Spark Plasma Sintering of Al_2O_3-TiC and Al_2O_3-TiC-Diamond Composites†

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Abstract

Spark plasma sintering characteristics of Al_2O_3-TiC and Al_2O_3-TiC-diamond composites were investigated. Samples prepared in the ratio of 70:30wt% of Al_2O_3-TiC and 67:23:10vol% of Al_2O_3-TiC-diamond were sintered at 1350 to 1500°C for 5 min under a pressure of 40MPa by the spark plasma sintering method. Diamond particles were coated with thin silicon carbide layer. No additive was used. Samples sintered were characterized in respect to microstructural and mechanical properties. The results revealed that nearly 99% of theoretical density in Al_2O_3-TiC composites was obtained, but densities are remarkably lower in samples with diamond. Contrary to this, the toughness of Al_2O_3-TiC – diamond composite in higher than that of Al_2O_3-TiC ceramics. Hardness of Al_2O_3-TiC-Diamond composite is also lower than Al_2O_3-TiC composites. These results were attributed to the lower thermal expansion coefficient of diamond and its tendency to convert to graphite.

KEY WORDS: (Al_2O_3) (TiC) (diamond) (spark plasma sintering) (microstructure) (hardness) (toughness) (density)

1. Introduction

The applications of ceramics as engineering parts have important attractions due to their advantageous properties as high hardness, superior chemical inertness, good strength and refractoriness in spite of their inherent brittleness. Al_2O_3-TiC ceramics generally exhibit good combination of high wear resistance, strength, fracture toughness and electrical conductivity. The combinations of Al_2O_3-TiC have been using as magnetic tape recording heads in the last decade, and it was also regarded to be a better component of cutting tools than monolithic alumina. Generally, sub-micron or ultra-fine raw powders of Al_2O_3, TiC and a small amount of sintering additives such Y_2O_3 and MgO etc. are necessary in order to improve the sintering process.[1] It was suggested that the industrial merit of this composite material can be further enhanced.[2] Similar thermal expansion coefficients of Al_2O_3 and TiC make them one of the harmonious couples. Their high hardness and melting point promote their use as anti-wear materials under heavy tribological conditions and their good electrical conductivity is useful for dissipating charge build-up in frictional contact.[3] These different uses need to have different levels of properties. But for each case, production of bulk material has some difficulties such as low fracture toughness, inadequate density, grain growth, etc...

In order to change the structure and properties of a ceramic material, the main ways are to change its composition and/or its processing route. Controlled dispersions of a second phase can improve material toughness and possibly the impact resistance.[4, 5] Second phase particles with high hardness are added frequently to the mixture for inhibiting grain growth in the matrix phase. In addition to this effect, if thermal expansion coefficient of second phase particle is significantly lower than that of the matrix phase, it increases fracture toughness of the ceramic. For instance, fine particles having a different thermal expansion to the matrix can produce very fine microcracks in the microstructure. Although this will probably decrease the strength of the matrix material, it can increase the strain tolerance of the overall composite and provide potential benefits in impact resistance and thermal shock resistance. Rather than a single catastrophic crack forming, the tiny microcracks in the region of loading all deflect slightly and essentially redistribute or absorb the load.[5]

Composites of Al_2O_3-TiC consist of finely dispersed titanium carbide grains in an alumina matrix. Their

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mechanical properties have also been an interesting subject for many researchers. During the last two decades, much attention has been paid to the toughness characteristics of Al_2O_3–TiC composites by noting the possible toughening effects resulting from the mismatch between the thermal and/or mechanical properties of Al_2O_3 and TiC grains.[6] In general, Al_2O_3-TiC composites exhibit high hardness and relatively low toughness. Therefore, it is important to increase toughness in a reasonable way. For this target, there have been many attempts to improve the properties of materials by distribution of diamond in recent years.[7, 8]

Spark plasma sintering system is a relatively new process that provides a means by which ceramic powder can be sintered very fast to nearly full density. It is carried out in a graphite die. It is considered that heating is accomplished by spark discharges in voids between particles generated by an instantaneous pulsed current directly applied through electrodes at the top and bottom punches of the graphite die. Via these discharges, the surface of particle is activated and purified, and a self-heat phenomenon is generated between the particles, thus the heat transfer and mass-transfer can be completed instantaneously.[9] The resistant heating through the sample and the mould is believed to contribute to the sintering as well. This method is not only convenient for processing of ceramics, also convenient for processing of other engineering materials such as metals, polymers and semiconductors.[10] This processing route has some unrivalled advantages like short time and relatively lower temperature to process and safety to work.

