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Enhancing the adhesion of diamond films on cobalt-cemented tungsten carbide substrate using tungsten particles via MPCVD system

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ABSTRACT

To increase the adhesion of diamond films and avoid the negative effects of using cobalt, previous treatments have employed tungsten particles to cover the surface of the 6 wt.% cobalt-cemented tungsten carbide (WC-Co) substrate. The surface of the tungsten particles is transformed into W_2C and WC, which attracts and traps carbon. Through the process of nucleation, the carbon forms around the tungsten particles, thereby satisfying the conditions necessary for the formation of diamond film. Using Raman spectroscopy, we determined that diamond films of good quality with excellent adhesive properties and a hardness level as high as 27.78 GPa could be produced following pretreatment with 2.0 μm tungsten particles. Rockwell indentation tests indicate that addition of tungsten particles promotes the interfacial adhesion of diamond films with WC-Co substrates. We determined that using smaller tungsten particles decreased the number of gaps and cavities on the surface of the substrate, thereby enhancing the adhesion of the diamond film.

1. Introduction

Cemented carbides are often applied to cutting tools, rotary tools, and various wear-resistant components [1,2], while diamond films deposited on cemented carbides by CVD can significantly prolong the lifespan of tools. Unfortunately, diamond films adhere poorly to the surface of sintered cobalt-cemented tungsten carbide (WC-Co) substrates, requiring manufacturers to use cobalt as a binder. The catalytic effect of the cobalt binder on sintered WC-Co has a detrimental effect on the growth of diamond films, favoring the formation of graphite or non-diamond phase carbon. Various approaches can be employed to avoid the negative influence of cobalt on mechanical tools, including chemical etching of the Co surface [3–6], forming stable Co compounds [7,8], and depositing a protective layer on the substrate [9–15]. Those surface modification methods improve the adhesion of diamond film by removing most of the cobalt from the surface of the substrate with a diluted acid solution. Thus, chemical pretreatments are efficient procedures to avoid the negative effects of cobalt. However, this process also creates corrosion layers and pits that detract from the mechanical properties of Co-cemented carbides [16,17].

In this study, we ignored chemical pretreatment methods, preferring to investigate how the size of tungsten particles alters the surface of WC-Co substrate. This method has never previously appeared in papers dealing with the preparation of diamond films on tungsten carbide. This study revealed that without acid pretreatment, tungsten replaced the Co to form a diamond film on the substrate. This provides a simple and environmentally friendly approach to enhance the adhesion of diamond film to WC-Co substrates by encouraging carbide species to form diamond phases around tungsten particles.

2. Experimental

2.1. Substrate pretreatment

The substrate samples used in this study were 6 wt.% cobalt-cemented tungsten carbide, measuring 10 mm × 10 mm × 1.5 mm. The samples were placed in an ultrasonic acetone bath for 5 min to remove oil and dirt particles from the surface. The surface of the substrate was subjected to hydrogen plasma for 2 h at a microwave power of 900 W, a pressure of 35 Torr, and a hydrogen flow rate of 60 sccm, in a microwave plasma system. Specifically, the hydrogen plasma treatment decarburized the WC-Co substrate to tungsten [2]. This step was intended to embed particles in the substrate for seeding diamonds, increase surface roughness, and enhance the adhesion of the diamond film. Following the hydrogen plasma pretreatment, the samples were cleaned ultrasonically with acetone for 30 min to remove any carbon soot from the surface. The samples were placed in beakers containing ethanol (50 ml) and tungsten powder (0.5 g). Macroscopically, the tungsten powder was homogeneously distributed on the surface of the WC-Co substrate using an ultrasonic bath with ethanol for 10 min (Fig. 1). The tungsten powder used to treat the surface was commercially available with particle sizes of 0.6, 0.8, 1.0, and

