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Study on interface between titanium-coated diamond and metal matrices①

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[Abstract] The XRD spectrum of titanium-coated diamond showed the existence of titanium carbide on the interface between diamond and its titanium coating. The diffusions between titanium coating and metal matrices were studied by SEM. The SEM photographs revealed that titanium can interdiffuse with nickel, cobalt, copper, iron and copper-based alloy to a great extent to lead to the disappearance of pure titanium layer and the formation of titanium diffusion layer. The results from transverse-rupture strength test showed that titanium coating on diamond improved the bonding strength between diamond and metal matrices by 3.2% for Co-based segment and 4.1% for Cu-10Sn based segment respectively.

[Key words] interdiffusion; transverse-rupture strength; titanium-coated diamond
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1 INTRODUCTION

Since the first synthetic diamond was successfully produced in 1950s, diamond tools have been widely used in many fields, such as stone processing, construction etc. In practice, strong bonding strength between diamond and matrix is very important to diamond tools. The tool life and efficiency, to a great extent, are determined by the retention of diamond grits[1,2]. The saw blade performance of uncoated diamond was compared with that of coated (with Ti and Cr) by Webb[3]. It showed that the improvement in retention is Cr-coated > Ti-coated > uncoated. Evens etc[4] studied the wetting and bonding of diamond with copper-tin-titanium alloys, and convinced the adhesion work W_a may be assessed by measuring the wetting of the surface of one phase by another that is in liquid state:

$$W_a = \sigma \cdot e_g (1 + \cos\theta) \quad (1)$$

where $\sigma \cdot e_g$ is the free energy of the liquid/gas interface and θ is the contact angle.

The transverse-rupture strength (σ_{bb}) test has been widely used to evaluate the fracture strength of the fragile materials such as cast iron, tungsten carbide and diamond segments[5~7].

$$\sigma_{bb} = 3p_0 \cdot L/(2b \cdot h^2) \quad (2)$$

where L, h and b are the length, thickness and width of the sample, and p_0 is the load applied.

2 EXPERIMENTAL

All the powders used in these tests were carbonyl iron powder, carbonyl nickel powder, carbonyl cobalt powder, < 75 μm copper-tin powder and < 75 μm tungsten carbide powder. The diamond types were JR5 250 ~ 300 μm diamond, uncoated and titanium-coated. Titanium coating was uniform, about 1 μm thick. The diamond was 8% in volume.

TRS sample sizes were 40 mm × 8 mm × 6 mm. Those samples were hot-pressed at the pressure of 25 MPa. The sintering temperature was 900 ℃ for cobalt-based bonds and 870 ℃ for copper-tin based bonds with the same holding time of 80 s. After the TRS tests, the fractured surfaces were observed with scanning electron microscope (SEM).

The titanium plate was hot-pressed with iron, nickel, cobalt, copper, copper-tin based alloy powders respectively, under 25 MPa, at 800 ℃, for 2 or 5 min in order to model the diffusion between titanium coating and metal matrices. Then, the diffusion layers were observed with SEM.

3 RESULTS AND DISCUSSION

3.1 XRD spectrum of titanium-coated diamond

Diamond was coated with titanium at 650 ~ 750 ℃ for 1 ~ 2 h in vacuum. The peaks of diamond, titanium carbide and titanium can be observed from the XRD spectrum of the Ti-coated diamond in Fig. 1. As we know, some carbide-forming elements can react with diamond at certain condition.

$$Ti + C_{(d)} \longrightarrow TiC$$

where $C_{(d)}$, referred to as diamond. An equation of free energy at 298 ~ 1 400 K takes the form[6]:

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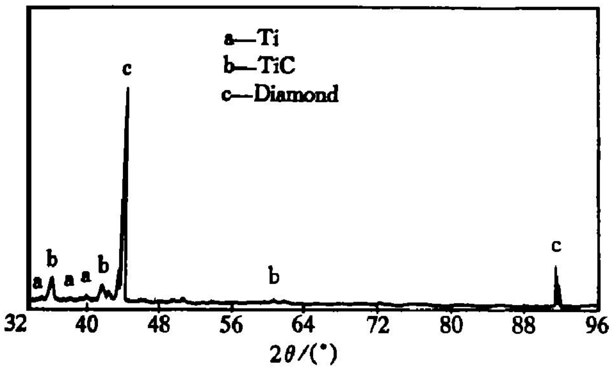

Fig.1 XRD spectrum of Ti-coated diamond

$$\Delta G = -185\,520.8 + 5.957\,34T \quad (3)$$

When the temperature is kept at about 950 K, $\Delta G<0$. That is to say, the process of transforming into titanium carbide is automatic. According to DTA curve[8], it is a heat generation reaction. The higher the reaction temperature is, the faster it processes. From Fig.1, it can be inferred that there exists a three-layer structure. In the course of titanium depositing in vacuum, titanium carbide, perhaps first forms on the interface between diamond and titanium. With the reactions processing, the carbon diffuses to the interface between titanium carbide and titanium, and titanium carbide epitaxially grows there.

