

Article

Enhancement of Oxidation Resistance via Chromium Boron Carbide on Diamond Particles

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Abstract: To improve the oxidation resistance of diamond, chromium boron carbide (Cr–B–C) coatings were synthesized through high temperature solid state synthesis and molten salt method on diamond particles in this paper. After holding the raw material at 900 °C for 2 h, the diamond surface was completely and uniformly covered by Cr–B–C coatings. Oxidation resistance of the diamond coated Cr–B–C was determined by the thermogravimetric analysis (TGA). The results revealed that the Cr–B–C coatings held the diamonds for 100%-mass in air atmosphere until 1151 °C, which was much better than the uncoated diamonds (720 °C) and the B₄C-coated diamonds (1090 °C). When Cr–B–C-coated diamond was annealed in air, Cr₂O₃ and B₂O₃ were formed as oxygen barrier layer to protect diamond from oxidation. The formation of B₂O₃ with high temperature fluidity was conducive to avoiding Cr₂O₃ delamination due to volume expansion during oxidation in air. Furthermore, the presence of Cr₂O₃ provided lasting protection by reducing the evaporation of B₂O₃. The oxidation products (B₂O₃ and Cr₂O₃) prove a complementary functional protection on diamond particles from oxidation.

Keywords: diamond; chromium boron carbide coating; thermogravimetric analysis; oxidation resistance



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1. Introduction

Diamond is renowned for its outstanding physical, electrical and mechanical properties, including high hardness (synthetic diamond, 70–100 GPa), highest thermal conductivity at room temperature (2×10^{13} W/m·K), and extremely low coefficient of thermal expansion (1×10^{-6} K) [1–3]. On the industrial front, it is remarkable to note that diamond is being exploited for both its mineral exploration and heat transfer applications, such as cutting tools, saw blade segments, grinding wheels, drill bits and heat sinks. Generally speaking, diamond is not devoted to working directly, but acts as the reinforcing phase of composites. As cutting elements or tools for heat transfer, these composites are frequently subjected the generation of high temperatures. Besides, it is worth mentioning that diamond metal matrix composites (MMCs) are generally manufactured under high temperature process [4]. However, diamond is easily oxidized at approximately 700 °C when annealed in oxidative atmosphere, leading to the oxidation products of diamond immediately escaping to external environment and a large amount of oxygen corrosion pits [5]. In addition, the defects cause serious loss of mechanical properties, which severely limits the lifetime and efficiency of diamond MMCs [3]. Therefore, the various applications of diamond tools at a high temperature requires a protective barrier without any damage to diamond particles.

According to previous research, enhancement in the oxidation resistance of diamond has been explored for decades to drive diamond for working efficiently or manufacturing