In this study, the optimum processing conditions and the mechanical and microstructural properties of alumina-titanium carbide-diamond (67:23:10 vol%) composite processed using spark plasma sintering system are investigated. Dispersion of diamond particles is expected to improve the wear resistance. The rapid sintering by spark plasma system may preserve diamond without graphitization.

2. Experimental Procedures

In this study, α-alumina of 0.3 micron (Sumitomo, AKP-30), titanium carbide of 1.3 micron (J. New Metal Co.) and diamond (0.5-2.0 micron-**1.25micron**- and 2.0-4.0 micron-**3micron**-) were used as starting powders. Before mixing, to prevent oxidation (or decrease oxidation tendency), diamond particles were coated by silicon carbide in a vacuum furnace. The details of the coating process were explained in reference.[11] Milled mixtures of Al_2O_3-TiC-SiC coated Diamond in ratio of 67:23:10% were put into a graphite die after compacting under pressure of 40 MPa. Spark plasma sintering was carried out in vacuum at different temperatures (1350-1400-1450 and 1500°C) for 5 min under 40MPa pressure using an SPS equipment (Dr. Sinter, SCM 1050) with a heating rate of 120°C/min. The temperature was measured by means of an optical pyrometer focused on a hole in the graphite die surface, which centered on the sample. **Figure 1** illustrates the SPS equipment used in the experiments. The density, and hardness and fracture

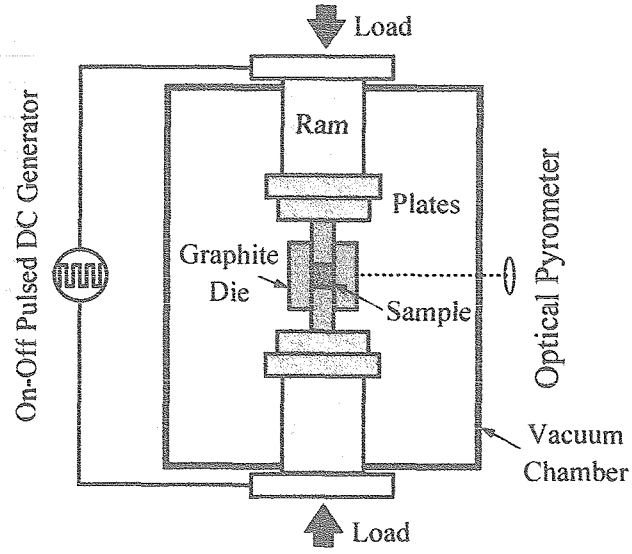


Fig.1 Schematics of spark plasma sintering equipment used in experiments.

toughness of samples were measured by Archimedes' method in distilled water and microhardness tester with a pyramidal indenter, and analysis were performed using optical microscopy, applying 20 kg load for 15s, respectively. Microstructural investigations and elemental scanning electron microscopy (SEM) and SEM-EPMA (JEOL 8600 Superprobe) on polished and etched specimens.

3. Results and Discussion

As it can be see from **Table 1** and **Fig.2**, though the relative density of the Al_2O_3-TiC composite is nearly constant at 99% of theoretical density, and doesn't show an important variation, relative densities of samples with diamond particles were increasing with sintering temperature for each particle size of diamond. Relative density was increasing with distribution of larger diamond particles in the Al_2O_3-TiC matrix as well. This is a surprise since common opinion assumes that it is better to use finer particles to obtain higher densities. Although there is no clear evidence, this kind of behavior can be related to surface areas of particles. Larger total surface areas of finer diamond particles (1.25 micron) present a larger oxidation surface. The silicon carbide coating on diamond particles can only improve the oxidation resistance of diamond, but does not prevent the oxidation completely. Oxidation takes place on the surface of diamond particles still, but it starts at higher temperature and develops slower (**Table 2**). For 1.25 and 3 micron of diamond, densities ranged from 94.9% to 96.5% and 96.7% to 97.1% for increasing temperatures, respectively. In latter case, variation in density is not so big.

Hardness values of Al_2O_3-TiC composite increased from 19.9 to 20.3 GPa, contrary to hardness values of samples with diamond particle which slightly decreased with sintering temperature for each particle size of diamond. Hardness values were changed in the range of 17.2 to 18.2 GPa and 17.9 to 18.3 GPa for 1.25 micron and 3 micron of diamond, respectively. These values are lower, by at least 2 to 3 units, than the hardness of Al_2O_3-TiC composite. The lower densities of the Al_2O_3-TiC composites when smaller diamond particles were dispersed and the decreasing tendencies of hardness with increasing sintering temperature for the dispersion of smaller diamond particles suggest that the surface of diamond particles is slightly converted to graphite. The graphitization of diamond would decrease the hardness, but increase the toughness because each diamond particle is covered with a thin graphite layer. It is difficult to identify the thin graphite layer because the EPMA can not distinguish between carbon atoms in diamond and graphite. However, these tendencies in density and hardness of Al_2O_3-TiC-Diamond associated with the sintering temperature suggest the graphitization of

Table 1 The density, hardness and fracture toughness of Al_2O_3-TiC, and Al_2O_3-TiC-Diamond (1.25 and 3 micron) composites processed by spark plasma sintering dependent on sintering temperature (for 5 min).