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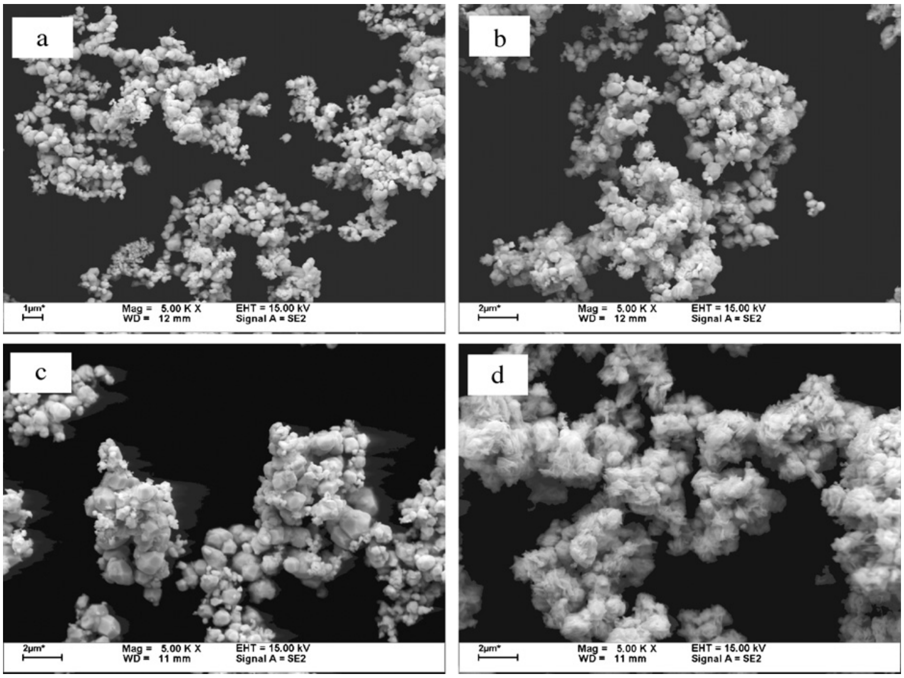

Fig. 1. FE-SEM images of tungsten particles with particle sizes of (a) 0.6 µm, (b) 0.8 µm, (c) 1.0 µm, (d) 2.0 µm.

2.0 µm (the 2.0 µm particle sizes was the limit suspension of the tungsten particle in ethanol).

2.2. *Diamond film deposition*

Diamond film deposition was performed using a 2.45 GHz microwave plasma chemical vapor deposition (MPCVD) system (ITRI, MP2000-DH2) with a 2 KW microwave source. Microwave power was maintained at 900 W and the pressure in the chamber was maintained at 70 Torr during deposition. A reaction gas mixture containing 300 sccm H_2 and 15 sccm CH_4 was maintained at a continuous flow for the entire 4 h deposition period. The surface temperature of the substrate was approximately 980 °C during deposition, as measured by infrared pyrometer.

X-ray diffraction (XRD, Rigaku TTRAXIII) was used to investigate changes in the chemical composition of the surface of the substrate. Field emission scanning electron microscopy (FE-SEM, Leo-1530) revealed the morphology of the diamond films formed around tungsten particles. A Raman spectroscope (Jobin Yvon, iHR-320) with a 514.5 nm He–Ne green light laser analyzed the physical properties and characterised the qualities of the diamond film. A nanoindenter (MTS, G200) with the depth set to 500 nm was used to test the hardness and Young's modulus of the diamond film. Finally, Rockwell-A hardness values were determined with a diamond indenter (Mitutoyo, ARK-600) to investigate the adhesive characteristics of the diamond films coated with WC-Co substrates. In many studies [3,7,14,18], Rockwell-A hardness measurements are used to detect the adhesion of diamond films, although a standard load for the test does not exist. In this study, we used a 60 kg load for the indentation test.

3. Results and discussion

3.1. *The transformation of the tungsten*

The size distribution of W particles was computed from FE-SEM images. From Fig. 1, it was calculated that photos (a)–(d) showed particle sizes of approximately 0.6, 0.8, 1.0, and, 2.0 µm, respectively, with little variation.

Fig. 2 shows XRD patterns from an untreated WC-Co substrate deposited with diamond film using tungsten particles of various sizes. The XRD patterns of the specimens produced with tungsten particles clearly exhibited extra W and W_2C peaks on the surface of the specimens, compared to samples without tungsten particles.

The (1 0 0) and (1 0 1) orientation of main WC peaks were at 35.69° and 48.42° in the XRD patterns. WC peaks in the specimens produced with tungsten particles showed a clear tendency to increase in size, compared to specimens without tungsten particles. The greater the number of tungsten particles that came into contact with the plasma, the greater the degree of change that was observed.

