Influence of heat treatment temperature on bonding and oxidation resistance of diamond particles coated with TiO₂ film

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Abstract. In this paper, TiO₂ films were coated on the surface of diamond particles using a sol–gel method. The effects of heat treatment temperature on the morphology, composition, chemical bonds, oxidation resistance and compressive strength of diamond particles coated with TiO₂ films were characterized through scanning electron microscopy, Fourier transform infrared, Raman spectroscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, thermogravimetric–differential scanning calorimetry and compressive strength test. The results showed that when the temperature reached 600°C, the amorphous TiO₂ on the diamond particles surface exhibited as a dense anatase film and the Ti–O–C bond formed between TiO₂ and the diamond substrates. When temperature reached 800°C, TiO₂ films were still in anatase phase and part of the diamond carbon began to graphitize. The graphitized carbon can also form the Ti–O–C bond with TiO₂ film, although TiO₂ film would tend to crack in this condition. Meanwhile, the temperature had a serious influence on the oxidation resistance of diamond particles coated with TiO₂ films in air. When the heat treatment temperature reached 600°C, the initial oxidation temperature of the coated diamond particles reached the maximum value of 754°C. When the diamond particles were oxidized at 800°C for 0.5 h in air, the weight loss rate reached the minimum value of 6.7 wt% and the compressive strength reached the maximum value of 15.7 N.

Keywords. Diamond; TiO₂ film; heat treatment temperature; anti-oxidation; mechanical properties.

1. Introduction

Due to its extremely high stiffness, diamond is an ideal material for manufacturing tools. When diamond particles and bonding powder are evenly mixed, the diamond tools with a specific shape and strength can be fabricated by the pressing and sintering process. However, the poor thermal stability makes the diamond prone to oxidation in the air and graphitization transition in a protective atmosphere in the sintering process, limiting the service life of diamond tools.^{1,2} Meanwhile, due to the poor wettability between diamond particles and the bonding agent, the surface of diamond usually needs to be coated with films to protect diamond particles from oxidation and graphitization transition. At present, the commonly used approach to surface modification of diamond particles is the electroplating method. By adding a direct current (DC) voltage to the plating solution, metal elements in the vicinity of the cathode are deposited on the diamond abrasive surface. In this way, some metal elements such as Cr, Ni, Cu, Al can be plated on the surface of diamond. But a large number of studies have shown that,^{3,4} due to the

poor physical bonding, metal coating is easily oxidized and prone to fall off during the sintering process of vitrified bond diamond tools. In addition to the poor wettability between metal coating and vitrified bond, the service life of diamond tools had only very limited development.

TiO₂ and TiO₂/Al₂O₃ films were prepared in previous studies^{5–7} on diamond particles by the sol–gel method. The results showed that, on one hand, a dense TiO₂ film on the surface of diamond particles could protect diamond particles from oxidation when it sintered in O₂. The incipient oxidation temperature of the TiO₂ and TiO₂/Al₂O₃ film-coated diamonds in air atmosphere was higher, 150–175°C, than that of the uncoated diamonds.^{5–7} On the other hand, the TiO₂ film could improve the wettability of bond to diamond particles in sintering, which could increase the service life of diamond tools. The grinding ratio of the TiO₂ and TiO₂/Al₂O₃ film-coated diamonds in air atmosphere was 220–50% higher than that of the uncoated diamonds.^{5–7} The effects of heat treatment temperature also have a great influence on the morphology, composition, oxidation resistance and compressive strength of diamond particles coated with TiO₂ films. However, few studies have been reported on these points.

In this paper, a dense TiO₂ film was prepared on the surface of diamond particles by the sol–gel method. We

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further discussed the influence of heat treatment temperatures on the morphology, composition and chemical bonds formed between TiO_2 film with diamond, as well as the oxidation resistance of diamond coated with TiO_2 films, making it a novel approach for the diamond surface modification.

2. Experimental

2.1 Raw materials

Raw materials used in this experiment are listed in table 1.

