Sintering and Toughening Behavior of Dense SiC-coated Diamond Dispersed WC/Co Composites†

ZHANG Lixue ***, MORISADA Yoshiaki **, MIYAMOTO Yoshinari *, JIN Zhihao ***

Abstract

Hard protective layers of nanometer sized SiC grains to protect against oxidation and graphitization were coated on diamond particles by the reaction of SiO and diamond. The SiC coated diamond particles were mixed in 20vol.% with WC-10wt.%Co and densified by using the SPS method. The sintering behavior in respect of the particle size of diamond, 8~16μm, 20~30μm and 40~60μm, was investigated. The relative densities of all composites reached 98%. The Vickers hardness increased slightly to 17.9GPa by dispersing 40~60μm size diamond, but did not differ so much from the matrix hardness of WC/Co, this suggests no direct bonding between diamond particles, and weak bonding between diamond and matrix. However, the indentation toughness increased from 9.4MPam$^{1/2}$ to 17.8MPam$^{1/2}$ with diamond dispersion. Crack deflection, debonding and stopping were clearly seen around diamond particles.

KEY WORDS: (Diamond), (SiC Coating), (SPS), (WC-Co), (Vickers indentation), (Toughness)

1. Introduction

Due to the outstanding properties of extremely high hardness, elastic modulus, thermal conductivity, and low friction coefficient with low sensitivity to wetness, diamond has been used for various mechanical applications such as wear resistant tools, cutting tools, milling tools, etc[1]. The composites containing diamond have been applied to machining graphite, ceramics, rocks, wood, concrete, glass and nonferrous materials. However, sintering of these composites is difficult due to the low thermal stability of diamond. Because diamond consists of the element carbon, it has a rather low resistance against oxidation. The oxidation starts at over 550°C in air. To overcome of the low oxidation resistance of diamond, many researches to add protective coatings such as Cr/Ni[2], Ti[3], TiN[4] on diamond surfaces have been reported. However, the problem of these coatings is reported to be the weak interface bonding with diamond[3]. Moreover, diamond is a high-pressure stable form of carbon, therefore graphitization occurs easily when the temperature is elevated if the pressure is not sufficient. The presence of solvent catalyst metals, such as cobalt, iron, or nickel facilitates the transformation between diamond and graphite[5]. It becomes more difficult to preserve the diamond when sintered together with these transition metals under low pressure.

In the present study, the above-mentioned shortcomings (oxidation and graphitization resulting from the corrosion of molten cobalt) of diamond powder was attempted to be solved by coating a SiC protective layer on the diamond particles through a simple reaction process of SiO and diamond[6]. The composites of WC/Co and SiC coated diamond particles were densified by a Spark Plasma Sintering (SPS) method. Cobalt cemented tungsten carbide is widely used for wear resistance and cutting tools due to its excellent hardness and toughness[7]. Diamond is difficult to sinter due to its high hardness and the low diffusivity of carbon atoms with strong covalent bonding. It is usually sintered with a cobalt binder under an extremely high pressure of 5~6Gpa and high temperature of 1400°C[8]. Therefore the sintered diamond is costly and limited in size and

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shape. If such composites of WC/Co with diamond could be fabricated under low pressure, it would produce a new material having higher performance than WC/Co and sintered diamond at low cost and free from size and shape limitation. The advantages of fast densification and low sintering temperature of SPS is expected to produce a high density preventing graphitization of diamond when sintering proceeds under a normal pressure[9]. The sintered samples were evaluated in respect of microstructure, density, Vickers hardness, and indentation toughness. Toughness is determined by measuring the extent of cracking associated with Vickers indentation because of the ease of specimen preparation and simplicity of the test procedure[10]. The toughness is important for performance of wear parts where impulsive or high impact forces are encountered.

2. Experimental procedure

Synthetic diamond powders (Showa Denko Co. Ltd.) with different particle sizes (8~16μm, 20~30μm and 40~60μm), and fine WC, Co powders (Japan new metals Co. Ltd.) were used. The diamond powders were coated by a SiC layer by the reaction between diamond and SiO granular (99% pure, Nacalai Tesue INC. Kyoto. Japan)[6].The coating process was carried out in a vacuum furnace at 1350°C under a pressure of about 0.03Pa.

The SiC coated diamond powders were mixed with WC-10wt%Co and a volume percent of 20%. For comparison, WC-10wt%Co without diamond powder was also prepared. The detailed properties of the powders and the composition of mixture were listed in **Table1**.

Table I Properties and compositions of the starting mixture.