Diamond deposition treatment transformed the tungsten particles and active carbon species into WC and W_2C phases; however, the intensity of W_2C peaks was not high. Nevertheless, previous studies have shown that hot filament chemical vapor deposition (HFCVD) treatment transformed the partial W_2C phase into WC phases after carbon deposition for 2 h at 800 °C [14,19].

The XRD patterns indicated the presence of crystalline structures in the diamond films produced with tungsten particles of various sizes. It was indicated that the diamond film had a (1 1 1) faceted orientation; however, none of the samples clearly showed the intensity of diamond peaks. The diffraction intensity of WC-Co substrate is higher than diamond; therefore, XRD generally shows the crystallization of the substrate more clearly. The XRD patterns

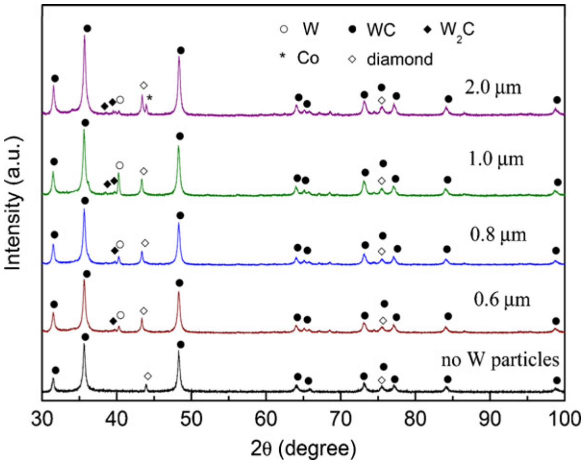

Fig. 2. XRD patterns of diamond films deposited on substrate with no tungsten particles and tungsten particles of various particle sizes.

