

Adjustment of residual stress and intermediate layer to BDD/porous Ti composite membrane*

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Diamond films are deposited on porous Ti substrates by hot filament chemical vapor deposition (HFCVD) method. For adjusting the residual stress of substrate and the titanium carbide (TiC) intermediate layer, the substrates are under annealing process firstly, then are put into alkaline solution with electricity oxidation, and finally composite membranes are obtained by HFCVD, which are characterized by X-ray diffraction (XRD), metalloscope and scanning electron microscope (SEM). Results show that the composite membranes deposited on unannealed substrates are cracked obviously in both sides and broken off easily. After annealing process, the membranes are no longer cracked easily, because the tensile stress distributed in substrates is significantly relieved. After passivation process, TiC generated between diamond film and substrate is less than that without passivation process.

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Diamond thin films have received great attention because of the excellent physical and chemical properties. Especially in recent years, compared with other traditional electrodes, boron doped diamond (BDD) as a new electrode is very suitable for wastewater treatment based on its significant advantages, such as wide potential window, high oxygen evolution potential and low background current.

Titanium (Ti) has been widely used in the fields of aviation, military and civilian industry with the properties of low density, high specific strength and wide range of working temperature. The electrodes made of BDD film and Ti plate have attracted more and more attention^[1-4] due to the excellent properties of the two materials above. However, there are a series of problems in BDD film grown on Ti^[5]. For example, TiC as an intermediate layer can be generated during deposition. Massive TiC can cause the poor adherent strength between the film and substrate, and the film falls off for its loose and porous structure^[6]. More and more relative researches have been done on BDD film grown on Ti plate^[7-9], which have great help to a further understanding of BDD Ti-based film.

As BDD film has good electrochemical properties, using it with membrane separation technology for controlling environmental pollution has increasingly become a hot area of research. In previous work, BDD film was deposited on porous Ti as the substrate to fabricate a kind of novel composite membrane. Compared with tradi-

tional membranes, its most significant feature is self cleaning, which exhibits the feasibility to solve membrane fouling^[10]. However, the correlational researches of BDD film deposited on porous Ti are very few. There are some new problems on porous Ti different from those on Ti plate, especially residual stress^[11], which causes the poor adherent strength and the effect of titanium carbide (TiC) intermediate layer. Hot filament chemical vapor deposition (HFCVD) has been a significant method in diamond deposition on Ti substrate^[12-18]. This paper shows how to deposit BDD films on porous Ti substrates by HFCVD. Meanwhile, annealing pretreatment and passivation on surface are performed.

The substrates for this experiment are porous Ti made of Ti metal powder by powder metallurgy. Experimental samples are divided into 5 groups named as A, B, C, D and E, respectively. All samples were put into suspension liquid of 50 mg/L diamond powder with grain size of 0.7 μm under ultrasonic treatment for 30 min to improve nucleation density^[19]. Ultrasonic cleaning of substrates was operated with acetone and deionized water for 5 min, respectively. Then the substrates were treated as follows. Sample A was done without annealing and passivation treatment. Put samples B, C and D into vacuum annealing furnace. Adjust the furnace temperature to 723 K and heat 20 min for B and C, then turn off the power. Change the temperature to 773 K for D. Make sure that the samples were cooled to room temperature, and then taken out of the furnace. Sample C was done without passivation

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process. Passivate three pieces of sample C named as C₁, C₂ and C₃ and sample D in sodium hydroxide liquor. Specific passivation conditions for sample C are shown in Tab.1. The power supply device is MOTECH LPS-305. Sample and stainless steel are as anode and cathode, respectively.

Tab.1 Specific passivation conditions for sample C

Passivation parameter	Sample		
	C ₁	C ₂	C ₃
Concentration	0.05 mol/L		
Time	20 min	30 min	40 min

The experiments were carried out by HFCVD, during which boric acid, hydrogen and acetone were used as boron source, carrier gas and carbon source, respectively. Six Ta wires with diameter of 0.6 mm were used as hot filaments. The six filaments were carbonized for 30 min before diamond deposition. The carbonization voltage was increased from 3 V to 15 V, then decreased to 3 V and turned off. Samples were put into deposition chamber to work after carbonization. Hydrogen flow rate was 240 cm³/min, and carbon flow rate was 70 cm³/min. Specific processing parameters are shown in Tab.2.