Sintering Temperature (°C)		1350	1400	1450	1500
Al_2O_3-TiC	Hardness, GPa	19.9±0.4	20.0±0.3	20.2±0.1	20.3±0.2
	Toughness, $MPam^{1/2}$	4,3±0.2	4.2±0.1	4.2±0.1	3.9±0.2
	R. Density, %	99.1	98.8	98.9	99.0
Al_2O_3-TiC-Diamond (1.25 micron)	Hardness, GPa	18.1±0.1	18.2±0.1	17.9±0.2	17.2±0.2
	Toughness, $MPam^{1/2}$	5.7±0.3	5.6±0.2	5.3±0.3	5.1±0.3
	R. Density, %	94.9	95.5	95.4	96.5
Al_2O_3-TiC-Diamond (3 micron)	Hardness, GPa	18.3±0.1	17.9±0.1	18.0±0.1	17.9±0.3
	Toughness, $MPam^{1/2}$	6.2±0.1	5.5±0.3	5.3±0.4	5.3±0.5
	R. Density, %	96.7	97.2	97.0	97.1

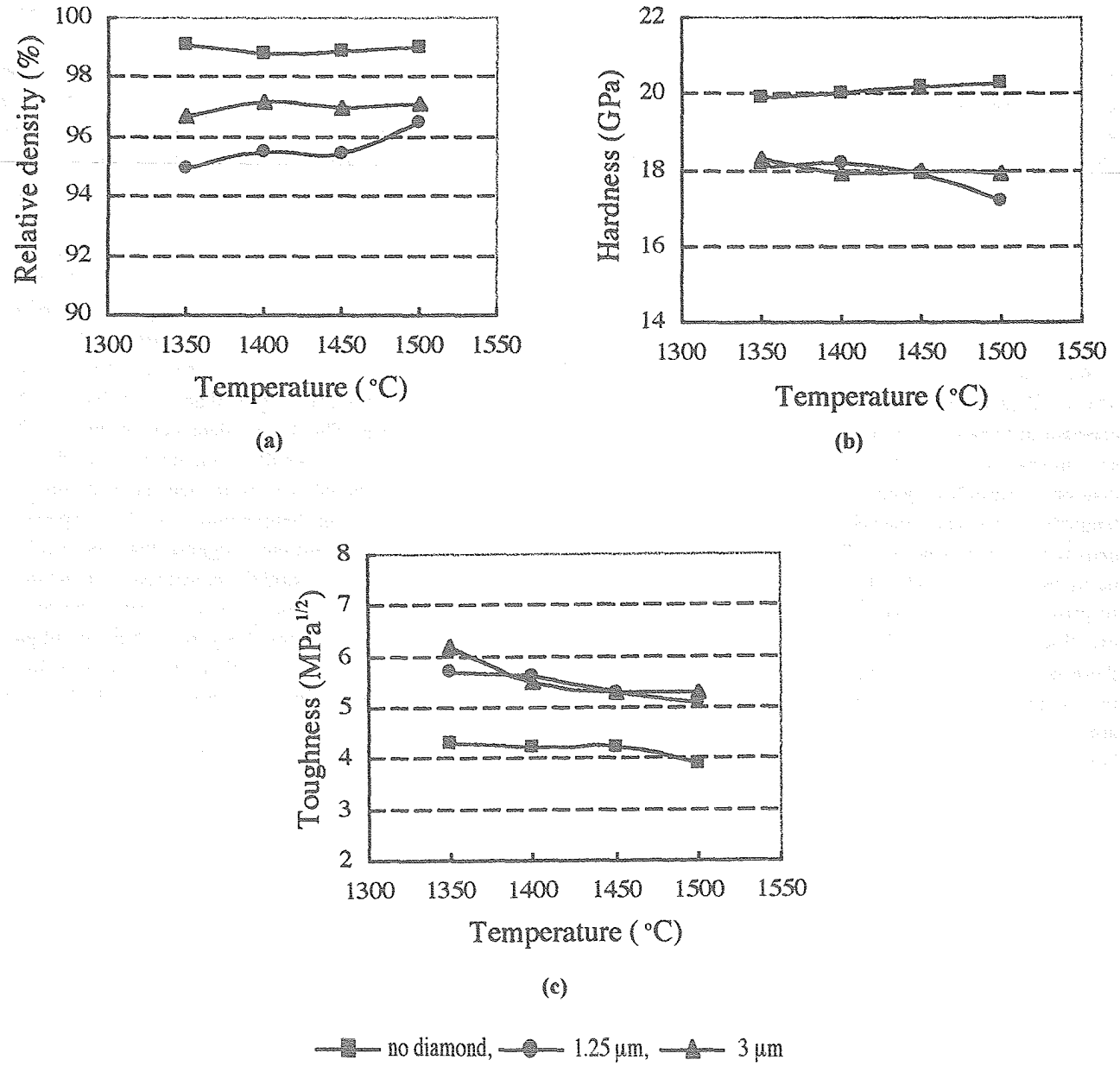
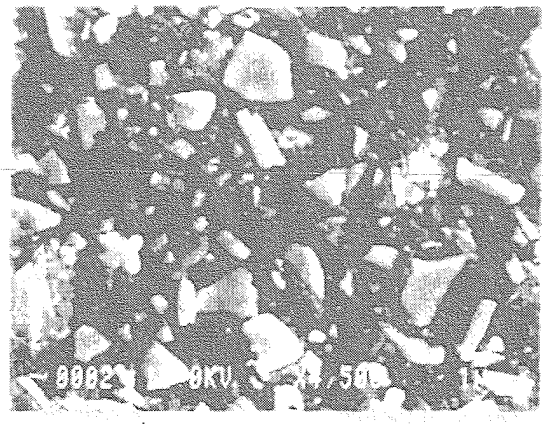