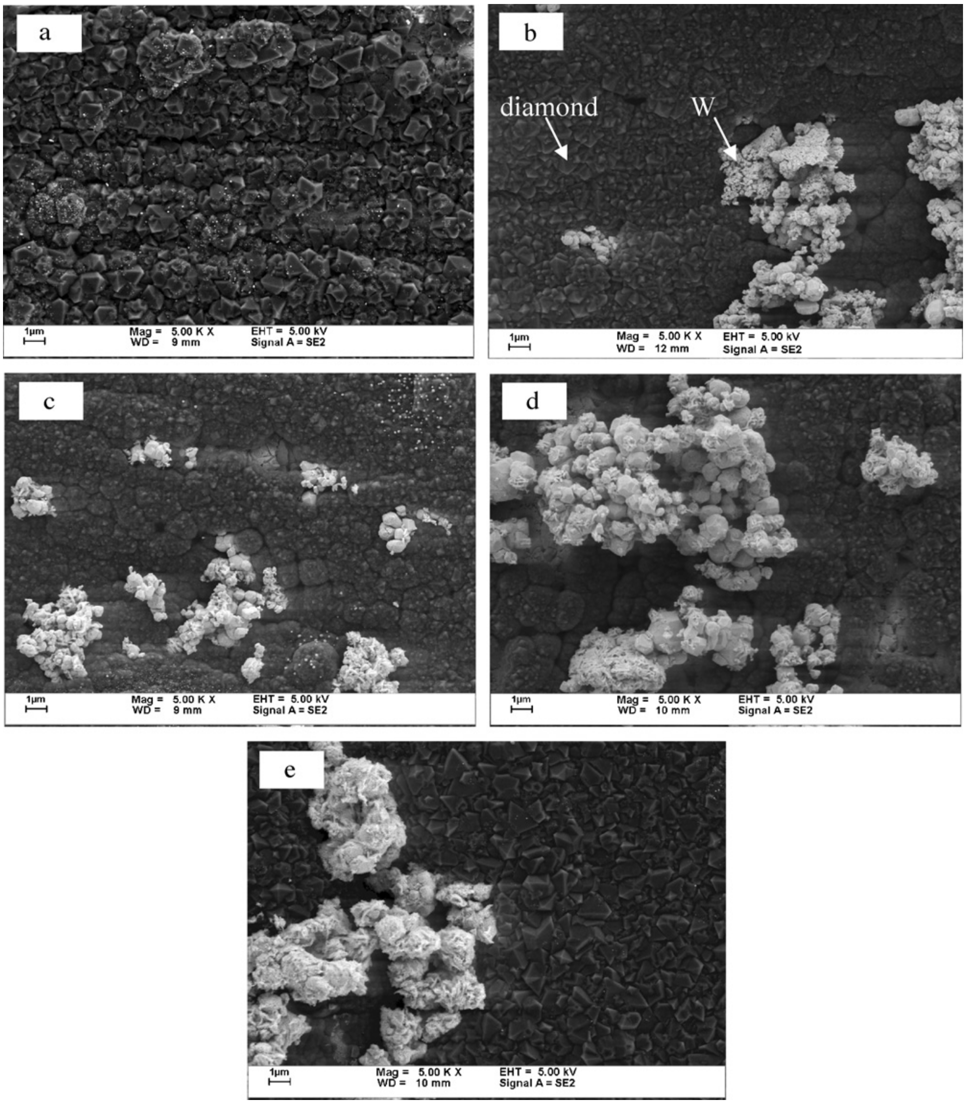

Fig. 3. FE-SEM images of diamond films with (a) no tungsten particles, (b) 0.6 μm, (c) 0.8 μm, (d) 1.0 μm and (e) 2.0 μm tungsten particles following diamond deposition.

showed diamond peaks at diffraction angles of 43.38° and 75.51°, corresponding to the (1 1 1) and (2 2 0) textured orientations. Moreover, the diffraction peak of (2 0 0) tungsten carbide orientation could not be distinguished from the diffraction peak of (2 2 0) diamond orientation, because the angles of the peaks were very close or overlapped one another.

The appearance of diffraction peaks of W was correlated with the amount of tungsten powder deposited on the surface of the substrate, which in turn, was related to the coverage of diamond film following the MPCVD process. Smaller tungsten particles (0.6, 0.8, and 1.0 μm) showed greater uniformity in suspension following ultrasonic vibration. For this reason, the particles of tungsten were distributed very densely across the surface. Because the diamond film covered the surface of the WC-Co substrate, no clear W peak for the tungsten particles of 2.0 μm was evident.

The cubic structure of Co disappeared from the surface of the substrate following extended thermal treatment. The thermal treatment not only assisted diamond growth, but also promoted the diffusion of Co crystals throughout the diamond film, due to a higher degree of sample coverage. At high deposition temperatures, cobalt regrouped on the surface of the substrate forming balls that moved during diamond deposition. This led to a diffusion of cobalt on the surface of the diamond coating [20].

3.2. *The morphology of diamond films*

Fig. 3 shows FE-SEM images of diamond film produced with tungsten particles of various sizes. Fig. 3(a) shows the morphology of the deposited diamond without tungsten treatment. After the MPCVD process, diamond facets became obvious. We assert that without tungsten particles, the substrate did not need to consume excess energy, and was therefore able to grow complete diamond facets in a fixed period of time. The tungsten particles were stacked and connected together, and did not find the single tungsten particle. Tungsten particles are softer than diamond, and diamond film does not cover clusters of tungsten particles totally, thus reducing the adhesive quality of diamond film. The simple solution is extending deposition time of diamond films, so that diamond films may grow and cover tungsten particles. The effect of tungsten particles on diamond film quality is discussed in Raman test.

Newly generated diamonds were ball-shaped [21–23], with few surface structures. The FE-SEM results show that the diamond particles had formed clusters around the tungsten particles and combined with the structure at high temperatures. The resulting diamond particles were approximately 0.4, 0.6, 0.8, and 1.0 μm, corresponding to tungsten particles of 0.6, 0.8, 1.0, 2.0 μm. The number of diamond balls increased with an increase in par-