Tab.2 Diamond deposition parameters

Processing parameter	Value
H ₂ flow (cm ³ /min)	240
Carbon flow in nucleation (cm ³ /min)	100
Boron doped quantity (mg/kg)	5000
Chamber pressure in nucleation (kPa)	1.5
Carbon flow in deposition (cm ³ /min)	70
Chamber pressure in deposition (kPa)	4
Power (W)	1350
Hot filament bias (V)	40
Hot filament temperature (°C)	2200
Substrate temperature (°C)	800
Deposition time (h)	5

The morphology and quality of passivated substrate and composite membrane were examined with XHC-SV1 metalloscope and JEOL JSM-6700F scanning electron microscope (SEM), respectively. The RIGAKU D/MAX-2500/PC X-ray diffractometer (XRD) was used to examine the substrate residual stress and the film component and phase. X ray source is Cu K α ray with wavelength of 0.15406 nm.

Porous samples were sintered by powder metallurgy, and the morphology is shown in Fig.1.

The XRD pattern of substrate is shown in Fig.2. It reveals that every lattice plane has an obvious peak with good crystallization. The diffraction peak angle of sub-

strate is smaller than that of nature titanium (PDF#:44-1294), which shows that porous substrate prepared by powder metallurgy has larger residual stress in the form of tensile stress^[20].

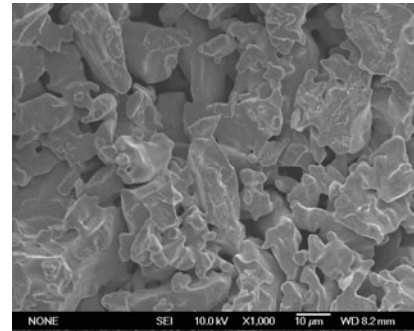


Fig.1 Top view of SEM image of porous Ti substrate

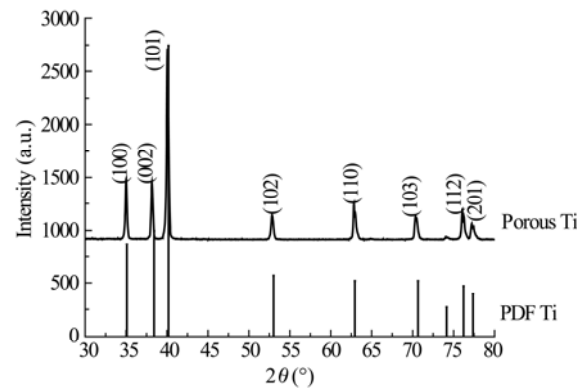


Fig.2 XRD patterns of the porous Ti substrate without annealing process and the nature titanium (PDF Ti)

Cooling process of composite membrane must be slow to avoid cracking, because the residual stress for porous substrate itself, the thermal stress and intrinsic stress formed during deposition all have bad influence on composite membrane^[21].

The sample of composite membrane deposited on sample A is shown in Fig.3. The result of sharp cooling process in 2 h is shown in Fig.3(a). The whole film was broken into fragment. The morphology cooling in 5 h is shown in Fig.3(b). The membrane surface was still cracked though the cooling rate slowed down, which has an enormous impact on composite membrane quality and lifetime.

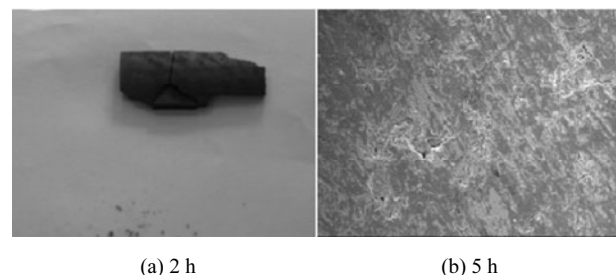


Fig.3 Top images of composite membrane without annealing after different cooling time values

Diamond film deposited by CVD on Ti shows compressive thermal stress, and Ti substrate shows tensile thermal stress, because their coefficients of thermal expansion are different. In addition, porous substrate fabricated by powder metallurgy shows large tensile stress itself. Both of them inevitably result in deformation and crack of porous substrate. The residual stress engendered by CVD process can not be controlled totally by adjustment of technological process. Therefore, it's necessary to release the residual stress of porous Ti substrate itself. If the residual stress is transformed to the compressive stress, the tensile stress caused by diamond deposition can be partially offset.

The annealing results of B, C and D are as shown in Fig.4. Compared with that of B, XRD pattern of sample C is better after annealing. When the temperature is up to 823 K, XRD pattern of sample D is not changed much more than that of sample C. Tab.3 shows the specific parameters of XRD diffraction peaks between sample B and sample C.

