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Deposition of tungsten-titanium carbides on surface of diamond by reactive PVD ①

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Abstract: The coatings of W-Ti carbides on the surface of diamond was obtained by using physical vapor deposition (PVD), during which WO_3 powders pre-treated with hydrofluoric acid were reduced by titanium hydride in vacuum at 850 ℃. The resistance of diamond to corrosion at high-temperature was investigated. The formation of W-Ti carbides on the surface of diamond was verified by X-ray diffraction analysis, the interface state between diamond and matrix in metal-base diamond composite was observed by scanning electron microscope. The results showed that the carbide coating is easy to be formed at low deposition temperature on the surface of diamond, while the resistance of diamond to corrosion at high-temperature and the strength of bonding between diamond and metal matrix are effectively improved.

Key words: diamond; physical vapor deposition (PVD); tungsten carbides; tungsten
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1 INTRODUCTION

Diamond tools are made generally by the powder metallurgical process. It is obvious that the interface energy between the diamond and ordinary metals or alloys is very high, and diamond crystals are unwettable to any low melting point metals and alloys, and its ability for welding is poor[1]. The studies[2~4]in many countries have shown that some carbophilic (that means affinity to carbon) metals or alloys deposited on the surface of diamond can react with diamond to form metal carbides[5], which have strong chemistry affinity to diamond and adhesion to metal matrix. In addition, the metals and carbides of metals deposited on diamond surface can prevent diamond from oxidizing at high temperature[6].

Physical vapor deposition (PVD) is a common method to deposit metals on the surface of materials, it can deposit some metals which are uneasily deposited in water solution, such as W, Ti etc. If some chemical reaction can take place in PVD, which is called reactive PVD, carbide coatings, such as WC, TiC etc can be obtained. In recent years, investigations[7~12] about deposition of carbophilic metals on the surface of diamond by PVD have been developed. Tungsten and titanium are all excellent carbophilic metals, depositing W-Ti on diamond surface can improve effectively the bonding strength between diamond and metal matrix. In the present work, the deposition of W-Ti carbides on diamond surface by reactive PVD is studied.

2 EXPERIMENTAL

Five grams of WO_3 powders and 0.1 mL of acetone solution containing 1% hydrofluoric acid were taken into porcelain crucible, and were blended well. Then about 10 g of JR_3 diamond grains and trace of titanium hydride, which was used as reducer, were added into the crucible and mixed fully with WO_3 powders. The crucible was subsequently placed into the vacuum system

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and heated to 850 ℃ at the pressure of less than 10^{-3} Pa. After heated for 60 ~ 90 min at a constant temperature of 850 ℃, an excellent coating of W-Ti carbides was deposited on the surface of diamond. The coated diamond was analyzed by X-ray diffraction. The composite of diamond and Cu alloy powders was prepared by hot pressing and sintering, and the state of bonding between the diamond and the metal matrix in the composite was observed by SEM.

3 RESULTS AND DISCUSSION

3.1 Mechanism of reaction

When W is deposited on the surface of diamond, a quite high temperature is needed to get a good coating due to the difficulty for tungsten to evaporate. In the technology presented in this work, WO_3 reacted with HF to form WF_6, and then WF_6 was reduced by hydrogen decomposed from titanium hydride to produce tungsten atom, which can react easily with carbon atom on the diamond surface to form tungsten carbide. Titanium decomposed from titanium hydride can also react with carbon atom on the surface of diamond to form titanium carbides. The chemical reaction concerned is as follows:

$$WO_3 + 6HF = WF_6 + 3H_2O(g) \quad (1)$$

$$TiH_2 = Ti + H_2 \quad (2)$$

$$3H_2 + WF_6 = W + 6HF \quad (3)$$

$$C + W = WC \quad (4)$$

$$C + 2W = W_2C \quad (5)$$

$$Ti + C = TiC \quad (6)$$

3.2 X-ray diffraction analysis of coatings on surface of diamond

In order to verify the deposition of carbophilic metals and the formation of carbides, X-ray diffraction analysis was carried out for coated diamond (Fig. 1). The results showed that the feature peaks of carbides of tungsten and titanium appear in X-ray diffraction pattern.