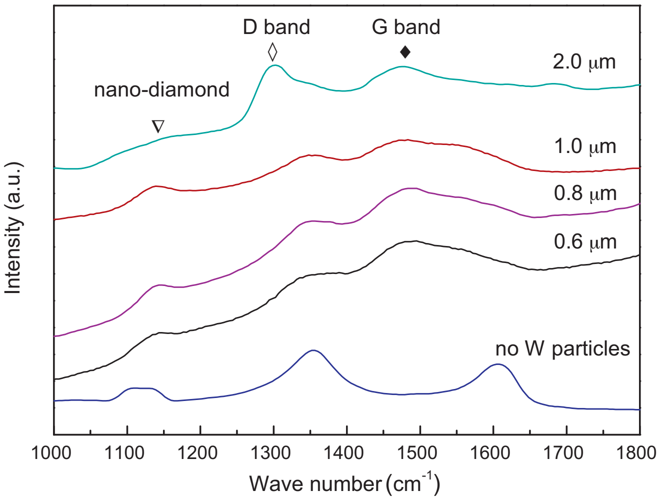

Fig. 4. Raman spectra of diamond films with and without pretreatment using tungsten particles of various sizes on substrate.

ticle size, leading to more complete coverage of the diamond film on the substrate.

Because the surface of the substrate was covered by the diamond film after 4 h deposition time, facets of diamond crystals appeared only at a particle size of 2.0 µm (Fig. 3(e)). Fig. 3 illustrates the special phenomenon of tungsten particles embedded in diamond films after 4 h deposition time, indicating that tungsten reacts easily with active carbon species and dissolves into the diamond. In summary, larger tungsten particles attract a greater quantity of carbon, thereby increasing the growth rate of the diamond film.

3.3. *The Raman of specimens*

Raman spectroscopy is the most widely used technique for characterising the composition of diamond films, because each phase specific peak identifies diamond, graphite, or amorphous carbon, in accordance with its characteristic vibration modes. The spectra contained both the D-band of diamond at 1332 cm^{-1} and the G-band of graphite at 1580 cm^{-1} [24]. Fig. 4 shows the Raman spectra of diamond films pretreated with tungsten particles of various sizes and film produced without tungsten treatment. In no W particles data, the wave numbers were 1360 and 1620 cm^{-1}, indicating an increase of approximately 30–40 cm. The peaks were slightly blue-shifted [14] due to compressive stress resulting from gaps between particles.

The morphology of amorphous diamond manufactured by diamond deposition showed that the D-band was not sharp in all samples. The 2.0 µm particles exhibited a sharp peak of sp^3 carbon hybridization, and the peak was slightly red-shifted compared to standard diamond phase (D-band, 1332 cm^{-1}). This shift might has been the result of tensile stress, probably due to the thermal expansion coefficient and vacancies caused during the deposition process. From the Raman and FE-SEM, it is clear that the 2.0 µm particles produced the highest quality diamond films among all of the samples employing tungsten pretreatment.

All Raman spectra exhibited a broad peak in the range of 1400–1650 cm^{-1}, corresponding to the amorphous carbon phase and the non-diamond phase (including G-band). Clearly, the tungsten treatment caused the production of low quality diamond films, just as in the growth period. Under these parameters, crystalline diamonds cannot be formed in the same period of time, because more energy is required to form crystals around the tungsten particles using a diamond deposition system such as this. Raman spectra clearly displayed another peak at approximately 1150 cm^{-1}. Previous research has shown that the feature at 1140 cm^{-1} is due to nano-crystalline diamond [25,26].

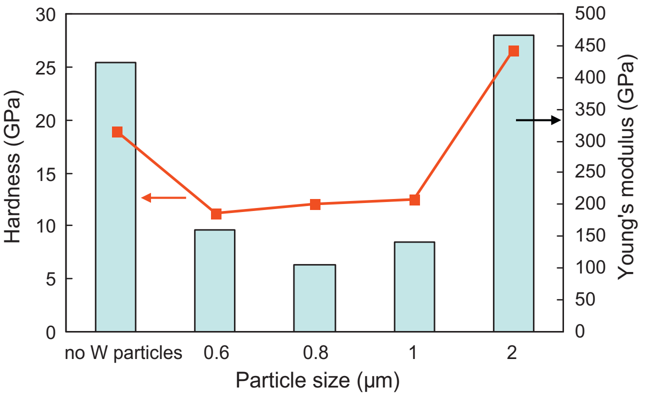

Fig. 5. The hardness and Young's modulus (*E*) of diamond film with and without pretreatment using tungsten particles of various sizes.