As soon as the titanium carbide is formed, the wetting situation of diamond by metals is changed. The wetting of titanium carbide by metal is better than that of diamond[9]. And that helps to sinter diamond segments.

3.2 Interdiffusion

Owing to the difficulties of investigation on the reaction between titanium layer on diamond and segments (This layer is too thin to be examined by normal equipment), titanium plate was used to substitute for the diamond coating in the following tests. Fig.2 is the SEM photographs of the diffusion layer between titanium plates and different metal powders.

From Fig.2, it can be demonstrated that under normal hot-pressing conditions, titanium and iron, nickel, copper, copper-tin alloy, cobalt can , to a great extent, interdiffuse to form a diffusion layer. The interdiffusion layer between titanium and nickel is comparatively thin, perhaps less than 1 μm (Fig.2 (b)), other interdiffusion layers are more than 2 μm, especially for copper-tin alloy and titanium, perhaps more than 5 μm. At 800 ℃, the equilibrium phases for titanium are α-Ti and little β-Ti. It can be inferred from those data[10] that interdiffusion coefficient D of nickel and titanium is one order of magnitude smaller than that of other metals. But One thing is very certain that titanium coating on diamond can still interdiffuse with nickel totally. It should be avoided that catalysts, such as iron, nickel and cobalt diffuse through titanium and titanium carbide layers to get in touch with diamond. They will accelerate the process of transforming diamond into graphite, weakening the bonding between diamond and metal matrices and deteriorating the strength of diamond.

3.3 Transverse-rupture strength (TRS) tests

The TRS difference value between the segments with and without diamond was often used to evaluate the bonding strength between diamond and matrices. Table 1 showed the results of TRS tests. Type A is a cobalt-based alloy, whereas type B is a copper-tin based alloy. From Table 1, it is showed that TRS for segments with diamond are about 20% smaller than those without diamond (we call them pure segments). The volume fraction of diamond is 8%, so the average linear density for diamond is $\sqrt[3]{0.08}\approx$ 0.43, the average density in area is $\sqrt[3]{0.08^2}\approx$ 0.186. If the diamond is not coated with titanium, during the hot-pressing process, catalysts (such as iron, nickel, cobalt) could contact with diamond and promote the graphitization of diamond. In addition, cobalt, nickel, iron are solvents of carbon, and they dissolve diamond at hot-pressing conditions, then graphite is separated out at room temperature. Both above actions to diamond weaken the bonding strength between diamond and metal matrix. In fact, there is little bonding strength between them. For the fracture strength of composite materials[11], there exists:

$$\sigma_b = \sigma_{b0}(1-\varphi_f) + \sigma_{bf}\varphi_f \quad (4)$$

where σ_b, σ_{b0}, σ_{bf} are the fracture strength of composite, matrix and reinforcement fibre, respectively, and φ_f is the volume fraction of fibre.

As to diamond segments, a similar equation is

Table 1 Results for transverse rupture strength

Type		TRS, σ_{bb}/MPa				Improvement of σ_{bb} after diamond coated with Ti/%
		Sample 1	Sample 2	Sample 3	Average	
A	Segments without diamond	902	896	889	896	
A	Segments with uncoated diamond	760	715	731	735	
A	Segments with Ti-coated diamond	778	745	743	759	3.2
B	Segments without diamond	943	976	925	948	
B	Segments with uncoated diamond	754	759	766	760	
B	Segments with Ti-coated diamond	821	788	793	791	4.1

