



Investigation on microstructure evolution and failure mechanism of boron doped diamond coated titanium electrode during accelerated life test



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ABSTRACT

For a long time, due to a lack of understanding on microstructure evolution of boron doped diamond (BDD) electrodes in application, there have been controversies on failure mechanism of the electrodes material. In this paper, A BDD coated titanium (Ti/BDD) electrode prepared by arc plasma chemical vapor deposition method was analyzed and accelerated life test (ALT) was carried out in 1 mol/L H₂SO₄ electrolyte at constant current density of 1A/cm². Various analyses techniques were combined to track the electrode failure process. The results showed that during the ALT process, the failure process of the Ti/BDD electrodes may be divided into two stages. In the first stage, defects existed in the coatings may lead to penetration of electrolyte into the BDD coatings, resulting in cracking and delamination of the coatings. Then in the second stage, corrosion of BDD grains and dissolution of intermediate titanium carbide layers occur accompanied by slow coatings delamination. Based on these analyses, possible ways to improve the service life of Ti/BDD electrodes are summarized.

1. Introduction

Boron doped diamond (BDD) has been considered as an ideal electrode material due to its high physical and chemical stability, wide potential window, low background current and non-toxicity [1, 2]. Specifically, BDD coated titanium (Ti/BDD), which could combine advantages of both Ti and BDD materials, possesses good potential in applications in the field of wastewater treatment [3–5]. Unfortunately, in terms of service life, Ti/BDD electrodes are found to be inferior to BDD coated niobium (BDD/Nb), tungsten (BDD/W) and silicon (BDD/Si) materials [6–8], and accelerated life tests (ALT) conducted under severe conditions demonstrated that Ti/BDD electrodes would show exfoliation of the BDD coatings as the primary reason of the electrode failure [8, 9].

Numerous investigations have been carried out to clarify failure mechanism of the Ti/BDD electrodes. Based on these investigations, different points of view have been given. To name a few, Chen et al. suggested that electrochemical corrosion of titanium carbide (TiC) interlayers formed between diamond coatings and Ti substrates would lead to delamination of the BDD coatings, when the electrolyte invaded the coatings through local defects [7]; Wei et al. suggested that poor quality and adhesion of BDD films would lead to short service life of the electrodes [10]; Tian et al. suggested that large residual thermal stress in BDD films should be the reason for the failure of the electrodes [11]; Chaplin et al. suggested that large coefficients of thermal expansion of

the corresponding oxides relative to the metallic substrates would result in delamination of diamond coatings [6]; and Guo et al. considered that the delamination of diamond coatings may be a complex process affected by many factors, among which dissolution of TiC layers, corrosion of diamond phase and high residual stress of the coatings may be main reasons [9]. Specifically, compared with those in BDD/W, BDD/Si and BDD/Nb systems, the bonding force between BDD coatings and Ti substrates is relatively weaker, and main influencing factors seem related with differences in thermal expansion coefficients between the substrate materials and nucleation characteristics of diamond on the substrate [12, 13]. However, all these conclusions have been drawn based on characterization of failed electrodes, and there has been no investigation aimed to track and analyze structural changes of BDD electrodes during their failure process. Due to the lack of such knowledge, there remain controversies on the failure mechanism of the electrodes.

In this paper, we report on experimental results obtained during an accelerated life test conducted on a self-prepared Ti/BDD electrode. A variety of characterization methods were applied to monitor its failure process. The change in microstructure of the electrode was recorded and analyzed to obtain information on the failure mechanism of the electrode. Results of the investigation may lead to improvement of our understanding on the failure mechanism of the Ti/BDD electrodes and provide routes to improve service life of the material.

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Table 1
Deposition parameters of the BDD coatings on the Ti substrates.

Gas flow rate (sccm)*	Nucleation/growth time (hours)	Temperature (°C)	Pressure (Pa)
Nucleation stage Ar\H ₂ \CH ₄ \B(OCH ₃) ₃	Growth stage Ar\H ₂ \CH ₄ \B(OCH ₃) ₃		
1800\100\10\0.4	1800\100\3\0.4	2/8	~750 500

* Standard-state cubic centimeter per minute.

2. Experimental process

2.1. Preparation of the electrode

Titanium plates of the size of 18 × 15 × 1.5 mm were prepared as the substrates. Surface pretreatment was applied to the substrates by mechanically grinding them with diamond powders, in order to facilitate nucleation of diamond on the substrates.

Deposition of BDD coatings was conducted by using a high current extended direct current arc plasma chemical vapor deposition (CVD) system [14, 15]. The reactive gas used was a mixture of argon (Ar), hydrogen (H₂) and methane (CH₄). Trimethyl borate (B(OCH₃)₃) was used as the source for element boron and it was fed into the deposition chamber through its evaporation. The deposition process of the BDD coatings consisted of both a nucleation and a growth stage [16]. Detailed process parameters for the deposition are given in Table 1. The deposition lasted for 10 h, and the thickness of the BDD coatings is about 2.5 μm.