3.4. *Hardness and Young's modulus*

Nanoindenters are well suited to measuring hardness and Young's modulus in film materials. The hardness and Young's modulus (*E*) of diamond film produced with and without pretreatment using tungsten particles are shown in Fig. 5. From this figure we can see the relative relationship between hardness and Young's modulus, in which both curves show the same trend. Diamond films produced without tungsten particles and those produced with pretreatment of 2.0 µm tungsten particles had hardness of 25.37 and 27.78 GPa, respectively. These values are two–three times greater than those of diamonds made with particles of other sizes were. According to FE-SEM and Raman, it is clear that the surface of crystalline diamond samples produced without tungsten particles and those made with tungsten particles of 2.0 µm had superior hardness performance compared with samples made with tungsten particles of other sizes.

3.5. *Adhesion test*

This study used the Rockwell-A indentation test to estimate the adhesion of diamond films on substrates using tungsten particles of various sizes. FE-SEM results (Fig. 6) revealed the morphology of the indentations for all samples under a 60 kg load. The indentation test may make diamond films fall off substrate. The comparison of peeling area of diamond films can determine the adhesive quality. Fig. 6(a) shows that diamond films which are not treated with tungsten powders peel in sheets. Fig. 6(e) shows that diamond films treated with 2 µm tungsten powders peel in flakes. The comparison of peeling area of diamond films above indicates that diamond films treated with 2 µm tungsten powders peel have higher adhesion than those without being treated with tungsten powders. As shown in Fig. 6(a), the indentation caused the propagation of cracks and many de-laminations in the area surrounding the contact between the diamond film and the substrate, in a raw sample without acid pretreatment or treatment with tungsten particles. However, the inclusion of tungsten particles of various sizes (Fig. 6(b)–(e)) produced smaller cracks with less surface peeling. For this reason, it was determined that specimens produced with smaller tungsten particles (0.6 and 0.8 µm) had superior adhesion; while specimens produced with larger tungsten particles (1.0 and 2.0 µm) had inferior adhesive properties. Although small tungsten particles have better adhesion than large tungsten particles, the latter is superior to samples which are not treated with tungsten powders as a whole. However, their application should take into consideration