2.2 Preparation of diamond coated with TiO_2 film

TiO_2 sol was prepared using butyl titanate, absolute ethyl alcohol, deionized water and diethanolamine as the starting materials. The chemical composition of aimed TiO_2 sol was $\text{Ti}(\text{OC}_4\text{H}_9)_4 : \text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HN}(\text{OC}_2\text{H}_5)_2 = 1 : 26.5 : 1 : 1$ (ratio in mol). The preparation process was as follows: firstly, butyl titanate was dissolved in absolute ethyl alcohol under stirring, followed by the addition of diethanolamine and the solution was mixed until a uniform solution was obtained. Then, a pre-mixed solution of $\text{H}_2\text{O} : \text{C}_2\text{H}_5\text{OH} = 1 : 10$ (v/v) was dropped into the uniform solution under severe stirring. Lastly, the mixture was stirred for 1 h and then kept stable for 24 h until a pale yellow sol was obtained.

Pre-treatment process of diamond raw material was as follows: firstly, certain amount of diamond particles were placed in a small reagent bottle and soaked in HCl (1 mol l^{-1}) for 1 h, then washed with deionized water and dried in an oven to remove all water. After that, it was immersed in an acetone solution for 1 h accompanied with the ultrasonic cleaning, followed with rinsing of deionized water again and dried in an oven for use.

Preparation process of diamond coated with TiO_2 film was as follows: the pre-treated diamond particles were firstly immersed in TiO_2 sol for 1 min, and dried for 5 min at 80°C in an oven. This process was repeated three times to obtain the diamond coated with TiO_2 film. After this, the further heat treatment was carried out in N_2 , the sample was dried at 100°C for 30 min, and then heated

with a heating rate of 5°C min^{-1} to different target temperatures and kept for 1 h at every target temperature. The diamonds coated with TiO_2 films treated at different temperatures were obtained after the natural cooling process after the heating.

2.3 Characterization

The morphology of TiO_2 film on the diamond particle's surface was imaged with a JSM-6700F scanning electron microscope (SEM) produced by Japan Electronics Corporation. Infrared absorption spectra of diamond particles coated with TiO_2 film were measured by the KBr table method in a Fourier infrared spectrometer (SPECTRUM one). Determined wavenumbers ranged between 4000 and 400 cm^{-1} . Raman spectra of diamond particles coated with TiO_2 film was tested with a LABRAM-010 laser confocal Raman spectrometer. The crystalline phase transition of diamond particles coated with TiO_2 film was determined using Raman vibration characteristics of the material samples. The wavelength is 514.5 nm , the scanning frequency is 10 and the power on the sample is 5 mW . X-ray photoelectron spectroscopy (XPS) analysis of diamond particles coated with TiO_2 film was carried out with the PHI Quantum 2000 type X-ray photoelectron spectroscopy analyzer, with the radiation source of $\text{AlK}\alpha$, experimental vacuum of 10^{-6} (Pa) and the working voltage of 20 eV . X-ray diffraction (XRD) analysis of diamond particles coated with TiO_2 film was carried out with a D8-ADVANCE X-ray diffractometer (German Brucker Company), with the radiation source of $\text{CuK}\alpha$ radiation, working voltage of 35 kV and working current of 30 mA . Thermogravimetric (TG) analysis of diamond particles coated with TiO_2 film was done with the NETZSCH-Thermogravimetric Analysis DIL402PC, with a heating rate of $10^\circ\text{C min}^{-1}$ and an air atmosphere. The test temperature ranged from room temperature to 800°C . The oxidation starting temperature was determined by the crossing point temperature, where the tangential line of the period of TG curves with the largest inclining rate crossed with the baseline. The oxidation weight-loss experiment was preformed as follows: a certain quantity of samples was placed into ceramic crucibles, and then the ceramic crucibles were transferred into a Muffle furnace,

Table 1. Raw materials used in this experiment.

Name	Chemical formula	Purity	Manufacturer
Diamond (45/50#)	C	Industrial grade	CRIMM superhard materials plant
Butyl titanate	$\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$	Chemical pure	Tianjin FuChen Chemical Reagent Factory
Diethanolamine	$\text{HN}(\text{OC}_2\text{H}_5)_2$	A.R.	China Pharmaceutical (Group) Shanghai Chemical Reagent Company Factory, China
Absolute ethyl alcohol	$\text{CH}_3\text{CH}_2\text{OH}$	A.R.	Aetna Fine Chemical Industry Co., Ltd., China
Hydrochloric acid	HCl	A.R.	Zhuzhou Institute of Chemical Industry, China
Acetone	CH_3COCH_3	A.R.	Aetna Fine Chemical Industry Co., Ltd., China

which was pre-heated to 800°C . The crucibles were then taken out to measure the residual sample at specified time intervals and then the samples oxidation rates for different oxidation times were calculated. Compressive strength experiment for 45/50 US mesh single diamond particles (Industrial grade, purchased from CRIMM superhard materials plant in China) was carried out with a JLK-rupture strength testing machine produced by Jinwei Measuring Instruments Co., Ltd., in which the diamond particles were oxidized at 800°C for 0.5 h in air. Data of the strength of samples were the result of an average of 10 times determinations.