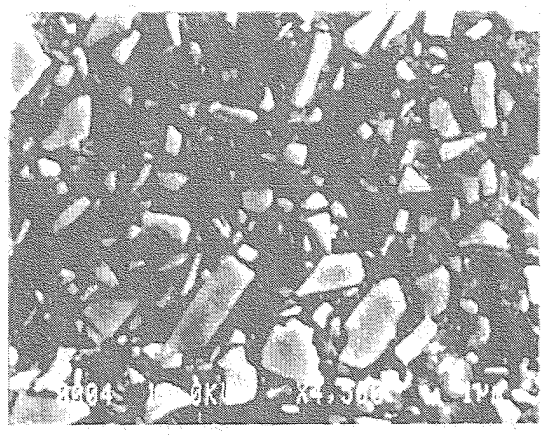
Fig.2 The variation of relative density (a), hardness (b) and indentation fracture toughness (c) of Al_2O_3- TiC-Diamond composite with sintering temperature for two different diamond particle size.

Table 2 Oxidation starting temperatures of diamond particles.

Particle size of diamond (μm)	~1.25	~3
Uncoated	492.2	508
SiC coated	617.1	635



(a)



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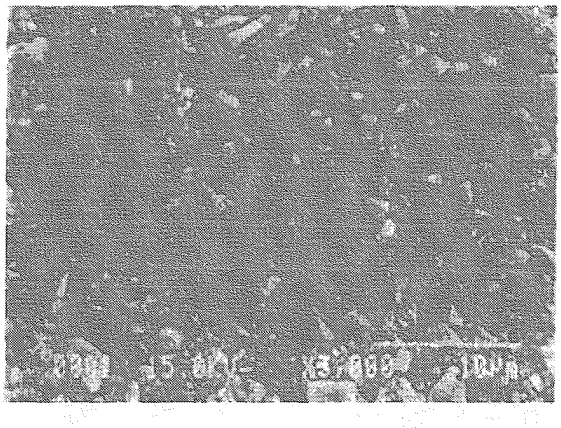