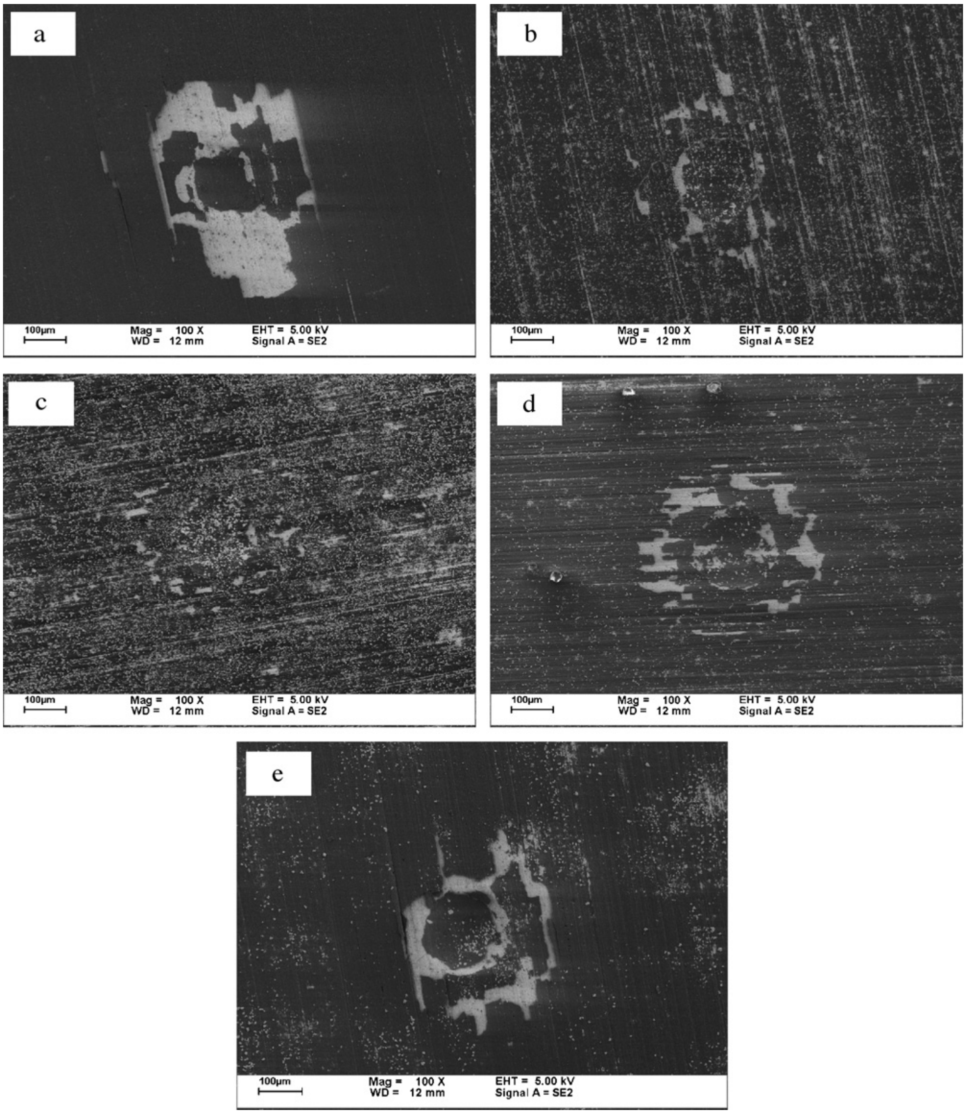

Fig. 6. Rockwell-A indentations showing the morphology of the diamond films with tungsten particles under a test load of 60 kg. The diamond films were coated with tungsten particles of various particle sizes: (a) no tungsten particles, (b) 0.6 μm, (c) 0.8 μm, (d) 1.0 μm and (e) 2.0 μm.

such diamond characteristics of crystallinity and hardness, so 2 μm tungsten particle is the best parameter in this experiment.

It can be observed from low-magnification of FE-SEM images, of which light color ones are tungsten particles and dark ones are diamond films, that all tungsten particles are evenly distributed. Macroscopically, small tungsten particles are densely distributed, and large tungsten particles are loosely distributed. As there is no effective dispersant for tungsten particles yet, tungsten particles may aggregate on samples. These samples were much better than samples produced without tungsten particles. Small tungsten particles produce small gaps, which improve adhesion after the growth of diamond film. The tungsten particles enhance adhesion by substituting a portion of the surface of the Co, where upon the W, WC-Co, and diamond bond with each other, following heat treatment.

From the TEM images, we observed the phenomenon in which tungsten particles combined and bonded with the WC-Co substrate (in Fig. 7). The carbon species formed diamonds along the upper edge of the tungsten particles and the surface of the tungsten carbide. Tungsten particles filled the gaps in which carbon atoms would be unable to enter to grow diamond. Spherical tungsten particles also caused many gaps, suggesting that reducing the number and size of gaps between the tungsten particles could enhance adhesion.

3.6. Discussion

We coated a WC-Co substrate with W particles to prevent a reaction between Co and carbon, and to promote the adhesion of the diamond film to the substrate. In pretreatment, we used ultrasonic vibration to distribute the tungsten particles on the surface of the sample. We used tungsten particles of various sizes to study the adhesion of diamond films to a tungsten carbide substrate. The WC-Co substrate facilitated the growth of diamond films in a CVD system. Through XRD, it was seen that the peaks in the intensity of WC increased, indicating a change from W to WC during the process of diamond deposition. The nucleus of diamonds in the vicinity of W grew and eventually covered the tungsten particles. Fig. 8 shows a schematic diagram of diamond films formed through a combination of tungsten particles with carbon species.