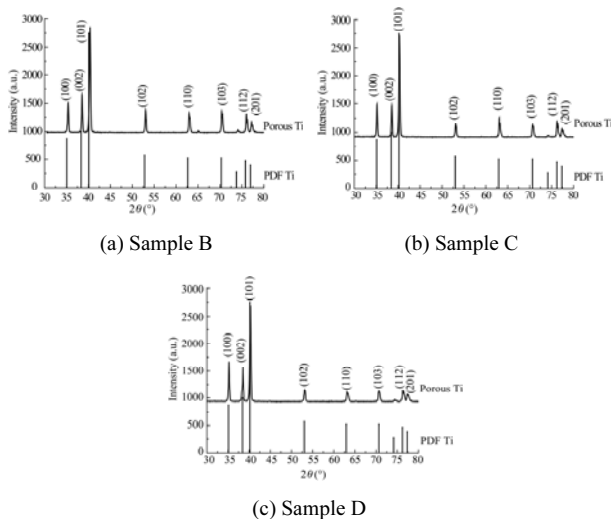


Fig.4 XRD patterns of the porous Ti substrates after annealing process

Tab.3 Comparison of XRD diffraction peaks between substrate and natural titanium before and after annealing process

<i>hkl</i>	<i>2θ</i> (°)		
	Pure Ti	Sample A (before annealing)	Sample C (after annealing)
100	35.09	34.94	35.14
002	38.42	38.12	38.49
101	40.17	40.04	40.24
102	53.00	52.75	53.03
110	62.95	62.88	63.07
103	70.66	70.34	70.68
112	76.22	76.08	76.23
201	77.37	77.16	77.37

Each diffraction peak angle is offset upward after annealing treatment. The internal stress of substrate is the compressive stress, which means the tensile stress is released and becomes compressive after annealing treatment according to Bragg equation

$$n\lambda = 2d \sin \theta, \tag{1}$$

where *n* (1, 2,...) is diffraction series, λ (nm) is X ray wavelength, *d* (nm) is interplanar spacing, and θ is the angle between incident ray and lattice plane.

Titanium itself is the strong carbide material, which reacts with operating gases to form titanium hydride (TiH₂) which is the first product and TiC at the beginning of diamond deposition. The intermediate layer generation is discussed^[6] in detail as diamond film is deposited on Ti plate. In initial stage, as shown in Fig.5, TiC grows quickly. Its rate slows down as diamond's deposition gradually increases, because the increasing area of diamond film prevents carbon into Ti substrate. After a while, TiC layer becomes thick and porous. The main reason is that titanium absorbs hydrogen and lowers the phase transition temperature from α to β . The transition temperature of β is about 600—700 °C, which causes the allegro formation of TiC because its formation is easier on temperature of β . TiH₂ is dehydrogenized at 600—800 °C under vacuum condition. So its production is less than TiC. Diamond nucleation and growth are based on the intermediate layer which is porous and stable at high temperature, while its existence can severely impact the service life when dealing with electrocatalytic degradation of organic matters.

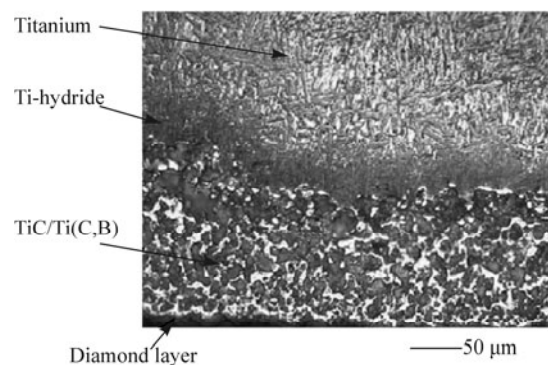


Fig.5 Intermediate layers between Ti substrate and diamond film

On that basis, this paper adopts a passivation process on porous substrate to form an oxidation layer before deposition in order to prevent the direct contact of titanium with carbon source and reduce the production of TiC. The morphologies of sample C before and after passivation are shown in Fig.6.

Substrate surface is sonicated by using diamond powder suspension liquid in order to protect oxidation layer and form scratching defect again like grinding effect. The XRD patterns of samples B, C₁, C₂ and C₃ after

deposition are shown in Fig.7.

