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Direct deposition of diamond films on steel using a three-step process

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Abstract

Diamond coatings were successfully deposited on tool steel substrates without using any external diffusion barrier layers. The diamond film deposition was performed in a hot filament chemical vapour deposition (HFCVD) reactor. In the first step, a high substrate temperature and a high methane percentage were used to achieve a faster critical carbon concentration and hence a shorter incubation time for diamond nucleation. Subsequently, the substrates were taken out of the reactor and subjected to ultrasonic scratching in diamond slurry in order to increase the diamond nucleation density. Then the final deposition was performed in the reactor under typical diamond growth conditions. X-ray diffraction analyses showed that Fe_3C was the dominant carbide phase formed on the steel surface after the first step. The carbides produced in the first step act as a diffusion barrier for both iron and carbon. Thus, they accelerate the diamond nucleation and help further diamond growth. Scotch tape adhesion tests showed that the diamond film adheres well to the substrate.

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1. Introduction

Deposition of a diamond film on steel offers the opportunity of enhancing the tribological properties and corrosion resistance of steel without losing the excellent characteristics of its own. By virtue of its high wear resistance and low coefficient of friction combined with its chemical inertness, a diamond coating will lead to enhanced performance and improved life time of a steel tool. Hence, diamond coated steel will open up many applications, extended tool life for example, in the industry.

A lot of efforts have been taken by several research groups to obtain diamond film on steel materials. Kozaki et al. [1] prepared a self-standing diamond film and then brazed it onto the steel substrate surface. However, this method is suitable only for flat substrates. Nakumara et al. [2] reported that high quality diamond can be obtained on steel substrates by optimizing the residence time of the carbon source gas in a HFCVD reactor. Yet, there was no evidence of continuous diamond film formation on the substrate. Narayan et al. [3] proposed a different method to enhance nucleation of

diamond on stainless steel. It involved carbon deposition on the substrate by pulsed laser evaporation followed by pulsed irradiation forming carbide phases and diamond micro crystallites, which provide nuclei for subsequent HFCVD diamond growth. Also here, no continuous film formation was shown.

There are several limiting factors making the diamond nucleation on steel troublesome. Metals such as tungsten, titanium, tantalum and zirconium react with carbon to produce carbides, while iron, cobalt, nickel and manganese dissolve carbon [4–6]. As a result, under diamond growth conditions, deposited carbon dissolves into the steel matrix to form a solid solution. Consequently, a prolonged time is required to reach the critical carbon concentration necessary for the diamond nucleation. Moreover, iron acts as a catalyst for the formation of graphitic phases. Also, the large difference in the thermal expansion coefficient of diamond and steel leads to very poor adhesion. Several diffusion barrier interlayer systems came into use to overcome some of the drawbacks mentioned above [7–12]. Unfortunately, this involves additional steps in substrate preparation and makes the diamond deposition process more elaborate. In our present work, we succeeded in the deposition of continuous and adherent diamond films on steel without using any external interlayers and our initial investigations are presented in this paper.

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2. Experimental details

The diamond films were grown on tool steel substrates (DIN—1.3247: Fe—74.3 wt.%, C—1.04 wt.%, Si—0.353 wt.%, Mn—0.251 wt.%, S—0.0126 wt.%, Cr—3.58 wt.%, Mo—9.08 wt.%, Ni—0.16 wt.%, Co—8.21 wt.%, Cu—0.129 wt.%, V—1.24 wt.% and W—1.54 wt.%). All the samples used were 18 mm in diameter and 3 mm thick. The average roughness, R_a , of the substrates, as measured by a profilometer (Perthen Perthometer M4P) was around 1.5 μm . The substrates were diamond coated following a three-step process. In the first step, the samples were subjected to a high methane concentration ($\text{CH}_4/\text{H}_2=4\%$) for 3 h. A conventional HFCVD reactor was used as described elsewhere [13]. The deposition temperature and gas pressure were kept at 850 $^\circ\text{C}$ and 5 mbar, respectively. The filament temperature was 2100 $^\circ\text{C}$ as measured by the infrared thermometer and the filament to substrate distance was maintained to be 8–10 mm. Next, the samples were taken out of the reactor and ultrasonically abraded in diamond slurry for 30 min to improve the nucleation density in the second step. The size distribution of the suspended diamond particles was 1–2 μm . In the third step, the diamond film was deposited in the HFCVD reactor for 4 h under the following conditions: CH_4/H_2 volume ratio 0.5%, substrate temperature 600 $^\circ\text{C}$, pressure 5 mbar and filament temperature ~ 2100 $^\circ\text{C}$.