3. Results and discussion

3.1 Effects of heat treatment temperature on the microstructure and composition of TiO_2 films

Morphologies of TiO_2 films on the surface of diamond particles treated at different temperatures are shown in figure 1.

Figure 1a shows that, before heat treatment, a smooth and uniform film could be observed on the diamond surface. When it was heated at 200°C , the dehydration and dealcoholization process took place, while this reaction

Figure 1. SEM images of TiO_2 films coated on diamond particles treated at different temperatures: (a) untreated; (b) 200°C ; (c) 400°C ; (d) 600°C ; (e) 700°C and (f) 800°C .

did not affect the morphology of the film (figure 1b). When the heat treatment temperature reached 400°C (figure 1c), the fine particles could be observed in the film although the film was still continuous. There were also large numbers of pores formed due to the volatilization of structural water.⁸ When treated at 600°C (figure 1d), the film was still uniform and dense, which was composed of TiO₂ particles ranging between 100 and 300 nm. Figure 1g is the sectional view in which the uniform TiO₂ film can be observed clearly. After being treated at 700°C (figure 1e), the second grain growth occurred and the original small particles among the TiO₂ interface began to sinter together and the cracks appeared in the film. After being treated at 800°C (figure 1f), the sintering phenomenon of TiO₂ particles in the film became obvious, the particles grew bigger, and more cracks could be observed in the film.

The XRD patterns of TiO₂ film on the surface of diamond particles treated at different temperatures are shown in figure 2. When the temperature was below 400°C, TiO₂ was amorphous. When it was increased to 600°C, some weak diffraction peaks of anatase phase appeared. When the temperature further increased to 700°C, the intensity of diffraction peaks gradually increased; which indicated that the crystalline degree of TiO₂ gradually improved.⁹ When at 800°C, all peaks became sharp, and no crystalline phase transformation emerged.¹⁰

The Raman spectra of TiO₂ film on the surface of diamond particles treated at different temperatures are shown in figure 3. When the temperature was below 400°C, no Raman peaks appeared indicating that the TiO₂ was amorphous. When the temperature increased to 600°C, three weak symmetry Raman peaks at 398, 515 and 640 cm⁻¹ were observed, which indicated that the amorphous film began to transit to the anatase phase, while the degree of crystallinity of TiO₂ was weak.

Figure 2. XRD patterns of TiO₂ films coated on diamond particles treated at different temperatures.

A further increase of temperature resulted in the high symmetry and gradual enhancement of Raman peaks at 398, 515 and 640 cm⁻¹, indicating that both the content and the crystallinity degree of anatase phase in film increased,¹¹ which was consistent with XRD results.

3.2 Effects of heat treatment temperature on the formation process of TiO₂ film chemical bonds

Infrared spectra of diamond coated with TiO₂ film treated at different conditions are shown in figure 4. As can be seen, the absorption peaks at 3080–3415 cm⁻¹ in

Figure 3. Raman spectra of TiO₂ films coated on diamond particles treated at different temperatures: (a) 400°C; (b) 600°C; (c) 700°C and (d) 800°C.