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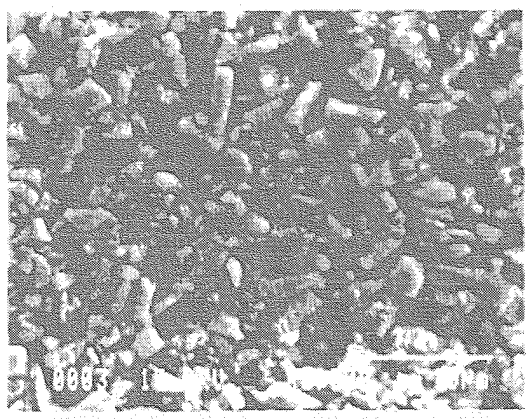
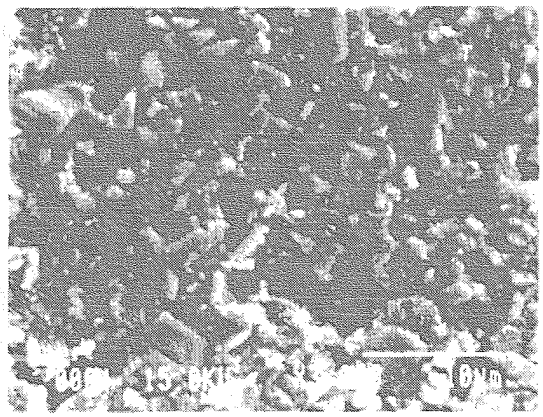
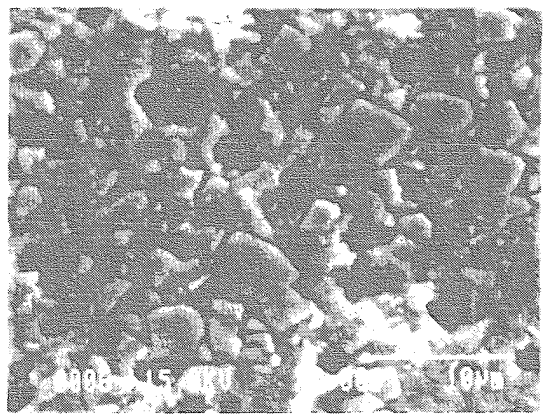


(d)



(e)

1350 °C



(f)

1450 °C

Fig.3 The SEM micrographs of samples: (a) Al_2O_3-TiC, 1350°C, (b) Al_2O_3-TiC, 1450°C, (c) Al_2O_3-TiC-diamond (1.25 micron), 1350°C, (d) Al_2O_3-TiC- diamond (1.25 micron), 1450°C, (e) Al_2O_3-TiC-diamond (3 micron), 1350°C, (f) Al_2O_3-TiC-diamond (3 micron), 1450°C.

diamond. If the degree of graphitization per unit surface area of a diamond is the same, the influence on the properties due to the smaller particles would be larger.

For all groups of samples, toughness decreased with sintering temperature. This decrease is only slight for Al_2O_3-TiC composites, but obvious for Al_2O_3-TiC-SiC coated diamond composites. The values of toughness of Al_2O_3-TiC-SiC coated diamond composites are nearly 25% higher (for 1.25 micron) and 40% (for 3 micron) than for the Al_2O_3-TiC matrix. These are the expected result from addition of diamond particles to the Al_2O_3-TiC composite. Because thermal expansion coefficients of Al_2O_3 and TiC are close to each other; there is no excessive residual stress to cause cracking in the matrix after sintering. In the case of the addition of diamond, which has much lower of thermal expansion coefficient, to this composite, tensile stress will arise around the diamond particles. Cracks will tend to deflect to diamond particles due to tensile stress around of them. This will decrease the crack energy requiring to be propagate. However, the effect of residual stress would be relaxed depending on the occurrence of the graphitization of diamond.

The microstructures were investigated by scanning electron microscope (SEM) on polished and etched specimens. All microstructures show that both TiC and diamond particles were uniformly distributed in alumina matrix (Fig. 3). The alumina grains were joined to each other very well. Because of the more ionic nature of the chemical bonding in oxides like Al_2O_3, grain boundary diffusion is enhanced and makes it even more difficult to control the grain growth during densification process than for non-oxide ceramics. Although it has been proved that the addition of a second phase does retard the matrix grain growth, it is still impossible to avoid it completely.[12] It is obvious that, grain growth occurred during sintering at higher temperatures. For example, the average grain size of alumina particles in samples sintered at 1350°C is 1 micrometer, whereas it is 3 micrometer for samples sintered at 1500°C. Diamond particles don't have a refining effect; that is, alumina particles grain sizes are nearly the same for both Al_2O_3-TiC and Al_2O_3-TiC-SiC coated diamond composites. As a result, as we mentioned above, the main role of diamond particles is to increase the toughness, not to increase the hardness and/or to refine the grains.

4. Conclusions

In this study, we examined the addition of diamond particles to Al_2O_3-TiC composite.

(1) The addition of diamond particles increases the fracture toughness up to 40% of the matrix. This improvement was attributed the lower thermal expansion coefficient of diamond and its extremly high hardness compared with.
(2) Hardness and relative density decreased with the addition of diamond.
(3) Diamond particles don't lead to the refining of the grains in the matrix.
(4) By using larger particle sizes of diamond, it is possible to obtain better results in fracture toughness, and density.

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