at a higher temperature, such as mineral exploration and heat transfer applications [6]. Due to the development of the diamond oxygen barrier, especially the protective coating on the diamond surface, the oxygen corrosion pits can be inhibited directly [3]. B_2O_3 is widely used to prevent oxidation of diamond, because of low oxygen permeability, good fluidity at high temperature and excellent wettability of carbon materials [7–9]. However, the hydrolysis of B_2O_3 at ambient humidity can cause the coating to peel off during heating owing to evaporation or expansion [10]. In our previous research, the boron carbide (B_4C) coating was covered on the surface of diamond particles by forming a B_2O_3 oxygen barrier layer which supplied a secondary protection of diamond to the enhancement of oxidation resistance during annealing. When the B_2O_3 oxygen barrier layer completely evaporated at 1000 °C for sustained heating time over 2 h, the coatings had no protective effect on diamond particles. Besides, tests for oxidation resistance at a higher temperature over 1000 °C were lacking [11]. Considering the ability of carbides to improve the oxidation resistance of diamond, the carbides coating materials prior to oxidation of diamond by forming an oxide layer are generally treated as available options generally [5,12]. Titanium carbide (TiC) coating was planted on diamond surfaces to protect the diamond particles from oxidation through delaying erosion temperature of diamond. Chagas et al. [13] studied the thermal damage of TiC-coated diamond under different heat treatment times (60, 180, 360 min). After 360 min of heat treatment, all uncoated diamonds were completely transformed into graphite, whereas the diamonds with TiC coatings exhibited sharpness and crystalline integrity. The TiC-coated diamonds had stronger protective effect than the uncoated diamonds during all the heat treatment time. It was worth mentioning that the diamond will lose its protection immediately due to the spalling of oxidation products. Sha et al. [14] reported that TiC-coated diamonds had a much higher onset temperature of mass loss (868 °C) compared to the uncoated diamonds (725 °C). In addition, the TiC coatings can also protect diamond particles from direct contact with cobalt, thereby reducing the occurrence of cobalt-catalytic graphitization. Yang et al. [15] researched that chromium carbide (Cr_7C_3) can take precedence over carbon to react with oxygen before the temperature reached 1048 °C. The use of Cr_7C_3 improved the oxidation resistance of ceramic refractories. However, the carbide coating was very easy to convert into oxide during heat treatment in air, and the oxide often caused the coating to fall off due to the internal stress caused by volume expansion, which showed weak adhesion to diamond. Therefore, to protect diamond better, we need to combine the dual advantages of B_2O_3 and carbides. The mutual protection mechanism of oxidation products is widely used in the field of ceramics and steel, but it is rarely used in diamond, except for the Ti–B–C coating on diamond which can be found in our previous research [16]. Moreover, the boride coating on diamond also has a small quantity of applications. Titanium boron carbide (Ti–B–C) coatings on diamond particles were benefited to hold the complete diamond morphology on 1000 °C for 1 h by forming TiO_2 and B_2O_3 [16]. The results revealed that oxidation resistance of borides on diamond was better than that of carbides, and the oxidation products (TiO_2 and B_2O_3) proved a complementary functional protection on diamond particles from oxidation. Therefore, metal borides coatings on diamond particles can immediately improve oxidation resistance at high temperatures. Considering that chromium carbide has a higher protective temperature (1048 °C) for diamond than titanium carbide (868 °C), therefore, Cr–B–C is a potential coating for improving oxidation resistance of diamonds.

The present study focuses on forming Cr–B–C coatings on diamond particles by high temperature process. The ability of Cr–B–C coatings on oxidation resistance has been investigated.

2. Materials and Methods

2.1. Materials and Preparation

Synthetic high pressure high temperature (HPHT) diamond particles (SCDF90, 90–116 μm , Zhengzhou Sino-Crystal Diamond Co., Ltd., Zhengzhou, China) were supplied.

The following reagents were used: chromium powder (Cr, 75 μm , purity 99.95%), boron powder (B, 10–20 μm , purity 99.0%), boric acid (H_3BO_3 , purity 99.5%), NaCl (purity 99.5%), KCl (purity 99.5%) which was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). For forming the chromium boron carbide coating on diamond particles, two steps were adopted. Firstly, in order to form boron carbide (B_4C) coating on diamond particles, 30.00 g diamond particles were immersed in a mixture of 39.60 g boron (B) and 27.60 g boric acid (H_3BO_3) powders. The diamond-powder mixture was strongly mechanically stirred at room temperature for 2 h. This mixture was placed in an alumina container and placed into a tube furnace under argon. B_4C coating was synthesized on diamond particles by heating diamond-powder mixture at 1200 $^\circ\text{C}$ for 6 h. Argon stopped flowing when the tube furnace reached room temperature. The samples were cooled in a tube furnace treated with dilute nitric acid to remove the soluble phases in the product. The coated diamonds were separated from the excess B powders by a sieve. Then, the mixture consisting of 8.70 g of Cr, 12.25 g of NaCl, and 17.60 g of KCl powders were grinded along a same circle direction for 2 h at room temperature before immersing 20.00 g of B_4C -coated diamond particles. This mixture was placed in an alumina container and placed into a tube furnace under argon. Cr–B–C coating was synthesized on diamond particles by heating raw material to 900 $^\circ\text{C}$ for 2 h. When the tube furnace was cooled, the samples were immediately immersed in water to remove inorganic salt. Finally, the coated diamonds were then separated from excess Cr powders by a sieve.