Name	Size (μm)	Molar Weight	Density (g/cm^3)	Wt. %	Vol. %	Coef. Lin. Expan. (10^{-6}/K)	Young's modulus (GPa)
WC	0.65	195.9	15.7	84.9	66.9	4.0	677
Co	_	58.9	8.9	9.4	13.1	12.3	211
Dia.	12-25-50	12.0	3.5	5.7	20.0	1.2	899

The mixed powders were milled for several hours. After compacting at room temperature the powder mixtures were filled into a graphite die. Spark Plasma Sintering was carried out in vacuum at different temperatures from 1000 °C to 1100 °C for 5 minutes under 30MPa pressure by using an SPS equipment (see **Fig.1**).

The sintering temperature was measured by an optical pyrometer. The sintered ϕ15mm × (4~5) mm compacts were polished to a flat surface by using a diamond wheel.

The SiC coated diamond powders were identified by XRD, the microstructure and composition were analyzed by 3D-SEM/EDX(Elionix, ERA-8800FE). The oxidation resistance was tested by TG/DTA(Regaku TG 8110).

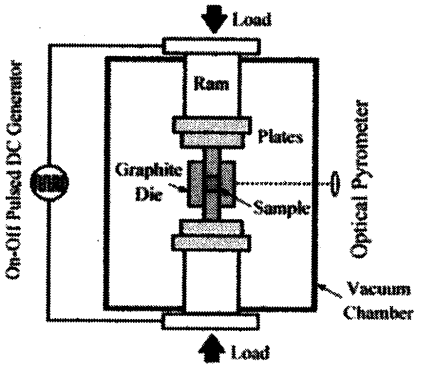

Fig.1 A schematic of SPS equipment

The SiC coated diamond powders of about 20mg were put into a ϕ5mm×5mm platinum crucible and heated up to 1200°C with a heating rate of 5 °C /min. in an airflow of 50ml/min.

The phase and composition of the sintered specimen were analyzed by XRD and 3D-SEM/EDX. The bulk density was measured in distilled water using Archimede's method. The relative density was calculated from the theoretical density based on the mixed rule. Vickers hardness and indentation toughness were measured 5 times on each sample using a Vickers hardness testing machine (AVK-C2 Akashi Corporation) under an indentation load of 50kgf for 10~15 seconds referring to the Japan Industrial Standard (JIS). The hardness expressed in GPa was calculated by the following equation:

$Hv=0.0018544(P/d^2)$,

where P is load (N), d is mean diagonal of indentation (mm). Fracture toughness was calculated using a simple equation given by K.Tanaka [10],

$K_{IC}=0.0725(P/C)^{2/3}$,

where P is indentation load (N), C is mean indentation induced crack length (mm) measured by optical microscope at a magnification of 200X from the center of the indentation to the crack tip. The indented surface and crack propagation was observed by 3D-SEM.

3. Results and Discussion

The SiC coating on diamond was identified to be β-SiC phase from the analysis by XRD. Each diamond particle was covered with nanometer sized SiC grains as seen in **Fig 2.**

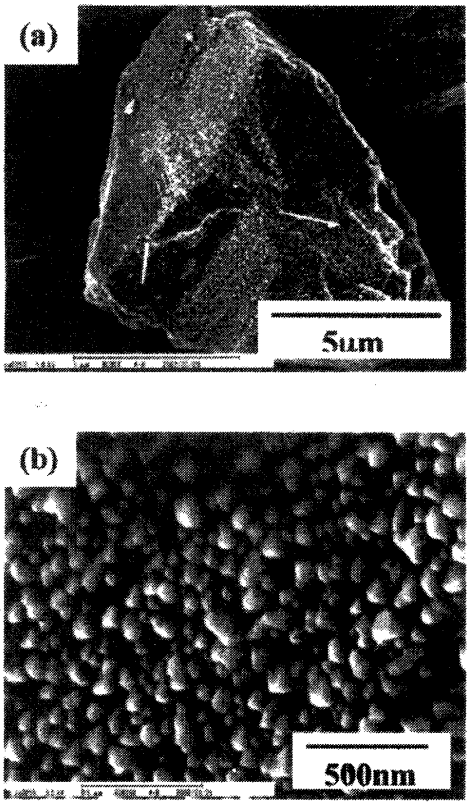

Fig.2 3D-SEM photos of a SiC coated diamond (a) and its coated layer of nanometer-sized SiC crystals (b).