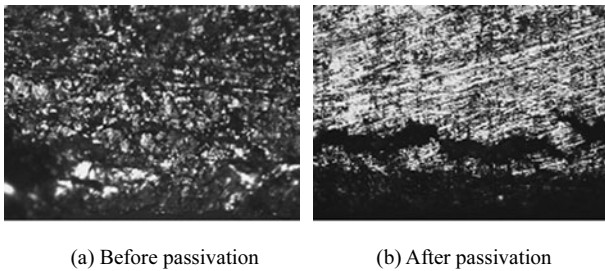


Fig.6 Metallographic microscope images of porous Ti substrates before and after passivation

From Fig.7, diffraction peaks of diamond at 43.9° and 75.3° can be identified clearly, corresponding to the (111) and (220) phases of diamond, and confirm its crystallinity presence with sharp peak and good crystalline. The peak at 43.9° is much higher than that at 75.3° , which indicates the preferred orientation is (111). The highest intensity peaks of two curves are both at 40.2° , and the relative intensity of TiC drops but not disappear after passivation treatment. The reason may be that the passivation layers are not so even that some small regions of the substrates aren't covered. In addition, the passivation layer isn't homogeneous, due to porous substrate itself is rougher than Ti plate. So central regions are bare somewhere along with diamond powder suspension liquid ultrasonic treatment. The relative ratios of TiC's peak intensities of sample B at 35.9° , 41.7° and 60.5° , corresponding to (111), (200) and (220), are 0.763, 0.660 and 0.298, respectively, and those of sample C₁ are 0.295, 0.230 and 0.090, respectively, while those of sample C₂ are 0.190, 0.178 and 0.066, and those of sample C₃ are 0.147, 0.134 and 0.049, respectively. The peak intensity of sample C₁ shows an apparent decline compared with that of sample B, which indicates content and coverage of TiC are substantially reduced. As passivation time extends, the degree of decline becomes more obvious. It demonstrates that the passivation layer inhibits the generation of TiC. When the surface of substrate is covered with a passivation layer, the generation of TiH₂ declines simultaneously, that is, the impact on the phase transition temperature from α to β becomes smaller. The generation of TiC can also be restrained. But the thickness and surface homogeneity are too hard to control to prevent TiC completely.

When the peak intensities of TiC decline, it can be seen that the peak intensity of diamond also declines. It is because the surface energy of diamond is always higher than that of any kind of substrate, and it's difficult for diamond to be deposited on the substrate directly. Titanium itself is the strong carbide material, which can react with operating gases to form TiC, so when carbon atoms combine with the dangling bonds of Ti surface, the free energy of Ti surface can be decreased, and thus diamond film can be deposited on Ti substrate. Therefore,

the passivation layer can not be as thick as possible in view of the quality of diamond deposition.

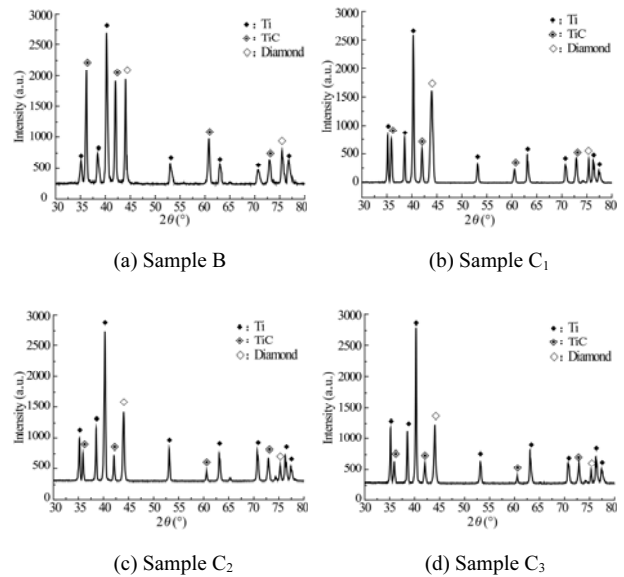


Fig.7 XRD patterns of composite membranes before and after passivation

The diamond film is deposited on porous Ti substrate using HFCVD. In order to eliminate the influence of residual stress of substrate from powder metallurgy, intermediate layer and thermal stress formed in deposition cooling process, annealing and passivation are all adopted so that the composite membrane can not be cracked and its lifetime can be improved. It is found that the residual stress of porous substrate itself is relieved significantly after annealing process at 773 K. When the temperature is up to 823 K, the result does not change much more. The original tensile stress of the lattice structure is adjusted as compressive stress, which narrows the thermal stress differences between diamond film and substrate. The fast-growing TiC forms an intermediate layer on the substrate in initial stage of diamond deposition. With the thickness of the layer increasing, TiC structure shows porosity, which is likely to cause diamond film off. Passivation process on the substrate before deposition can prevent carbon source from directly contacting with the Ti substrate. When the passivation layer becomes thicker and thicker, the quality of diamond deposition is affected. So the thickness of passivation layer should be controlled.

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