2.2. Experiments and Characterization

The microstructure of the samples was characterized by a Bruker D8 (Bruker, Karlsruhe, Germany) with a Cu $\text{K}\alpha$ source X-ray diffraction (XRD). The surface morphologies and topographies of the coatings were characterized by Hitachi S-4800 scanning electron microscope (SEM, Tokyo, Japan). Thermalgravimetric analysis (TGA) was performed using a Netzsch STA449F3 (Selbu, Germany). The temperature of the TGA was increased from room temperature (20 $^\circ\text{C}$) to 1200 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C}/\text{min}$ in air atmosphere.

3. Results and Discussion

3.1. Phase Analysis

Figure 1 demonstrates the XRD patterns for the uncoated, B_4C -coated and Cr–B–C-coated diamond particles. As shown in Figure 1, the peak located at 43.92 $^\circ$ was observed in all the patterns, which corresponded to diamond (JCPDF#06-0675). In order to clearly observe other peaks of coating on diamond particles, the high-intensity peak of single crystal diamond substrate was truncated partially. Three peaks located at 23.49 $^\circ$, 34.95 $^\circ$ and 37.82 $^\circ$ can be assigned to the B_4C structure in comparison to the standard PDF cards (JCPDF#35-0798). To identify the two-step synthetic composite coatings, five peaks located at 44.93 $^\circ$, 46.16 $^\circ$, 56.32 $^\circ$, 63.38 $^\circ$, and 75.69 $^\circ$ were observed which corresponded to the CrB structure (JCPDF#32-0277), and four peaks located at 39.19 $^\circ$, 42.54 $^\circ$, 44.16 $^\circ$ and 50.19 $^\circ$ were observed which corresponded to the Cr_7C_3 structure (JCPDF#36-1482). Therefore, the coatings of the Cr–B–C synthesized at 900 $^\circ\text{C}$ consisted of CrB and Cr_7C_3 .

Figure 2 shows the SEM images for the diamond particles with different coatings. After a high temperature process, a complete coating coverage is obtained at the B_4C -coated diamond and Cr–B–C-coated diamond, and no cracking or spalling is found on the diamond surface. As shown in Figure 2b, a large number of small particles are deposited on the surface of diamond due to the formation of B_4C particles. As a contrast, the Cr–B–C-coated diamond (Figure 2c) shows a relative smoother surface without any obvious particles. In addition, B_4C -coated diamond can still maintain polyhedron shape, but the shape of the Cr–B–C-coated diamond has changed from sharp corners to nearly spherical. This also indicates that the two-step synthesis method of Cr–B–C coatings continue to grow on the basis of the B_4C coating, and the thickness of the coating is greater than that of B_4C .