Figure 3 compares the starting temperatures of oxidation for SiC coated and uncoated diamond with different particle sizes. The uncoated diamond particles start oxidation at 550 °C~600 °C, while the SiC/Dia showed at least 150 °C higher oxidation temperature. The oxidation temperatures increased with increasing diamond particle size. This is explained by considering that the larger the diamond particles, the less surface for oxidation in case of the same mass.

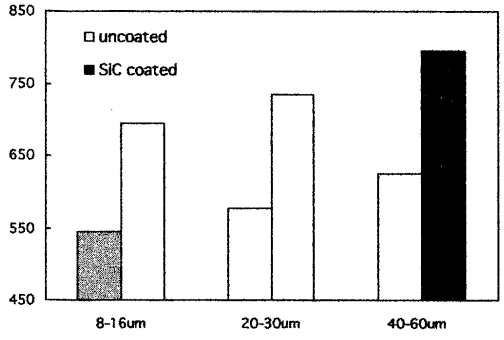

Fig.3 Comparison of the starting temperature of oxidation for SiC coated and uncoated diamond with different particle sizes.

Figure 4 shows microstructures of the polished composites of SiC/Diamond with different particle sizes of diamond dispersed WC/Co. The relative density was calculated to be almost 98% under the optimized sintering condition. The high density resulted from the role of SiC coating layer, which must protect the diamond particles from corrosion by molten cobalt and produce no graphitization.

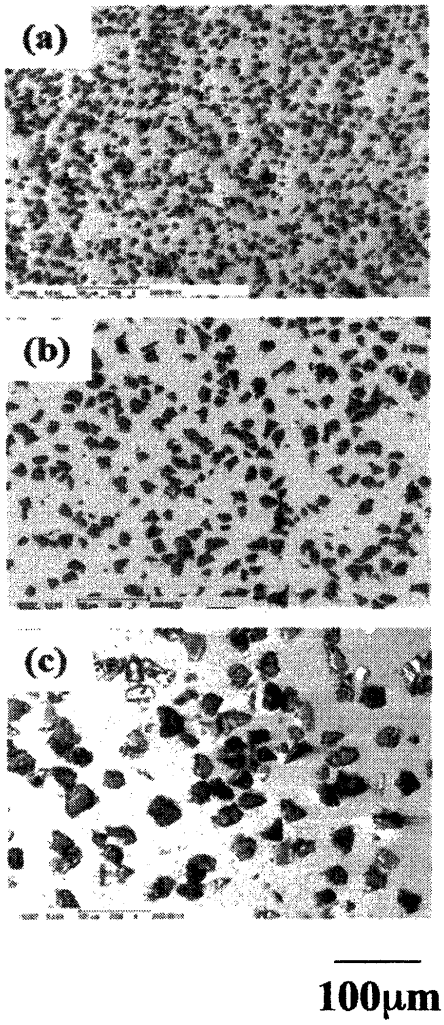

Fig.4 Optical micrographs of the SiC coated diamond dispersed WC-Co with different sizes of diamond particles, (a) 8-16μm, (b) 20-30μm,(c) 40-60μm. The content of diamond is 20 vol%.

Figure 5 shows XRD patterns of the SiC-Dia/WC-10wt%Co and the WC-10wt%Co. In the SiC-Dia /WC-10wt%Co, a diamond peak of (111) was observed, but no other diffraction peak was detected

Diamond particles were distributed uniformly in the WC-10wt%Co matrix. The interface of the diamond/matrix was clear as seen in **Fig.6**.

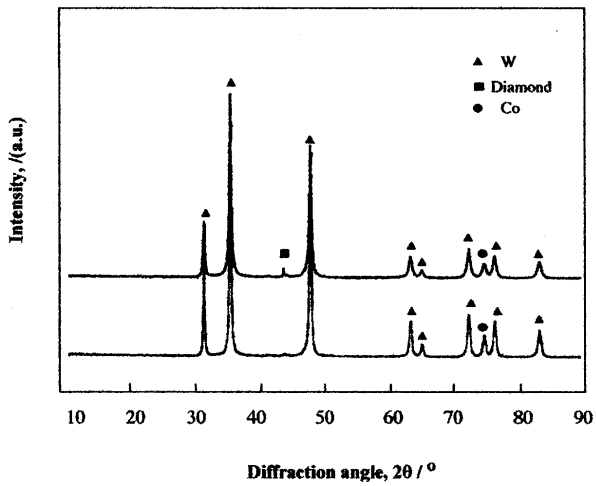

Fig.5 XRD patterns of the WC-Co and the SiC coated diamond (40-60μm) dispersed WC-Co.