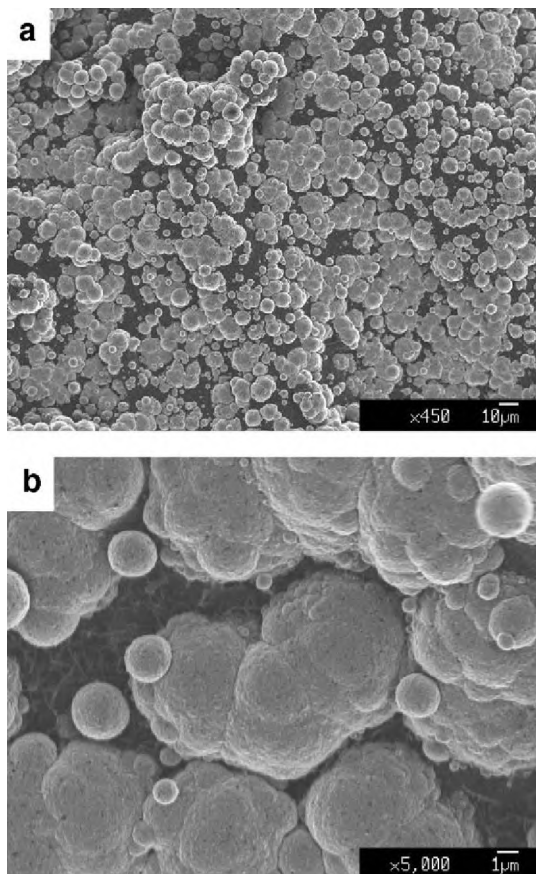


Fig. 1. SEM image of the tool steel surface after the first deposition step of the three-step process. (a) Low magnification, (b) high magnification.

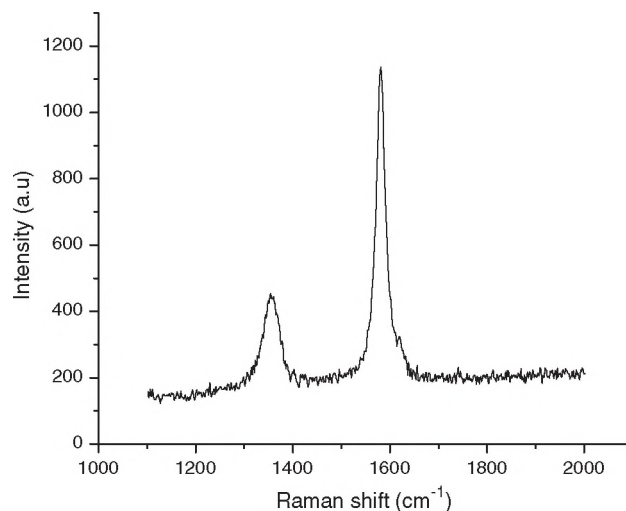


Fig. 2. Raman spectrum of a diamond film deposited on tool steel using the three-step process after the first step.

Raman spectroscopy, using an Ar ion laser (514.5 nm) with an output power of 50 mW and a focused beam diameter of 2 μm (Renishaw system 1000), was used to reveal the quality and the stress state of the deposited films. X-ray diffraction was performed with a Bruker-AXS D5005 diffractometer to analyze the phases present in the substrate surface before and after deposition. Scanning electron microscopy (JEOL JSM 6330 F) was employed to examine the surface morphology of the substrates after each step. Scotch tape adhesion tests were carried out to examine the adhesion of the films.

3. Results and discussion

SEM images in Fig. 1 show the formation of many ball shaped features after the first step of the three-step deposition process. In the Raman spectrum obtained after the first step, three peaks are observed (Fig. 2). The peak at 1581.1 cm^{-1} is the first order E_{2g} mode for graphite, known as the G band. The peaks centered around 1354.1 cm^{-1} and 1620.2 cm^{-1} are also first order lines, which are generally referred to as the D and D' modes of microcrystalline graphite, respectively [14]. There is no diamond Raman peak noticed. The preferential formation of graphitic phases can be explained by the catalytic effect of iron for graphite nucleation and growth.