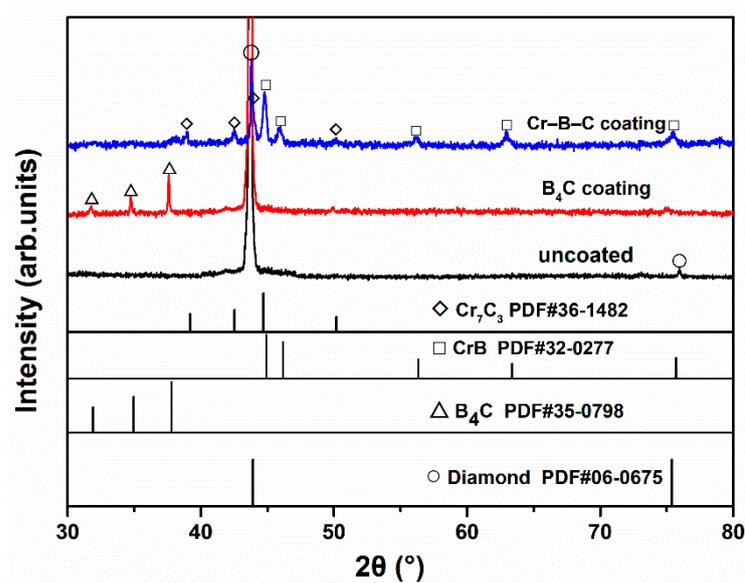


Figure 1. XRD patterns for uncoated diamond particles, diamond particles with B_4C coating, Cr-B-C coating, respectively.

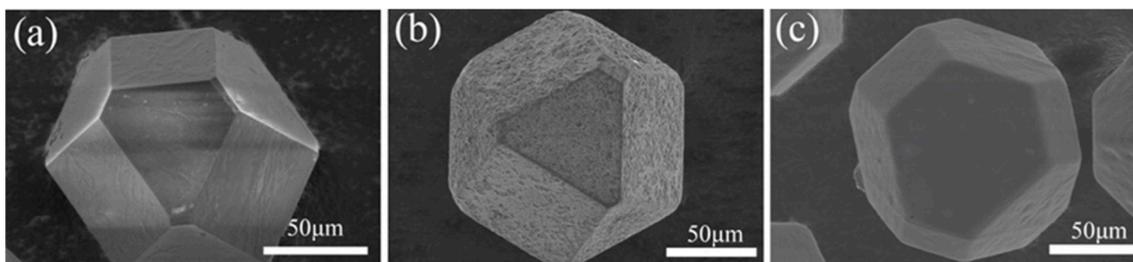


Figure 2. SEM images for (a) uncoated diamond, (b) B_4C -coated diamond, (c) Cr-B-C-coated diamond.

Possible reaction equations between diamond, Cr and B_4C are listed as follows:



Effects of temperature on the Gibbs free energy (ΔG) of reactions (1)–(4) are shown in Figure 3. It is well known that a reaction can only occur when its ΔG is below zero, and a smaller ΔG gives rise to an easy reaction. The Equation (1) showed that B_4C was formed by diamond and Cr since the $\Delta G < 0$ at 1200 °C. At the heating process of the Cr-B-C system, the inorganic salt (NaCl and KCl) added in the raw mixture acted as a catalyst that cannot participate in the reaction actually, and chromium was immediately reacted with B_4C to form CrB (as shown in Equation (2), the $\Delta G < -50$ kcal from 0–900 °C) and Cr_7C_3 (as shown in Equation (3), the $\Delta G < 0$ when temperature > 500 °C). In the meantime, the formed Cr_7C_3 transformed to CrB continuously as the temperature rose further to 900 °C (as shown in Equation (4), the $\Delta G < -60$ kcal). Finally, when the mixture maintained 900 °C for 2 h, the formed CrB was the end product, with a small amount of Cr_7C_3 that had not yet reacted completely, which agreed well with the results of the XRD patterns (Figure 1).