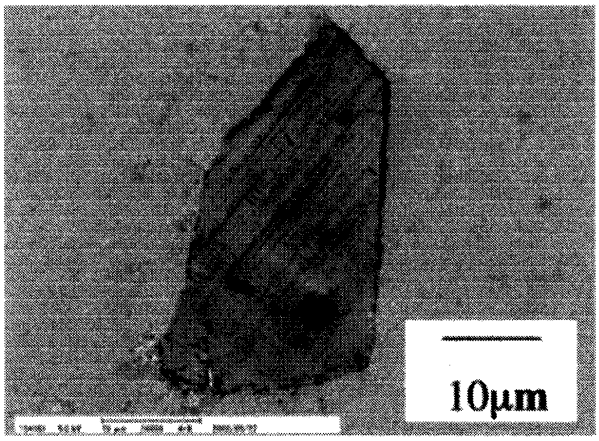

Fig.6 A SEM photo of a SiC coated diamond (40-60μm) in the WC-Co matrix.

Figure 7 (a) shows the relationship between the Vickers hardness and the particle size of diamond for the SiC-Dia/WC-10wt%Co composites. The hardness of a specimen including 8~16μm diamond particles is 16.3GPa, which is lower than that of the WC-10wt%Co (16.7GPa). It increases slightly to 17.9GPa when the diamond particle size is 40~60μm. No large effect of hardness increase by incorporating diamond into the WC/Co matrix suggests that the direct bonding of diamond particles is not formed due to the rapid sintering under low pressure. The interface bonding between the WC/Co matrix and diamond would be weak because of the low wetting ability of diamond to molten cobalt[11]. It is considered that the composites have such a microstructure in which diamond particles are almost isolated and embedded. Therefore the measured hardness of the composites reflects mainly the hardness of the WC/Co matrix. The Vickers hardness is measured at the pyramidal area of ~200μm in diagonal length. The dispersion of large diamond particles (20vol.%) of 40~60μm size would affect the hardness.

Figure 7 (b) shows the relationship between the indentation toughness and the particle size of diamond. The toughness increased markedly from 9.4 $MPam^{1/2}$ to 16.1 $MPam^{1/2}$, 16.8 $MPam^{1/2}$ and 17.8 $MPam^{1/2}$ due to the existence of diamond with the particle sizes of 8~16μm, 20~30μm and 40~60μm, respectively.

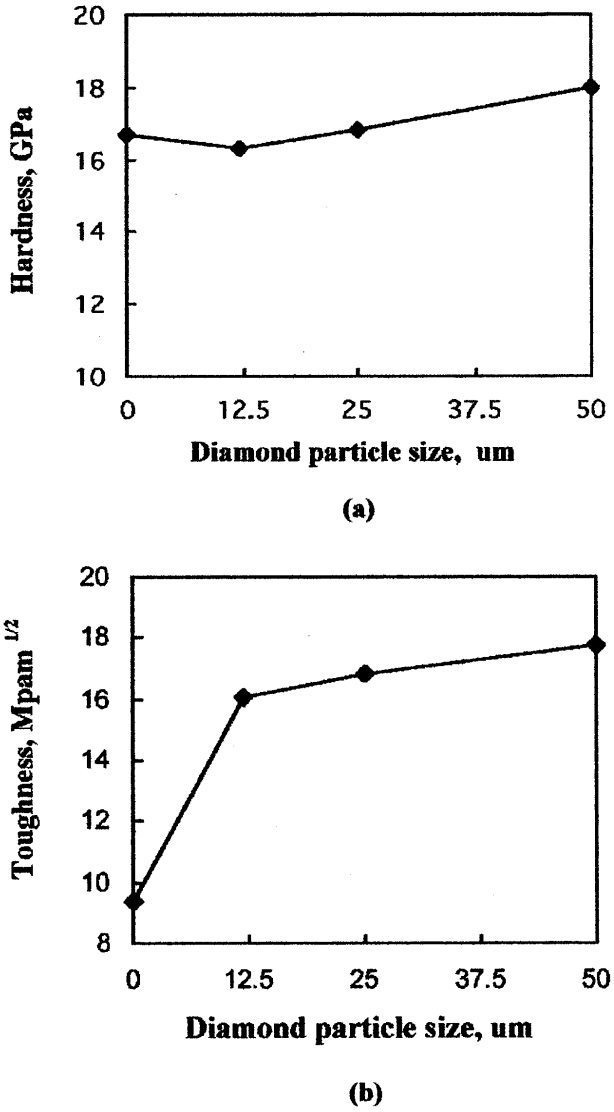

Fig.7 Vickers hardness (a) and indentation toughness (b) of the SiC coated diamond dispersed WC-Co as a function of diamond particle sizes.