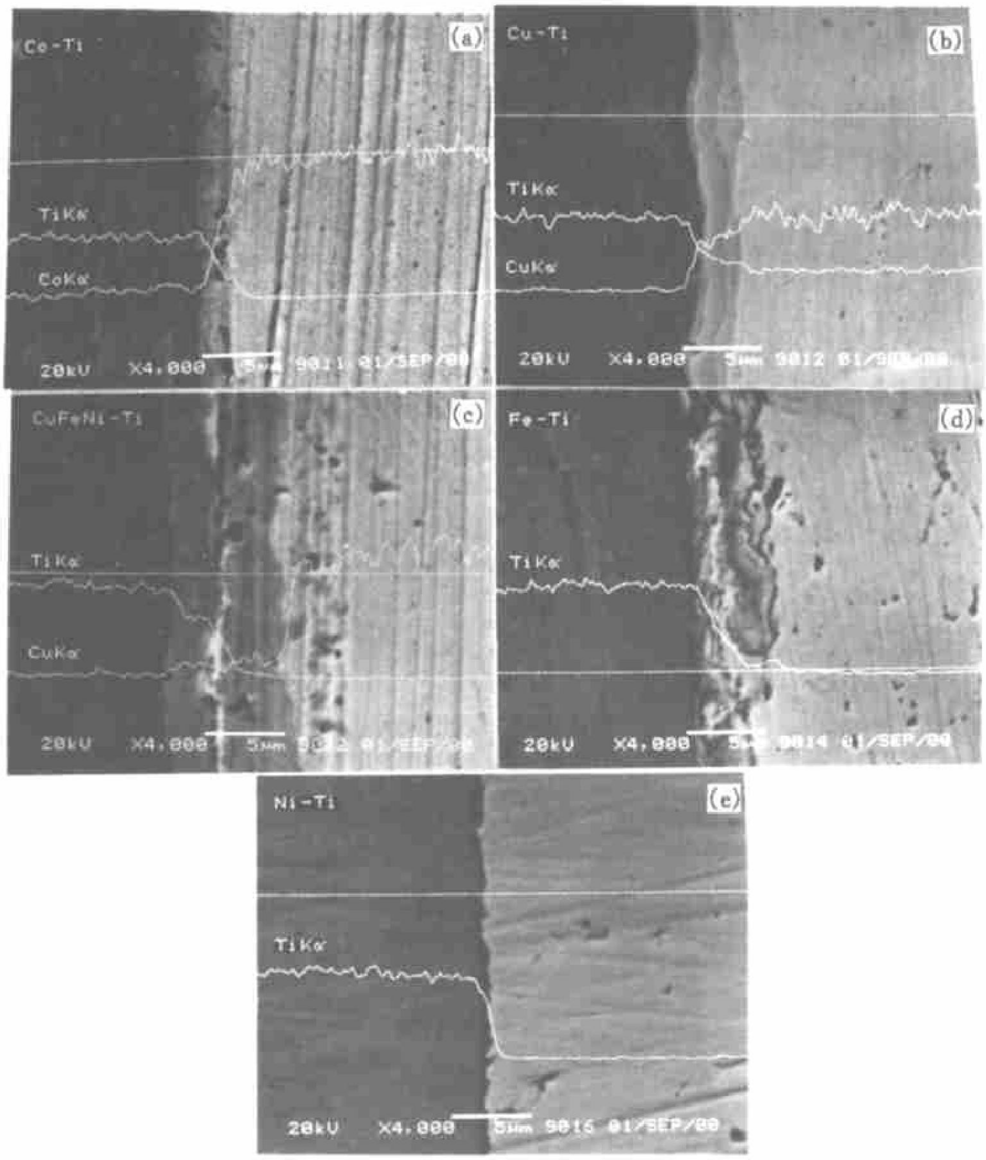

Fig. 2 SEM photographs of interfaces between titanium plates and metal powders (800 ℃, 25 MPa)
(a)—Titanium and cobalt (2 min); (b)—Titanium and copper (2 min); (c)—Titanium and copper alloy (2 min);
(d)—Titanium and iron (2 min); (e)—Titanium and nickel (2 min)

put forward:

$$\sigma_{bb} = \sigma_{bb0}(1 - S_d) + K\sigma_{bbd} S_d \quad (K > 0) \qquad (5)$$

where σ_{bb0}, σ_{bbd}, σ_{bb} are TRS of matrix, diamond and segment, respectively, and S_d is the density of diamond in area.