2.2. Electrode characterization and accelerated life test

Morphology of the samples was examined by using an FEI Quanta 450 field emission scanning electron microscope (FE-SEM), equipped with an energy dispersive spectrometer (EDS) analyzer for elemental analysis. Structure of the BDD coatings was characterized by Raman spectroscopy conducted using a Raman 2000 spectrometer. A D/MAX 2000 X-ray diffractometer (XRD) was used to analyze phase components of the Ti/BDD electrodes.

A Ti/BDD electrode was prepared by sealing a BDD coated Ti sample into a self-made polytetrafluoroethylene groove, and an effective electrode area of 1 cm² was defined by using a fluorine rubber sealing ring. ALT on the electrode was carried out in 1 mol/L H₂SO₄ electrolyte at room temperature. A TRADEX MPS 302 power source was used to provide a constant current of 1 A/cm² density to the Ti/BDD electrode. The Ti/BDD sample and a stainless steel plate of the size of 40 mm × 30 mm × 2 mm were used as the anode and the cathode, respectively. The distance between the two electrodes was set at 15 mm. During the test, the cell voltage of the electrolytic cell was monitored, and electrode morphology, phase components and surface composition of the electrode were analyzed.

3. Experimental results and discussions

3.1. Characterization of the BDD electrode

Surface morphology of the as-prepared Ti/BDD electrode is shown in Fig. 1. It can be seen from the figure that the surface of the BDD coating is smooth and compact, and no obvious voids, cracking and delamination of the diamond coating could be noticed. The size of the diamond grains is relatively uniform, and it is in the range of about 1 μm. The faceted diamond grains show primarily triangular (111) surfaces, consistent with the result of Gerger et al. that proper boron doping would favor formation of (111) textured diamond films [17].

Fig. 2 shows the Raman spectrum of the BDD coated electrode. Two broad peaks at around 500 cm⁻¹ and 1200 cm⁻¹ were suggested as due to amorphous diamond. The downshift and disappearance of the

characteristic diamond peak at 1332 cm⁻¹ were attributed to the Fano effect [18, 19]. Such a Raman spectrum is typical for a heavily boron doped diamond film. Generally, with the increase in boron doping concentration, the peaks of 500 cm⁻¹ and 1200 cm⁻¹ downshift and their relative intensities increase, while the peak at 1332 cm⁻¹ downshifts and decreases [19].

Applying the following formula:

$$[B] \text{ cm}^{-3} = 8.44 \times 10^{30} \exp(-0.048x) \quad (1)$$

derived by Bernard et al. to estimate boron concentration in BDD films and valid for boron doping in the range of about $2 \times 10^{20} \sim 10^{22} \text{ cm}^{-3}$ [19], it is estimated that the boron concentration in the BDD coating of the electrode is on the order of $2.3 \times 10^{21} \text{ cm}^{-3}$. In above formula, x denotes the Raman shift of the Lorentzian component of the Raman peak at around 500 cm⁻¹.

3.2. Results of the accelerated life test

Fig. 3 shows variation of the cell voltage during the whole ALT process. This test lasted for 127 h. We see that initially, there appeared a moderate decrease in the cell voltage, which may be attributable to the formation of oxygenated functional groups on surface of the electrode with a decrease in over potentials of the electrolytic reactions [20]. With the further increase in electrolysis time, the cell voltage remained stable for a long period, and only a slight increase could be observed during this period. Then, after about 100 h, the cell voltage increased obviously, and after about 120 h, it entered a rapid increasing stage and the cell voltage changed from its initial value of about 5 V to 30 V, signifying the failure of the electrode.

Fig. 4 shows the change in macromorphology of the Ti/BDD electrode during the ALT process. From Fig. 4(a) we see that the surface of the as-prepared electrode was uniform and defect-free. Then, after 4 h of electrolysis, Fig. 4(b), we see that macroscopically there remained no obvious coating exfoliation. After 24 h of ALT, we see from Fig. 4(c) that the BDD coating started to show isolated areas of exfoliation. Then after 55 h of electrolysis, Fig. 4(d), the exfoliation areas of the BDD coating was enlarged and interconnected each other. And after 100 h of electrolysis, there remained only a few isolated regions of BDD coating left on the substrate surface. And at last, the BDD coating vanished completely from the sample surface and the electrode failed, as shown in Fig. 4(f).

Fig. 5 shows variation of percentage of delaminated area of the BDD coating with the electrolysis time calculated from Fig. 4 with Image-Pro Plus 6.0 software. It may be seen from the figure that the delamination area amounted to about 8% at 24 h, it increased to nearly 66% at 55 h, and at 100 h it increased to about 90%. From the figure we could notice that the rate of the coating delamination between 24 and 55 h was significantly higher than that after 55 h.

Fig. 6 shows two microscopic images of the tested electrode after 4 h of electrolysis. It can be seen from the figure that microscopically delamination of the BDD coating has already occurred after only 4 h of testing. We see from Fig. 6(a) that cracking has appeared around a local defect, and from Fig. 6(b) we see that a delamination area of the coating propagated upward by further cracking.

Fig. 7 shows SEM images of the BDD coating observed at different electrolysis times. It can be seen from the figure that the morphology of

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