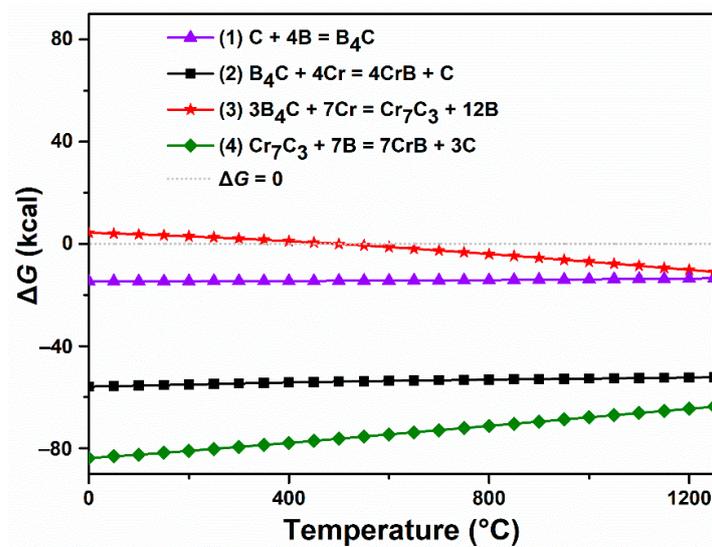


Figure 3. Relationships of temperature on Gibbs free energy (ΔG) of the reactions (1)–(4).

3.2. Oxidation Resistance

Oxidation resistance of the uncoated, B_4C -coated and Cr–B–C-coated diamond particles was determined by the TGA. As shown in Figure 4, for the uncoated diamond particles, the TGA curve displays an obvious protection failure while the heating temperature reaches 720 °C, indicating the oxidation resistance of the uncoated diamond can reach 720 °C. The TGA curve for the B_4C -coated diamond displays a weight gain from 700 to 855 °C, and slowly decreases to 100% in weight until 1090 °C. The weight gain was attributed to the formation of B_2O_3 , and the fast weight decrease due to the evaporation of B_2O_3 according to our previous research [11,16]. For the Cr–B–C-coated diamond particles, the TGA curve shows that the weight increases from 599 to 1118 °C, and then decreases directly to 100% mass at 1151 °C.

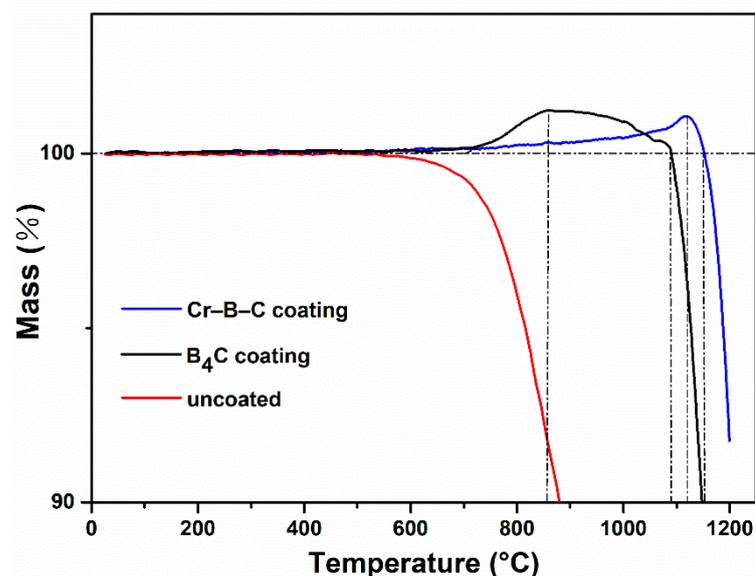


Figure 4. TGA results for the uncoated diamond particles, diamond particles with B_4C coating, Cr–B–C coating, respectively.

The inflection points of the curve in Figure 4 are made into the data histogram as shown in Figure 5. From the initial temperature of weight gain, the Cr–B–C coating (599 °C) and B_4C coating (700 °C) are both lower than the oxidation temperature of diamond in air

(720 °C), indicating that the coatings can play a protective role before diamond oxidation. From the initial temperature of weight loss, the Cr–B–C coating (1118 °C) and the B₄C coating (855 °C) are much higher than that of the uncoated diamond (720 °C) as well, indicating that both Cr–B–C coating and B₄C coating had good protective effect, and the Cr–B–C coating has better effect on delaying the oxidation of diamond than the B₄C coating. From the initial temperature of protection failure, when the diamond mass loss is reduced to 100%, Cr–B–C coating (1151 °C) is better for maintaining the quality of diamond than B₄C coating (1090 °C). In summary, the Cr–B–C coating exhibits the best protection of diamond particles from oxidation in this research.