The X-ray diffraction pattern of the tool steel surface after the first deposition step at a high methane percentage is given in Fig. 3. The dominant phase as observed from XRD is Fe_3C , while there is also a considerable amount of Cr_3C_2 . The formation of carbide phases during the first step is believed to provide an effective solution to the main problems, diffusion of carbon atoms into the iron matrix and iron atoms to the surface, in coating diamond film on steel. The carbides act as a diffusion barrier for both iron and carbon. Thus the critical carbon concentration is reached faster and a short incubation time for nucleation has become possible.

Additional experiments demonstrated that ultrasonic pre treatment, which is the second step in the three-step deposition process, has a considerable influence in terms of increasing the

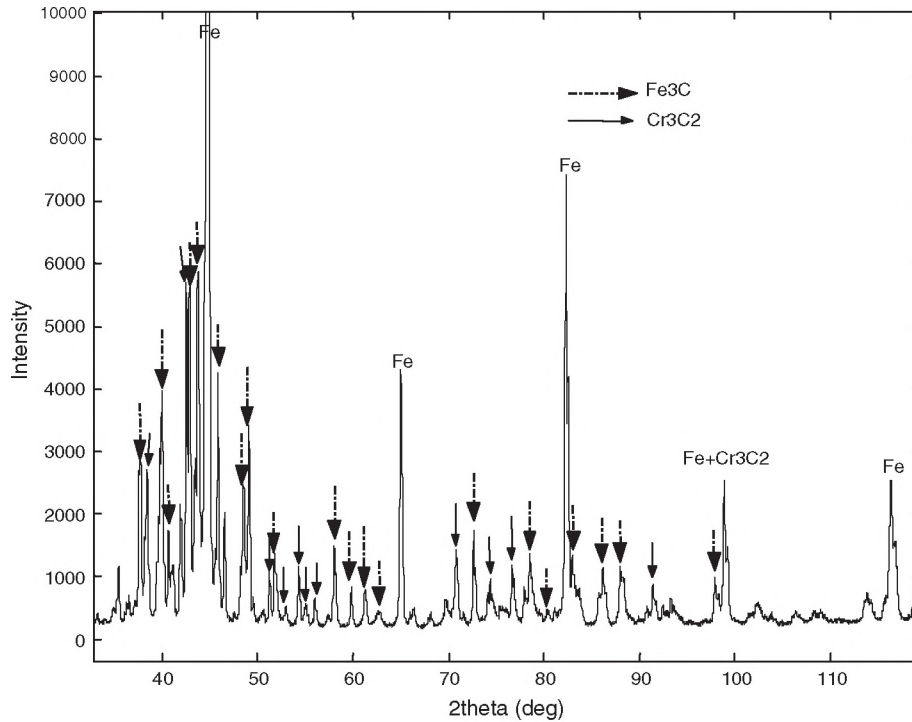


Fig. 3. XRD pattern obtained after the first step of the three-step process for diamond coatings on tool steel.

nucleation density. The samples subjected to the final deposition step without ultrasonic pre treatment show growth on a few areas as shown in Fig. 4, while the pretreated substrates are found to have growth throughout the surface as can be seen in Fig. 5.

The SEM micrographs in Fig. 5 display the morphology of a diamond thin film obtained on a tool steel substrate after all the three steps. As can be seen in Fig. 5a, the deposited diamond film is continuous and the formation of well faceted diamond crystallites is evidenced from the high magnification picture in Fig. 5b. The morphology of the diamond film after the third step indicates that the final diamond layer has replicated the initially formed ball shaped layer (Fig. 1) of graphite. So, these graphite phases seem to act as nucleation centers for the diamond growth in the subsequent deposition. This is in

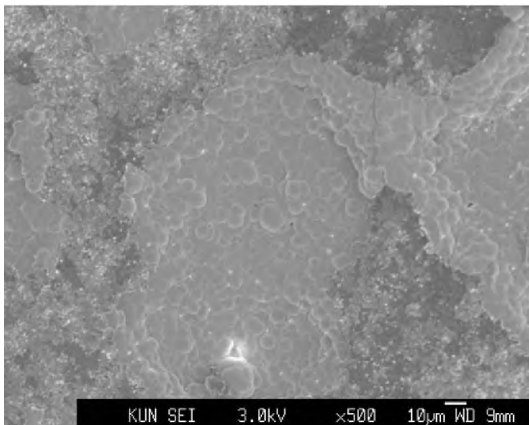


Fig. 4. SEM image of a diamond film deposited on tool steel without ultrasonic pretreatment.