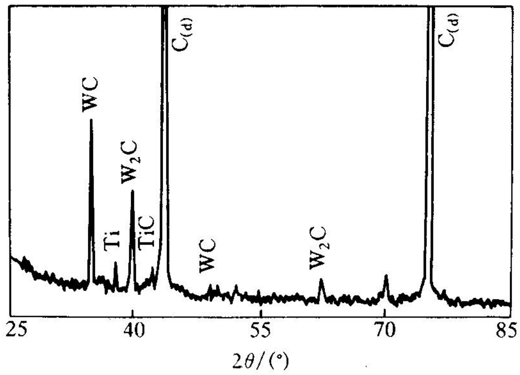

Fig. 1 XRD pattern of W-Ti carbides coating on surface of diamond

3.3 Resistance of diamond to corrosion at high temperature

After heat treatment at 900 ℃, 1 050 ℃ in atmosphere, the uncoated and coated diamond were analyzed by SEM, and the shapes of the diamond surfaces are shown in Fig. 2 and Fig. 3. The oxidization process and corrosion mechanism of diamond could be realized from the changes of the shapes of the diamond surfaces after heat treatment.

Fig. 2 showed that the uncoated diamond was subjected to severe corrosion after heated at 900 ℃ and more severe corrosion at 1 050 ℃ with a lot of etching pits on the surface of diamond. However, the diamond deposited with coating of W-Ti carbides was subjected to very faint corrosion at 900 ℃ and 1 050 ℃ (Fig. 3), only a bit of small and shallow etching pits appeared on the diamond surface, which illustrated the diamond deposited with coating of W-Ti carbides had strong resistance to corrosion and oxidization at high temperature.

3.4 Bonding strength between diamond and metal matrix in metal-base diamond composite

The diamond and powder of copper alloy were mixed and made into composite by hot pressing and sintering, then a face of the composite was ground and polished to expose the section of the diamond grains. The state of bonding between the diamond and the metal matrix was observed by SEM (see Fig. 4). The results showed that there were obvious rifts between the uncoated diamond and the matrix, which

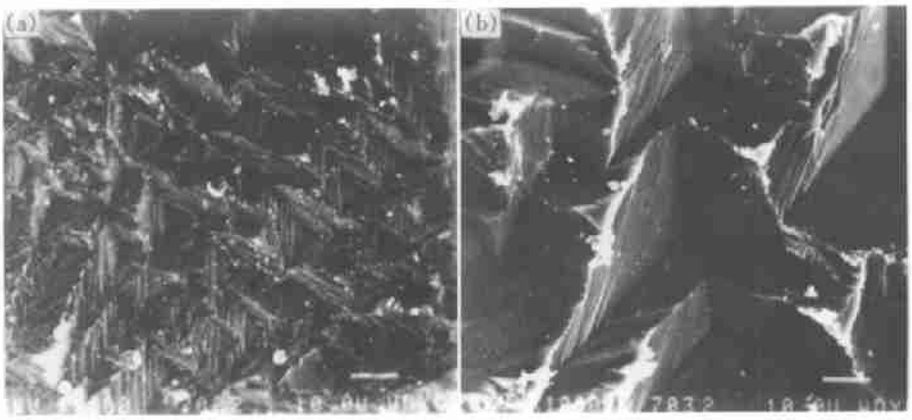

Fig.2 Surface shapes of uncoated diamond after heated for 10 min in atmosphere
(a)—At 900 ℃; (b)—At 1 050 ℃

