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Effect of phosphorus content on the properties of Ni-P coated diamond

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ABSTRACT

Ni-P coated diamond (NPCD) with different phosphorus content was prepared by electroless plating through adjusting NaH_2PO_2 concentration in plating bath. Effect of phosphorus content on the properties of NPCD as surface microstructure, phase structure and heat resistance was studied and compared with that of diamond with no Ni-P coatings. The surface microstructure and the chemical composition were determined by environmental scanning electron microscope (ESEM). The phase structure was observed by X-ray diffraction (XRD). The results demonstrated that a lower phosphorus content of NPCD corresponds to better surface properties with lower roughness and higher heat resistance. A higher phosphorus content, on the contrary, leads to worse overall performance of Ni-P coating.

1. Introduction

Diamond has been extensively used in many industries to fabricate items such as abrasive tools, architectural ornaments, optical and electronic devices and in other fields due to its excellent characteristics such as high hardness, wear resistance, great compressive strength, good heat conduction and electrical insulation [1–3]. Currently, it is difficult to meet the industrial demands using just natural diamond due to resources scarcity; because of this, synthetic diamond is used in the vast majority of industrial applications. Compared with natural diamond, however, synthetic diamond also has some drawbacks, such as poor thermal resistance at high temperature and worse corrosion resistance [4–6].

Diamond tools are generally prepared by electroless plating or electroplating processes, using diamond as reinforcing particles co-deposited in a metal or alloy matrix; it is undesirable to deposit unmodified diamonds due to their high interfacial energy with most metallic surfaces. This results in poor cohesion with the matrix; consequently diamond particles can easily fall off the matrix, thus reducing tools' working life greatly [7,8]. Grech et al. [9] used electroless plating techniques to make diamond particles coated with an interface of Ni-P alloys, with uniform coverage and tailored nano-metric thickness. Ahn et al. [10] reported that the adhesion of a nickel coating layer and diamond particle surface was greatly improved by metallizing the diamond surface with Ni-P fines. Qiu et al. [11] showed that the metallization of a diamond surface, with the formation of a stable chemical metallurgical structure with the matrix can reduce the interfacial energy and enhance the cohesion between the diamond and the matrix. In addition, diamond surface metallization can also improve the strength, heat resistance and corrosion resistance of diamond and the working life of tools. Dong et al. [12] fabricated Ni-P coated diamond (NPCD) by using electroless plating; their results showed that the diamond coated with Ni-P films exhibited higher thermal stability than the diamond with no coating.

Electroless plating is one of the methods commonly used in surface metallization; through this, a metal layer of uniform thickness and strong cohesion can be grown on the diamond surface through a redox reaction [13]. At present, many metals were tested for diamond electroless plating, such as nickel, cobalt, copper and tungsten; metal matrices such as Ni-P [9,10,12], Ni-Zn-P [14], Ni-Cu-P [15] and Ni-W-P [16] were also tested. In such matrices, phosphorus is an important element due to the fact that it improves the overall performance of coated diamond; indeed properties such as hardness, density and strength are positively affected. However, to present, no systematic study was ever performed on the effect the phosphorus content on the properties of the matrix.

In the present paper, NPCD specimens with different phosphorus contents have been made by varying NaH_2PO_2 concentration in an electroless bath. The effect of the phosphorus content on the properties of NPCD surface microstructure, phase structure and heat resistance was studied.

2. Experimental procedures

The size of diamonds used in this experiment is from 10 μm to 20 μm, as shown in Fig. 1. Since the pretreatment of diamond has considerable importance for the successful electroless plating, the following procedure was followed: the diamonds were immersed into a flask containing 5 g/L sodium hydroxide (NaOH) at 95 °C for 30 min, to remove oil

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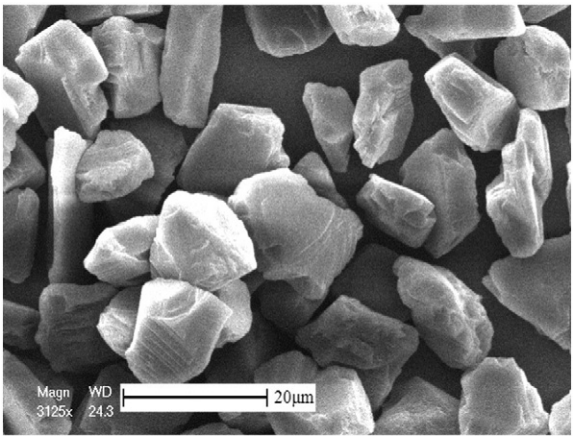

Fig. 1. Microstructure images of diamond particles used in experiments.

stains from the surface, washed in distilled water and then rinsed with 20% HNO_3 at 90 °C for 20 min for surface roughening. After further washing with distilled water, a mixed solution containing 10 g/L $SnCl_2 \cdot H_2O$ and 40 ml/L HCl was used for surface sensitizing at room temperature for 10 min, with ultrasonic vibration. Subsequently, etching in 0.5 g/L $PdCl_2$ and l0 ml/L HCl mixed solution was performed to activate the surface; this was done at room temperature for 10 min with ultrasonic vibration. Before electroless plating, reduction treatment in a solution of 30 g/L $NaH_2PO_2 \cdot H_2O$ at room temperature for 10 min was also done. To ensure cohesion between the Ni-P coating and diamond, the specimen was put into the plating bath immediately after pretreatment. The composition of the electroless plating bath provided different phosphorus contents (3–13%), as mentioned in Table 1. The pH was adjusted to 5, and electroless Ni-P plating lasted for 30 min at a temperature of 95 °C during this process. After completion of the coating, the specimens were removed from the bath and rinsed with distilled water.