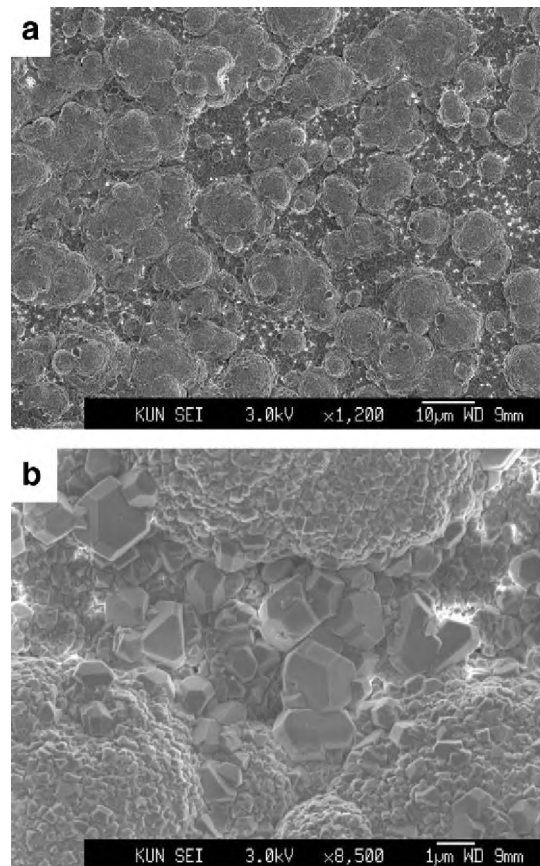


Fig. 5. SEM image of a diamond film obtained after the third step. (a) Low magnification, (b) high magnification.

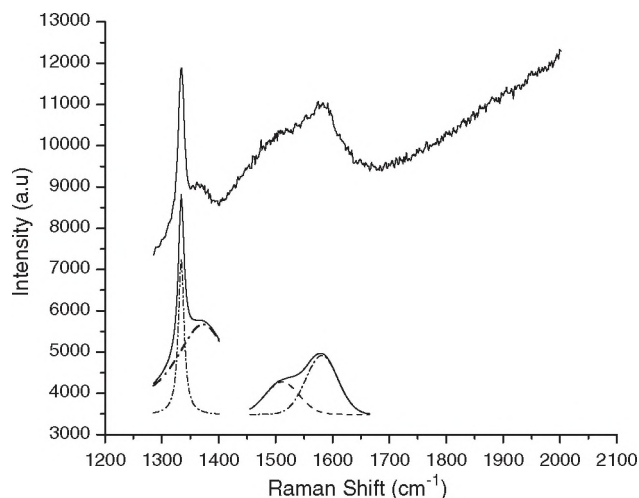


Fig. 6. Raman spectrum of a diamond film deposited on tool steel sample after the third step.

agreement with the result of Chenault et al. who found that graphitic deposits provide excellent diamond nucleation sites [15]. The occurrence of these ball-shaped features also account for the roughness of the film.

Fig. 6 shows the Raman spectrum of the diamond film shown in Fig. 5. There are four Raman modes present. A sharp non-splitted diamond Raman peak is observed at 1334.7 cm^{-1} . The slight upward shift (Raman diamond peak for natural diamond is 1332.5 cm^{-1}) is an indication for the presence of compressive stress of about 1 GPa. The distinctive band centered at around 1575.2 cm^{-1} corresponds to the G mode of graphite, while around 1364.7 cm^{-1} , the weak signature of disordered graphite D band is observed. Furthermore, a weak broad band at 1506 cm^{-1} , the characteristic of amorphous carbon, is also detected. It should be noted that the large contribution of the non-diamond carbon modes in the spectrum can be related to the fact that the scattering efficiency of sp^2 carbon is 50 times higher than that of sp^3 carbon [16].

The adhesion of the films obtained using the three-step deposition process was tested using scotch adhesion tape. The test results showed that the diamond film adheres well to the substrate. There was no peeled-off diamond found on the scotch tape while viewed under the optical microscope.

4. Conclusion

Continuous and adherent diamond films are successfully prepared on tool steel substrates without the use of any external

diffusion barrier interlayers. This was achieved in a three-step process that involved deposition at a high methane concentration (4%) in a HFCVD reactor, subsequent ultrasonic treatment with diamond slurry outside the reactor and final deposition of the diamond film using the typical methane percentage of 0.5%. The graphitic phases formed in the first step and the pretreatment in diamond slurry were found to be very essential to obtain a high nucleation density. In addition, the carbide layers formed in the first step act as diffusion barrier layers for both iron and carbon and helped to achieve a short incubation time for diamond nucleation.

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