Figure 4. IR spectra of TiO₂ films coated on diamond particles treated at different temperatures: (a) 200°C; (b) 400°C; (c) 600°C and (d) 800°C.

figure 4a–d were corresponding to the –OH group stretching vibration, owing to the surface-adsorbed water of the particles. Absorption peak at 1639 cm⁻¹ corresponding to H–O–H bending vibration was due to the structure of water. Absorption peak at 1450 cm⁻¹ was caused by C–O vibration in CO₃²⁻.⁶ Absorption peak at 2862–2922 cm⁻¹ (figure 4a) was due to the bending vibration of methylene –CH₂–, which did not appear in other curves, indicating that the organic groups were excluded when temperature reached 400°C. The absorption peak at 1075 cm⁻¹ (figure 4a) represented characteristic vibration of the Ti–O–C bond, which was due to the reaction between TiO₂ and free carbon from its surface organic group at 200°C. When temperature reached 400°C, most of the free carbon did not form the Ti–O–C bond, resulting in the disappearance of the characteristic peak (figure 4b). After being treated at 600°C, a strong absorption peak at 1086 cm⁻¹ (figure 4c) appeared, which was caused by the characteristic vibration of Ti–O–C groups and the carbon in this group came from diamond substrate.⁶ This peak moved 10 cm⁻¹ to the left in figure 4c compared to that in figure 4a, which was due to the change of chemical environment of carbon in TiO₂ surface organic group. After being treated at 800°C, a strong absorption peak at 1071 cm⁻¹ (figure 4d) appeared and was also caused by characteristic vibration of Ti–O–C groups, which moved 5 cm⁻¹ to the right compared to that in figure 4c.

The Raman spectra of diamond coated with TiO₂ film treated at different temperatures are shown in figure 5.

Figure 5. IR spectra of diamond particles coated with TiO₂ films treated at different temperatures (a) 600°C and (b) 800°C.

When the temperature was 600°C, a sharp peak at 1325 cm⁻¹ corresponding to the characteristic vibration peaks of diamond crystal appeared. When increased to 800°C, broadened characteristic peaks (figure 5b) appeared at 1372 and 1597 cm⁻¹, which were produced by the graphite, diamond, diamond-like carbon and carbon.¹⁰ Raman spectra indicated that, when the diamond coated with TiO₂ film was heat-treated at 800°C, part of diamond transformed to graphite, and part of graphite C and Ti elements in TiO₂ film formed the Ti–O–C bond. These changes caused the movements of infrared absorption peak.¹²

XPS analysis of Ti element in TiO₂ film treated at different temperatures is shown in figure 6. When treated at 400°C, large amounts of Ti⁴⁺ and Ti³⁺ and only a small amount of Ti²⁺ existed in the TiO₂ film. When the temperature exceeded 600°C, large amounts of Ti⁴⁺ and Ti²⁺ film and a small amount of Ti³⁺ existed in TiO₂.¹³ The change of Ti chemical valence was due to the removal of the free carbon in the film, Ti–O–C bond formed between TiO₂ film and diamond substrate during this process; thus, the Ti³⁺ content in the film decreased and Ti²⁺ content increased.

3.3 Effects of heat treatment temperature on oxidation resistance and mechanical properties of diamond coated with TiO₂ film

Oxidation weight-loss data of diamond coated with TiO₂ film treated at different temperatures are listed in table 2. It can be seen that the temperature of TiO₂ film had a great influence on the oxidation resistance of diamond particles. Compared with the uncoated diamond particles, when the temperature reached 200 and 400°C, the initial oxidation temperature of coated diamond only had a slight improvement (figure 7a), as the large number of pores existed in the film (figure 1b and c). When it reached

Figure 6. XPS spectra of Ti in TiO₂ films treated at different temperatures: (a) 400°C; (b) 600°C and (c) 800°C.

Table 2. Anti-oxidation of diamond particles coated with TiO₂ films treated at different temperatures.

Heat treatment temperature (°C)	Initial oxidation temperature (°C)	Weight loss rate of diamond oxidized at 800°C for 0.5 h in air (wt%)	Weight loss rate of diamond oxidized at 800°C for 2 h in air (wt%)	Compressive strength of diamond oxidized at 800°C for 0.5 h in air (N)
Untreated	687	24.3	74.7	0
200	692	21.4	72.8	2.4
400	702	16.7	68.4	5.3
600	754	6.7	60.2	15.7
700	748	8.9	63.9	12.3
800	727	10.1	65.2	10.7

Figure 7. DSC–TG curves of diamond particles coated with TiO₂ films treated at different temperatures: (a) 400°C; (b) 600°C and (c) 800°C.

Figure 8. Weight loss of uncoated and coated diamond treated at different temperatures and oxidized at 800°C for 2 h in air.