After 4 h of diamond deposition, only the surface of the sample pretreated with 2.0 μm tungsten particles had a clear diamond phase, while samples produced with tungsten particles of other

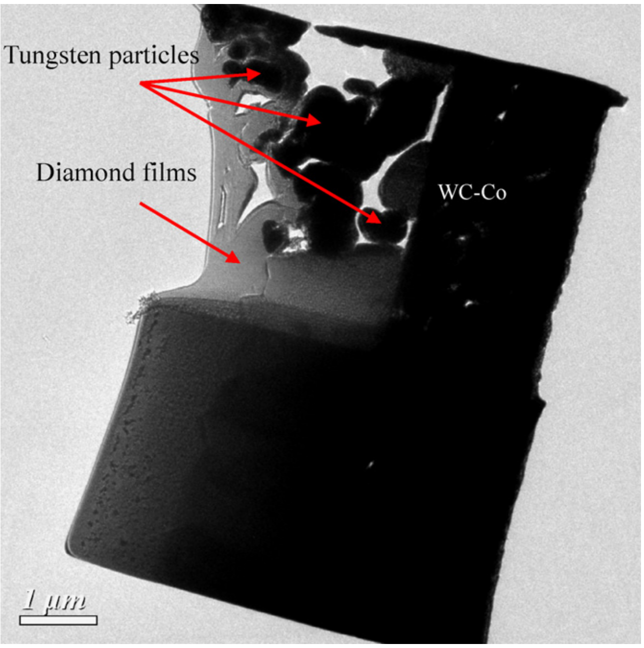

Fig. 7. TEM image of 0.6 μm tungsten particles processed specimens after diamond deposition.

sizes did not. This is a clear indication that larger particles of tungsten encourage the growth of diamond, preferring to grow on the surface of crystalline diamond films. However, all of the diamond deposition reactions required more energy to transform the tungsten into WC. Therefore, when the surface of the sample was covered with too many tungsten particles in the preview experiment, the diamond film did not grow on the surface, even under the same conditions.

Pretreatment with smaller tungsten particles provided superior adhesion, as the gap between the particles was reduced, due to a more compact arrangement. The tungsten particles bound with the WC-Co substrate to provide a degree of adhesion. Clearly, distributing appropriately tungsten particles on the WC-Co substrate improves the adhesion of diamond film. When the space between tungsten particles was reduced, the adhesion of the diamond films to the WC-Co substrate considerably improved. In this study, the adhesion of all samples pretreated with tungsten particles improved. According to Raman and adhesion data, we determined that pretreatment with 2.0 μm tungsten particles was optimal for this application in a fixed period of time.

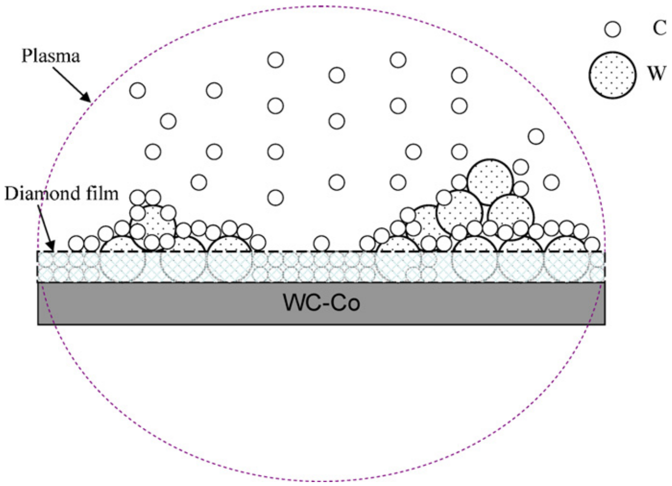

Fig. 8. Schematic diagram of diamond films formed by tungsten particles and carbon species.

4. Conclusions

The growth of diamond film on tungsten carbide tool steel can enhance abrasion resistance. We applied tungsten particles of various sizes to the production of diamond film to determine the ideal parameters for the enhancement of adhesion between the film and substrate. Following diamond deposition, tungsten particles transformed into W_2C and WC, and the availability of WC as carbon and CH_3^- made it highly conducive to the growth of diamond. Larger particles of tungsten produced larger diamond particles with improved crystallinity.

Pretreatment with 2.0 μm tungsten particles proved ideal for the production of crystalline diamond film. The degree of adhesion between the diamond film and substrate appears to be inversely proportional to the quantity and size of gaps between the tungsten particles. Diamond films produced with tungsten particles of 2.0 μm showed the highest hardness of 27.78 GPa and good crystallinity. Therefore, this study considers pretreatment using tungsten particles of 2.0 μm to be the optimal approach for the enhancement of abrasion resistance in industrial products through the application of diamond films.

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