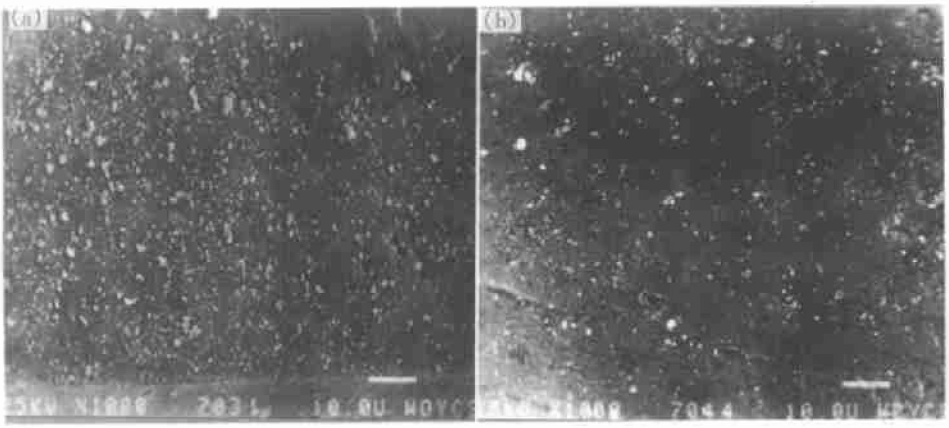

Fig.3 Surface shapes of diamond deposited with coating of W-Ti carbides after heated for 10 min in vacuum
(a)—At 900 ℃; (b)—At 1 050 ℃

implied the poor strength of bonding between the uncoated diamond and the matrix, however only tiny crack appeared between the coated diamond and the matrix. This fact may be explained as follows: As the interface energy between the metal matrix and the diamond is very high, and the crystal of diamond is unwettable to the metal matrix, the bonding between the diamond and the metal matrix may be thought to be inlaid mechanically. As a result, the matrix metals around the diamond can be worn away easily, and rifts and cracks appear between the diamond and the matrix. In another aspect, the coated diamond can be bound chemically with the metal matrix because W, Ti deposited on the surface of diamond can react with carbon atoms on the crystal of diamond at high temperature to form carbides, which can strengthen greatly the adhesion between the diamond and the metal matrix.

4 CONCLUSION

WO_3 powder treated chemically by hydrofluoric acid was used as test material, and titanium hydride was used as reducer, the W-Ti

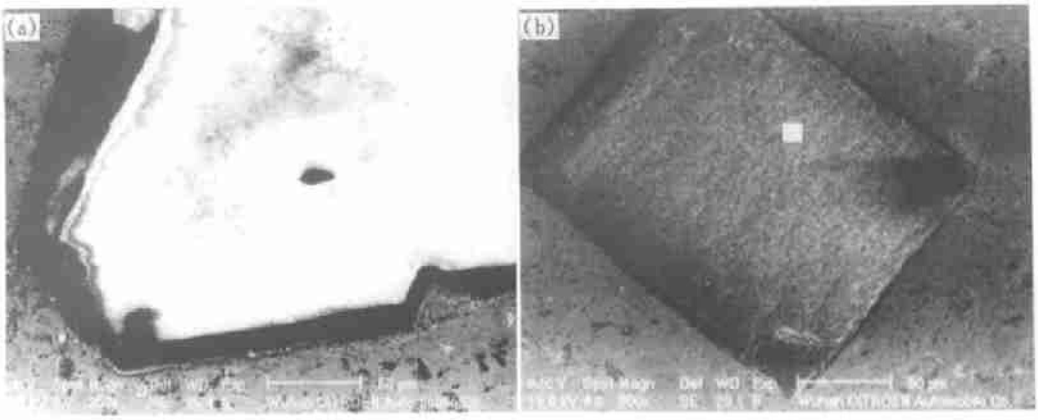

Fig.4 SEM photographs of interface between diamond and metal matrix in diamond composite
(a)—Uncoated diamond; (b)—Coated diamond

carbides coating was deposited on the diamond surface in vacuum at 850℃ by PVD. The results of X-ray diffraction analysis of the coated diamond had testified the formation of tungsten-titanium carbides on the diamond surface, carbides formed on the surface of diamond can improve effectively the bonding strength between diamond and metal matrix, as well as the resistance of diamond to corrosion at high temperature.

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