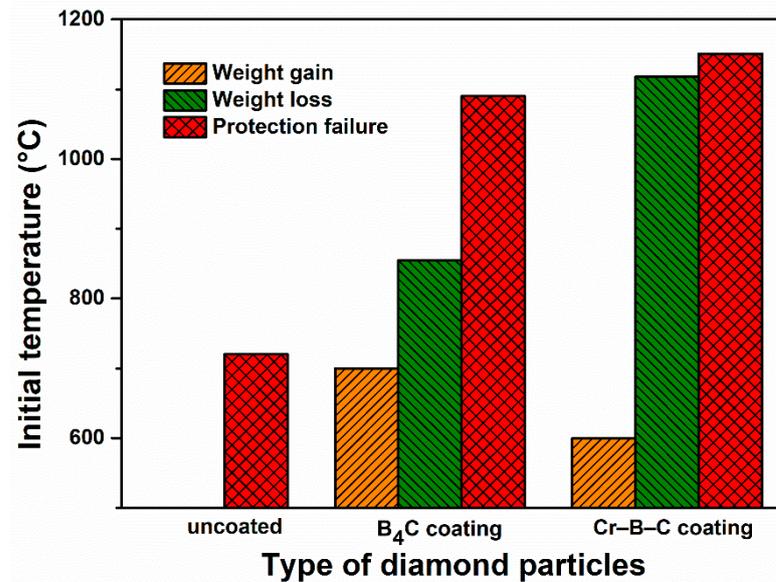


Figure 5. Initial temperature of the three types of diamond particles in TGA results.

The Cr–B–C-coated diamond particles after annealing at 1151 °C with a heating rate of 5 °C/min in air, were observed of four peaks located at 33.68°, 36.32°, 41.18°, 54.88° which corresponded to Cr₂O₃ (JCPDF#38-1479) and other four peaks located at 39.19°, 42.54°, 44.16° and 50.19° can be corresponded to Cr₇C₃ (as shown in Figure 6). Therefore, the Cr–B–C coatings after annealing at 1151 °C were composed of Cr₂O₃ and part of Cr₇C₃ that has not been oxidized.

As shown in Figure 7, after annealing at 1151 °C in air, the edges and corners of the uncoated diamond were confusion, which displayed a severe surface corrosion (Figure 7a). A similar phenomenon occurred on the B₄C-coated diamond (Figure 7b), but displayed a pitting corrosion. In contrast, the Cr–B–C-coated diamond possessed a complete coverage of edges and corners, and stayed a large area of squama structure stayed on the diamond surface (Figure 7c).

In order to visually observe the Cr–B–C coating after oxidation in Figure 7c, the sample was enlarged to obtain the SEM images shown in Figure 8a–c. It can be seen from Figure 8 that the crystal form and angular region of the diamond maintained very well. On the surface of the Cr–B–C coating, large squama structures appeared, which was related to the oxidation of coating components at high temperature. When the oxidation product on the diamond surface evaporated and exfoliated, the original fluid B₂O₃ showed holes and voids, bringing new oxygen flow channels to the diamond which damaged the protection of the coating.