Figure 8 shows the behavior of crack propagation for the composite samples with different size diamond particles. In WC-10wt%Co, the indentation crack propagates directly and straightly, while in diamond dispersed composites (Fig. 8 (b) ~ (d) and (f) ~ (h)), the cracks are deflected or blocked by diamond particles, resulting in a short crack lengths. The uniform distribution of diamond particles in the WC-Co matrix also promotes this effect. Generally crack deflection is caused by residual strains in a composite, which arises from elastic modulus and/or thermal expansion mismatch between the matrix and the particulate phase[12]. In this study, the secondary phase of diamond particles has a much higher elastic modulus and lower coefficient of thermal expansion compared with the WC-10wt%Co matrix. The matrix shrinks more than diamond particles when cooling down from the high sintering temperature. This induces tensile strains near the SiC-Dia./WC-Co interface, causing the indentation crack to deflect toward the diamond particles. The debonding of diamond from the WC/Co matrix is seen in Fig.8 (f ~ h), which can increase the toughness as well[11]. Larger diamond particles would act effectively to stop the crack propagation.

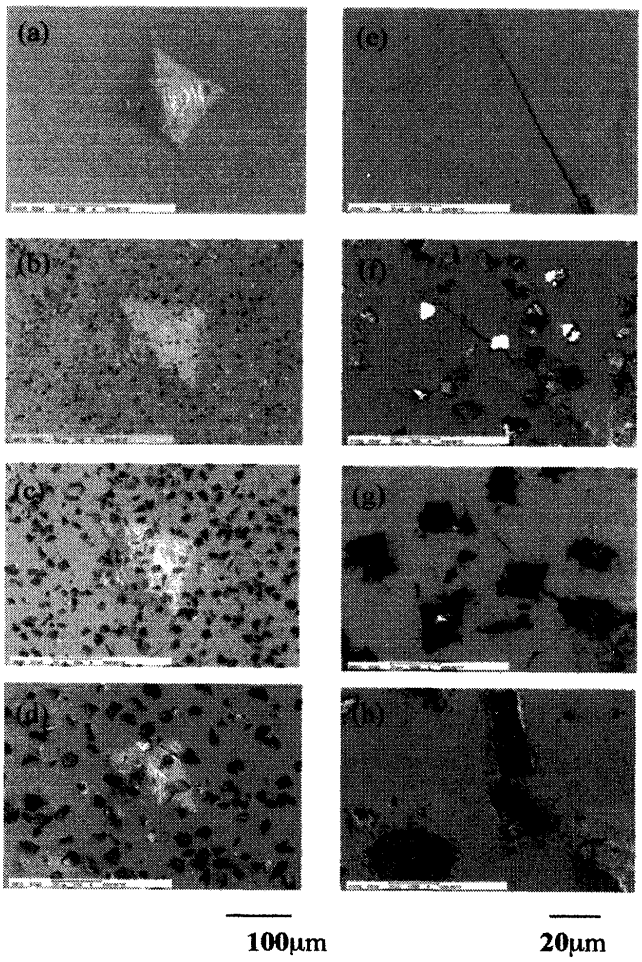

Fig.8 Indentation surface and crack propagation in the WC-Co compact and the SiC coated diamond dispersed WC-Co. (a) WC-10wt%Co, (b) SiC coated diamond dispersed WC-Co with diamond particle size of 8-16μm, (c) 20-30μm,(d) 40-60μm. (e)~(h) are higher magnification images.

Conclusions

The sintering ability of SiC/Diamond dispersed WC-10wt%Co composites was investigated by using on SPS method. The results obtained can be sammarised as follows.

(1) Nanometer-sized SiC coatings protected diamond effectively from graphitization resulting from the corrosion of molten cobalt during high temperature sintering under normal pressure.

(2) The WC-10wt%Co matrix dispersed with diamond particles can be sintered to a high relative density of about 98% at 1050°C for 5 minutes.

(3) The mechanical properties of WC-10wt%Co were improved by the addition of SiC coated diamond particles, especially toughness, which increased about 90%. The mismatch of CTE and elastic modulus between diamond and WC-10wt%Co matrix leads to this significant improvement. The variation of particle size of diamond was considered to have little effect on the improvement of toughness.

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