintered at 1550°C for 2 h as a function of MgO content.

Fig. 1 The microstructure of Al_2O_3 -5 vol% ZrO_2 composite sintered at 1500°C for 2 h without HE ball milling.

Fig. 4 The relative density and the relative content of m- ZrO_2 in Al_2O_3 -5 vol% ZrO_2 composites against the sintering temperature.

Fig. 5 An SEM micrograph of Al_2O_3 -5 vol% ZrO_2 nano-composite sintered at 1550°C for 2 h.

Fig. 6 TEM micrographs of Al_2O_3 -5 vol% ZrO_2 nano-composites sintered at (a) 1500°C and (b) 1450°C for 2 h.

shown by an SEM micrograph in Fig. 5 and those sintered at 1500 and 1450°C are shown by TEM micrographs in Figs. 6(a) and (b), respectively. ZrO_2 particles show a white contrast in SEM micrograph, but dark contrast in TEM micrographs. In all specimens, even though most of the ZrO_2 particles were still observed along grain boundaries and at triple points of the Al_2O_3 grains, some ZrO_2 particles were found embedded in the matrix grains. It is noted that these intra-granular particles are relatively small and nearly spherical.

The average grain size of Al_2O_3 grains observed by SEM is plotted against the sintering temperature in Fig. 7. The de-

Fig. 7 The average grain size of Al_2O_3 in Al_2O_3 -5 vol% ZrO_2 composites against the sintering temperature.

Fig. 8 The XRD pattern of Al_2O_3 -5 vol% ZrO_2 powders (a) before and (b) after HE ball milling for 1 h.

pendence of grain size on the sintering temperature was considerably high. The grain size of the specimen sintered at 1450°C was only $0.6\mu\text{m}$, which was smaller than $1/3$ of the Al_2O_3 /non-oxide nano-composites. The composite sintered at 1450°C is therefore expected to have improved mechanical properties due to the small matrix grains incorporated with intra-granular nano-sized tetragonal ZrO_2 particles.

4. Discussion on the Role of HE Ball Milling

An intra-granular nano-composite of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ system was successfully fabricated by using Zr alkoxide for the second phase and HE ball milling. It has been shown that HE ball mill was essential for making nano-particle dispersion in the matrix grains. The probable effect of HE ball milling on the present system are suggested to be as follows: (1) mechanical alloying or amorphous formation, (2) refinement of Al_2O_3 particles, and (3) introduction of strain into the Al_2O_3 particles.

Figure 8 shows the XRD patterns of Al_2O_3 -5 vol% ZrO_2 powders before and after HE ball milling for 1 h. The broad peak at 30° (2θ) representing (111) reflection from t- ZrO_2 disappeared with HE ball milling. This is either due to the disso-

Table 1 Crystallite size and lattice strain of Al_2O_3 powder in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ mixtures with various treatments and fractional number of intra-granular nano- ZrO_2 particles in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nano-composites.

	Crystallite size, D/nm	Lattice strain (%)	Fractional number of intra-granular nano- ZrO_2 particles* (%)
Before HE ball milling	115	0.03	—
After 1 h-HE ball milling (Sample 1)	68	0.11	9.2
Sample 2	59	0.20	11.8
Sample 3	62	0.02	5.6

*Only ZrO_2 particles below 200 nm were counted.

Fig. 9 The lattice parameter of Al_2O_3 in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ mixtures as a function of ZrO_2 content.

lution of ZrO_2 into Al_2O_3 or its transformation into an amorphous state. If the former was the case, the lattice parameter of Al_2O_3 should increase because of the larger ionic radius of Zr^{4+} than Al^{3+} . However, the lattice parameter of Al_2O_3 treated with HE ball milling hardly changed with ZrO_2 doping (Fig. 9). Thus, the disappearance of the ZrO_2 peak was interpreted as the transformation of ZrO_2 into an amorphous state. The HE ball milling also resulted in a significant change in the Al_2O_3 grains. The crystallite size of Al_2O_3 measured by XRD was reduced to nearly half the initial size and the lattice strain was also significantly increased (See Table 1).

In order to clarify the contribution of each effect to the formation of intra-granular nano-particles, two modified processes were adopted for powder preparation. Namely, only Al_2O_3 powder was HE ball milled before ZrO_2 addition through Zr alkoxide and the same process as above but the Al_2O_3 powder was annealed at 700°C for 2 h before alkoxide addition. HE ball milling of only Al_2O_3 eliminated the possibility of MA or amorphous transformation of ZrO_2 and the annealing in the latter process would further remove the strain in Al_2O_3 grains introduced by HE ball milling. The samples prepared by the original method and by the modified methods are referred to as sample 1, sample 2 and sample 3, respectively. Accordingly, sample 1 includes all of the effects (1)–(3), sample 2 includes effects (2) and (3), and sample 3 includes effect (2) only. The crystallite sizes and lattice strains of these powders are listed in Table 1.

All powders were sintered at 1550°C for 2 h and the size distribution of ZrO_2 particles were measured separately for the inter- and intra-granular particles. As illustrated in Fig. 10, the size distributions of the inter-granular particles were nearly the same for both samples 1 and 2, with an average size around 400 nm, while that for sample 3 was slightly

Fig. 10 The particle size distribution of intra-/inter-granular ZrO_2 particles in the samples.

narrower with a smaller average size. The size distribution of intra-granular particles appeared slightly different from one another, but the significance was not clear because of the limited counting number. Nevertheless, the number of intra-granular particles in sample 3 was significantly less than those in the other two (Table 1).

Regarding the role of HE ball milling in producing intra-granular nano-particles, these could not be produced by precipitation reaction since HE ball milling did not result in the dissolution of Zr into Al_2O_3 matrix. Indeed, much smaller particles should have been observed if this were the case. Instead, fine ZrO_2 particles seem to have been engulfed by the growing Al_2O_3 grains. In order that this mechanism should effectively operate, smaller initial grain size of Al_2O_3 seems to be favorable to the grain growth. In the present case, ZrO_2 particles seem to have been quite small from the very beginning of its formation, because of the alkoxide-root method. Thus, the main role of HE ball milling seems to be the refinement of Al_2O_3 particles. The larger number of intra-granular particles in samples 1 and 2 compared with sample 3 suggests that the strains of Al_2O_3 caused by HE ball milling was also favorable for yielding intra-granular particles. This is probably because the strained particles had a stronger tendency to grow and thus greater chances to engulf ZrO_2 particles. However, further investigation will be necessary to clarify the detailed mechanism.

5. Summary

An Al₂O₃-5 vol%ZrO₂ micro/nano-composite was successfully fabricated by using the HE ball mill mixing of commercial Al₂O₃ powder and Zr alkoxide. The mixed powders could be sintered to a nearly full density at 1450°C in the ambient atmosphere. The microstructure consisted of fine dispersions of ZrO₂ particles, both intra-granular type of ~50 nm and inter-granular type of ~0.2 μm, with an Al₂O₃ matrix grains of ~0.6 μm. The role of HE ball milling in the present nano-composite formation was primarily the refinement of the Al₂O₃ grains and the introduction of strains in them. The production of the intra-granular particles was most likely due to the engulfment of ZrO₂ particles by the growing Al₂O₃ grains during sintering.

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