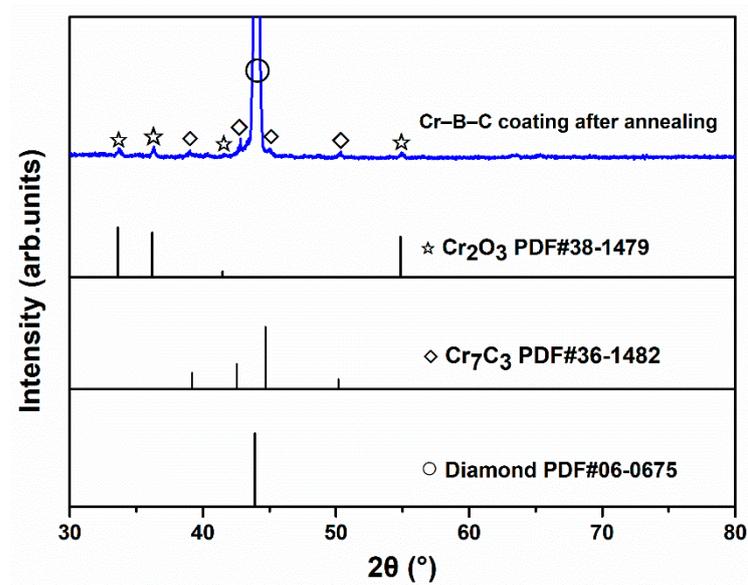


Figure 6. XRD patterns for the Cr-B-C-coated diamond particles after annealing at 1151 °C.

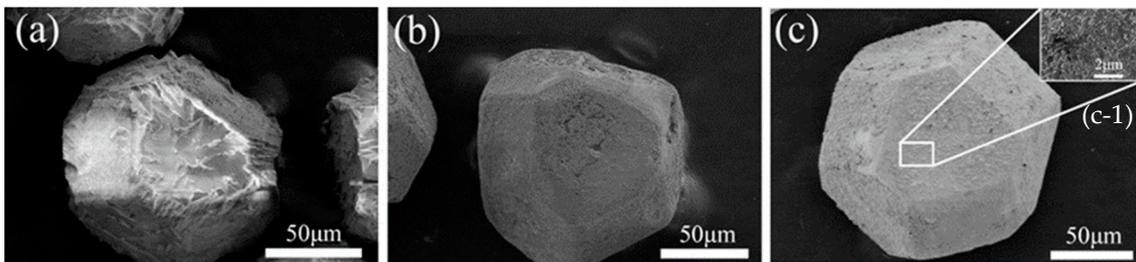


Figure 7. SEM images for (a) uncoated diamond, (b) B_4C -coated diamond and (c) Cr-B-C-coated diamond, after annealing at 1151 °C: (c-1) the squama on diamond surface.

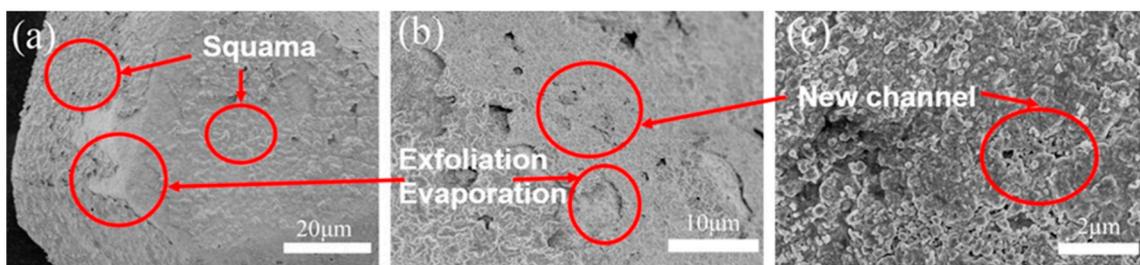


Figure 8. SEM images for Cr-B-C coated diamond after annealing at 1151 °C: (a) the squama on diamond surface; (b) the exfoliation and evaporation of coating; (c) the new channel for oxygen.