600°C, the initial oxidation temperature of coated diamond reached a maximum value of 754°C (figure 7b). The obvious improvement might be caused by the dense TiO₂ film on diamond surface, which was composed of the fine grain size anatase (figure 1d). When being treated at 800°C, initial oxidation temperature of diamond dropped to 727°C (figure 1c), which was caused by the cracks and the decrease of bonding between TiO₂ film and diamond (figure 1f).

Before oxidation, the compressive strength of single 45/50# diamond uncoated with TiO₂ film was 24.6 N. As for uncoated diamond particles, when oxidized at 800°C for 0.5 h in air, number of deep cracks and holes generated on the diamond surface owing to the oxidation of diamond (figure 9a), resulting in serious damages to the diamond particles. Then the compressive strength decreased to 0 N. A dense TiO₂ film formed on diamond particles surface when the heat treatment

Figure 9. Surface morphology of uncoated and coated diamond treated at different temperatures and oxidized at 800°C for 0.5 h in air: (a) uncoated; (b) 400°C; (c) 600°C and (d) 800°C.

temperature was 600°C. It increased the initial oxidation temperature and protected diamond particles from the oxidation. So the compressive strength improved and reached 15.7 N.

The weight-loss curves *vs.* oxidation time at 800°C in the air are shown in figure 8. As for the sample treated below 600°C, when the oxidation time was 0.5 h, the mass loss rate decreased with the increase of sample's temperature. When sample's temperature equaled to 600°C, the mass loss reached the lowest value of 6.7 wt%. When the temperature increased, the mass loss of samples increased.

Figure 9 showed the surface morphology of uncoated and coated diamond treated at different temperatures and oxidized at 800°C for 0.5 h in air. The oxidation corrosion on the surface of uncoated diamond (figure 9a) was serious. Surface of some diamond particles showed deep oxidation corrosion cracks and some particles even broke into pieces. As for the diamond particles coated with TiO₂ film and treated at 400°C (figure 9b), the oxidation resistance was improved, while cracks appeared in the film and some of them tended to fall off. The particle edges were completely oxidized, and the original smooth surface of the diamond particles showed some steps and circular holes due to the presence of large amounts of screw dislocation defects in diamond, which preferentially reacted with oxygen.¹⁴ As for the coated diamond treated

at 600°C (figure 9c), continuous TiO₂ film still existed on the diamond surface after oxidation, while the film had cracks, some of which tended to fall off. As for the coated diamond treated at 800°C (figure 9d), the surface was oxidized into rugged shape. The edges of particles still existed, and the generated spherical particles on the surface were identified to be TiO₂ by energy-dispersive spectroscopy. It could be inferred that, with the increasing oxidation time, TiO₂ film on the diamond particles surface tended to fall off completely and was no longer able to protect the diamond surface. Thus when the oxidation time exceeded 0.5 h, the oxidation was obviously accelerated (figure 8).

4. Conclusion

Heat treatment temperature has a great influence on the morphology and phase of diamond particles coated with TiO₂ film. When temperature was below 600°C, TiO₂ film was amorphous, and a large number of pores appeared in the film. At 600°C, the film transformed to a dense anatase phase film. When temperature reached 800°C, TiO₂ was still in anatase phase, but the cracks emerged in the film.

When the coated diamond particles were treated at 400°C, there was no bonding formation between TiO₂

film with diamond, and a large amount of Ti^{4+} , Ti^{3+} but only a small amount of Ti^{2+} existed in the TiO_2 film. When the coated diamond particles were treated at 600°C , Ti-O-C bond formed, and the amount of Ti^{2+} increased slightly. When being treated at 800°C , the carbon on the surface of the diamond particles transformed to graphite. The carbon from graphite could also form Ti-O-C bond with TiO_2 film.

The heat treatment temperature had a significant influence on the oxidation resistance of diamond particles. When coated diamond particles were treated below 600°C , the initial oxidation temperature of particles increased with the increase of temperature. When being treated at 600°C , the initial oxidation temperature of coated diamond particles reached a maximum value of 754°C . When the diamond particles oxidized at 800°C for 0.5 h in the air, the weight loss rate reached the minimum value of 6.7 wt% and the compressive strength reached the maximum value of 15.7 N. As the temperature further increased, the initial oxidation temperature of coated diamond particles decreased. When treated at 800°C , the initial oxidation temperature of diamond decreased to 727°C .

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