Heat resistance tests were conducted in electric furnace at 600 °C for 30 min, and the weight change of each specimen was measured before and after test by using an electrical balance with 0.1 mg weight scale accuracy. The surface microstructure and the chemical composition of NPCD with different phosphorus contents were observed by environmental scanning electron microscope (ESEM, XL-30, Philips, Netherlands); such analyses were performed before and after the heat resistance test. The phase structure of NPCD was determined by using X-ray diffraction (XRD, D8 ADVANCE, Bruker AXS, Germany) with Cu Kα radiation ($U = 40$ kV, $I = 40$ mA). Diffraction patterns were recorded in the 2θ ranging from 20° to 90° at a step size of 0.02° s^{-1} and a scanning speed of 0.1 s $step^{-1}$.

3. Results and discussion

3.1. Surface microstructure of NPCD

Table 2 reports the description of the 4 different samples prepared, with the corresponding phosphorus content; the phosphorus values ranged from 3.7 wt.% to 12.7 wt.%. Fig. 2 and Fig. 3 show the chemical composition and the microstructure images of various. It can be clearly seen from Fig. 3 that NPCD is rougher than the original diamond, which has a smooth surface and distinct edges; the surface of the low phosphorus content NPCD, on the contrary, is smoother than that of the one with a higher phosphorus content. Some fine globules with sizes from 0.25 μm to 0.6 μm were uniformly distributed on the MP-NPCD surface, as shown in Fig. 3(b). Such globules can create adhesion problems with the metal matrix, as they could be loosely attached to the interfacial film [9]. A higher phosphorus content for NPCD enhances the size and amount of the globules and promotes the globules to agglomerate into floccules, thus resulting in a greater roughness of the MHP-NPCD surface (see Fig. 3(c)). It is evident from Fig. 3(d) that the globules further increase in the size (from 1.5 μm to 3 μm) and agglomerate as clusters during the electroless process in the sample with the highest phosphorus content (12.7 wt.%); consequently, surface roughness of the HP-NPCD increases as well. The mechanism proposed in the electroless bath is reported below [17]:

Table 1
Bath composition for electroless Ni-P coating.

Components of plating bath	Concentration
$NiSO_4 \cdot 6H_2O$	25 g/L
$NaH_2PO_2 \cdot H_2O$	8–30 g/L
$C_2H_4O_2$	20 ml/L
CH_3COONa	15 g/L
CN_2SH_4	1.8 mg/L

Table 2
Description of the NPCD samples, with the corresponding phosphorus content.

Sample name	Phosphorus content	Sample description
LP-NPCD	3.7 wt.%	Low phosphorus content NPCD
MP-NPCD	8.7 wt.%	Middle phosphorus content NPCD
MHP-NPCD	11.3 wt.%	Middle high phosphorus content NPCD
HP-NPCD	12.7 wt.%	High phosphorus content NPCD

$$Ni^{2+}_{ads} + H_2PO^-_{2ads} + H_2O \xrightarrow{cat} Ni + 3H^+ + HPO^{2-}_3 \quad (1)$$

$$H_2PO^-_{2ads} + H_2O \xrightarrow{cat} HPO^{2-}_3 + H^+ + 2H_{ads} \quad (2)$$

$$H_2PO^-_{2ads} + H_{ads} \xrightarrow{cat} P + H_2O + OH^- \quad (3)$$

$$2H_{ads} \xrightarrow{cat} H_2 \quad (4)$$

The formation of Ni-P coating on diamond is a consequence of the chemical reduction of Ni^{2+} and $H_2PO_2^-$ to Ni and P in the presence of NaH_2PO_2 as a reducing agent. The reactions (1) and (3) are enhanced with increased $H_2PO_2^-$ concentration, due to the increase of $NaH_2PO_2 \cdot H_2O$ dosage in bath; this results in increased phosphorus content in the Ni-P coating. Ni-P globules, on the other hand, are formed when the deposition rate of the Ni-P coating is rapid in a high NaH_2PO_2 concentration bath, and they agglomerate when the $NaH_2PO_2 \cdot H_2O$ dosage is as high as 30 g/L; in these conditions $NiHPO_3$ sediments are easily formed, leading to the presence of oxygen element as an impurity in the Ni-Ps (see Fig. 2).

3.2. Phase structure of NPCD

Fig.4 shows the XRD patterns of NPCD with different phosphorus contents. It can be seen that the original unmodified diamond is single crystal and it is oriented along the {111} plane, as the peak at 43.86° is much higher than that at 75.24°. The straight baseline indicates that no crystal impurities are present in the diamond. After coating with the Ni-P alloy, the intensity of the diamond peaks reduces and some wide and weak intensity peaks are observed at about 43°; this indicates that the NPCD is polycrystalline but with a low crystallinity of the Ni-P coatings. A weak intensity peak of elemental nickel can be found at 44.02° in the pattern of HP-NPCD, due to the high concentration bath causing a rapid deposition of nickel. The intensity of the diamond peaks in LP-NPCD and MP-NPCD is significantly lower than in the other two samples. Under the same scanning conditions, in fact, samples MHP-NPCD and HP-NPCD show a diamond peak with higher intensity (Fig. 3(c) and 3(d)); this is because these two deposits have poor surface coverage, due to the presence of globules.