At an arbitrary cross section, owing to little bonding strength between diamond and matrix, diamond doesn't undertake the load it should do, so the TRS decreases a lot. In Table 1, the TRS of the uncoated diamond decreases by 18% for type A and by 19.8% for type B. These values are very close to 18.6%, the density of diamond in area. That is to say, for the TRS of uncoated diamond, there exists

$$\sigma_{bb} = \sigma_{bb0}(1 - S_d) \qquad (6)$$

When the diamond is coated with titanium, the titanium layer, to some degree, prevents catalysts or solvents (Ni, Co, Fe) from contacting with diamond. So, on one hand, it abates the graphitization and dissolution of diamond; on the other hand, titanium is a carbide-forming element, it could react with diamond into titanium carbide, in the process of sintering, the titanium layer and metal matrix could interdiffuse to form a diffusion layer. Because of the above reasons, the titanium coating on diamond improves the bonding condition between diamond and matrix and improves the transverse-rupture strength. The figures from table 1 show that the TRS of segments with Ti-coated diamond have an increment of 3.2% for type A and 4.1% for type B.

Both in copper-tin based and in cobalt based alloyed matrices, the pull-out pits of the uncoated diamond are very smooth (Fig. 3(a), 3(c)), whereas those of the Ti-coated diamond are very rough (Fig. 3(b), 3(d)). The rough pits should result from the strong bonding strength between diamond and matrices. When the segments fracture, the Ti-coated diamonds leave the segments with small parts of metal matrix.

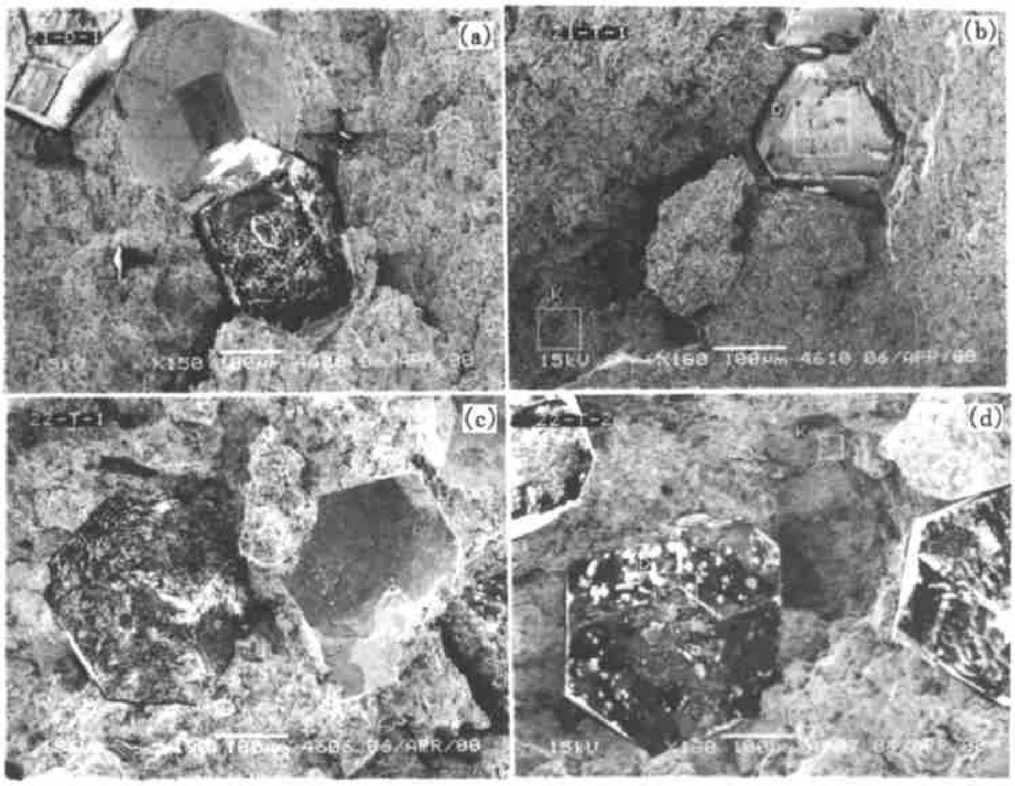

Fig.3 SEM photographs of fracture sections from TRS tests
(a)—Co based segment, uncoated diamond; (b)—Co based segment, Ti-coated diamond;
(c)—Cu-Sn based segment, uncoated diamond; (d)—Cu-Sn based segment, Ti-coated diamond

To sum up, after hot-pressing, a four-layer structure is formed.

Here, the wetting of diamond by metal should be told from the bonding strength between diamond and metal . For example, nickel, cobalt, and iron could wet diamond better than many other metals, but they accelerate the graphitization of diamond, so weakening the bonding strength[12]. The good wetting of diamond by carbide-forming elements is the result of the change of the objective of wetting, from diamond into carbide.

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