Combined with above results, the Cr-B-C coating fully covers on the diamond surface (Figure 2c). The Cr-B-C coating is oxidized to a layer of B_2O_3 and Cr_2O_3 (Figure 6) during annealing. The weight is increased due to the Cr-B-C coating absorbing oxygen atoms above 599 °C (Figure 5, the initial temperature of weight gain with Cr-B-C coating). Figure 9 illustrates the oxidation mechanism of Cr-B-C coating on diamond particles. The Cr-B-C coating consisted of CrB and Cr_7C_3 will be oxidized prior to diamond. When the temperature of anneal increases gradually, the fluid of B_2O_3 (fusion point, 450 °C) efficiently releases the stress caused by the expansion of Cr_2O_3 , which prevents the desquamate of Cr_2O_3 from volume expansion. In addition, B_2O_3 heals the exfoliation of Cr_2O_3 which might lead to the defects on the diamond surface. Moreover, the evaporation of B_2O_3 is suppressed due to

the coverage of Cr_2O_3 . The oxidation products (B_2O_3 and Cr_2O_3) prove as complementary functional protection on the diamond particles from oxidation. As the temperature reached $1151\text{ }^\circ\text{C}$, the squama (Figures 8a and 9) on the diamond surface is caused by the evaporation of B_2O_3 completely (Figure 8b, agree with the XRD result that the diamond surface is covered by Cr_2O_3 after annealing), revealing a new channel (Figure 8c) for oxygen through the barrier and corroding the diamond particles, leading to a directly protection failure (agree well with the Figure 4). Thus, the Cr–B–C-coated diamond remains intact after annealing in air and reveals the best protection against oxidation of diamond particles.

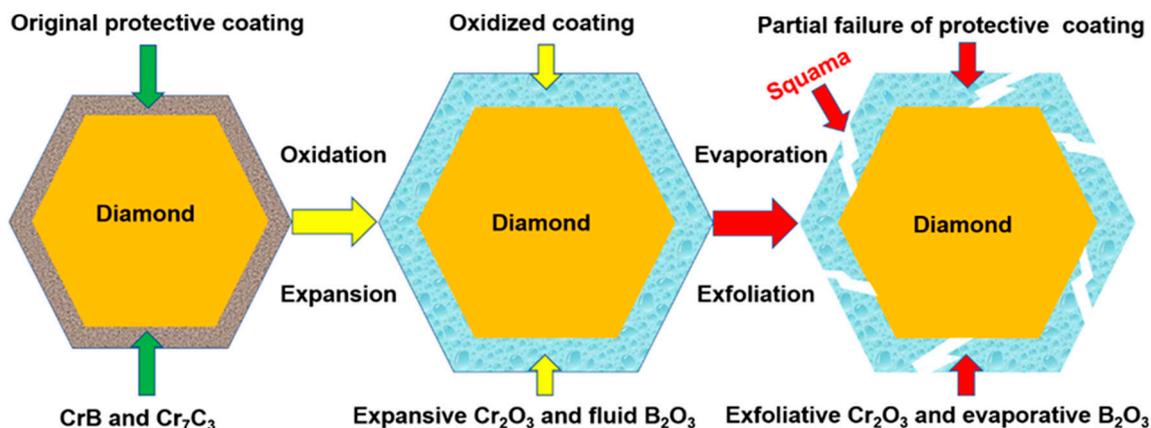


Figure 9. Schematic illustration of the oxidation mechanism related to the Cr–B–C coated diamond.

4. Conclusions

After holding the raw material at $900\text{ }^\circ\text{C}$ for 2 h, the diamond surface was completely and uniformly covered by Cr–B–C coatings consisting of CrB and Cr_7C_3 . The results of TGA revealed that the Cr–B–C coatings can effectively prevent the diamond from being oxidated during heating in air. The formed B_2O_3 and Cr_2O_3 acted as oxygen barrier layers to protect the diamond from oxidation. Furthermore, the formation of B_2O_3 with high temperature fluidity was conducive to avoiding Cr_2O_3 delamination due to volume expansion during oxidation in air. In addition, the presence of Cr_2O_3 provided lasting protection by reducing the evaporation of B_2O_3 . The enhancement of oxidation resistance via chromium boron carbide on diamond particles is of great significance for various applications with elevated temperature, such as mineral exploration and heat transfer applications.

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