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High adhesion and quality diamond films on steel substrate

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Abstract

A process to deposit a diamond coating on steel substrates has been successfully developed. It includes the electroplating of nickel by using an electrolyte dispersed with micro-diamonds, and then a diamond deposition through a microwave plasma chemical vapor deposition system. The diamond films were characterized by Raman and CL spectroscopy, XRD, SEM and SEM line scanning. The results show a high diamond crystal quality, low residual stress (about 0.67 GPa) and high nucleation density. The adhesion of the films was evaluated by a cutting test and an interface examination. The results show that the retentivity of the diamond grits in the films after the cutting test is much better than that in the commercial electroformed diamond tools. The advantages of the process are: (1) the formation of nickel–carbon–hydrogen alloys to enhance diamond nucleation and growth, (2) the micro-diamonds acting as the seeds for diamond nucleation and growth, and forming effective mechanical interlocking with the nickel interlayer, and (3) the formation of good diffusion bonding of the nickel interlayer with the steel substrate. © 1998 Elsevier Science S.A.

Keywords: Diamond films; Microwave plasma CVD; Interlayer; Adhesion

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1. Introduction

Diamond is an exceptional material with extreme hardness, good wear resistance, low friction coefficient and high thermal conductivity. Therefore, one of the potential applications is for tribological situations, such as machining or wear-resistant coatings. However, the most important requirements for these applications are to solve the film adhesion problems and to find a cost-effective and fast fabrication method. One way to solve the adhesion problem was to sacrifice the diamond quality for a better film adhesion. However, in terms of cutting performance, diamond films with good diamond crystal quality will possess stronger and sharper edges for cutting, which was a factor to consider. Another way to solve the adhesion problem was interlayer applications. For example, a process with good diamond film adhesion on steel substrate was successfully developed by Hoffman et al. using a nitridized Cr film as the interlayer [1]; but the diamond quality of the their films was not good enough, as shown by their Raman peak profiles. Diamond coatings on steel substrates were also investigated by many other researchers owing to the availability and low cost of steel [2–8], but were not quite satisfactory. This is due to the fact that iron can consume the carbon species on the substrate surface to inhibit diamond nucleation. Another problem is the existence of film internal stress owing to high thermal stress and intrinsic stress [9–13].

Recently, a new process to synthesize a high quality of diamond at low pressures was successfully developed by using mixtures of various forms of carbon and with one of several metals (Au, Ag, Fe, Cu, Ni, etc.) as a starting material on the substrate in hydrogen plasma at 600–1100 °C [14]. The main idea of the process was to form liquid metal–carbon–hydrogen alloys in the presence of plasma to enhance diamond nucleation and growth. In our research, a process has been developed to deposit diamond films on the tool steel substrate with good adhesion, low residual stress and diamond quality by using a similar idea.

2. Experimental details

The substrate for diamond deposition was JIS-SKD11 tool steel with nominal compositions of 1.4–1.6% C, 11.0–13.0% Cr, and 0.8–1.2% Mo. In order to compare with the regular insert for further cutting tests, the

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specimen for the substrate was designed to be a triangular shape with each side measuring 15.0 mm and a thickness of 4.1 mm. After mechanical polishing, the substrate was electroplated with a layer of nickel by using an electrolyte, which is dispersed with micro-diamonds, at a current density of 1.0–1.4 A cm^{-2} under a temperature of 30–40 °C for 1 h. The micro-diamond powders were commercial grade HPHT synthetic diamonds with an average size of 16 μm in diameter and irregular shapes. The electrolyte consists of nickel sulphamate (600 g l^{-1}), nickel chloride (4.4 g l^{-1}), boric acid (40 g l^{-1}) and few drops of H_2O_2.

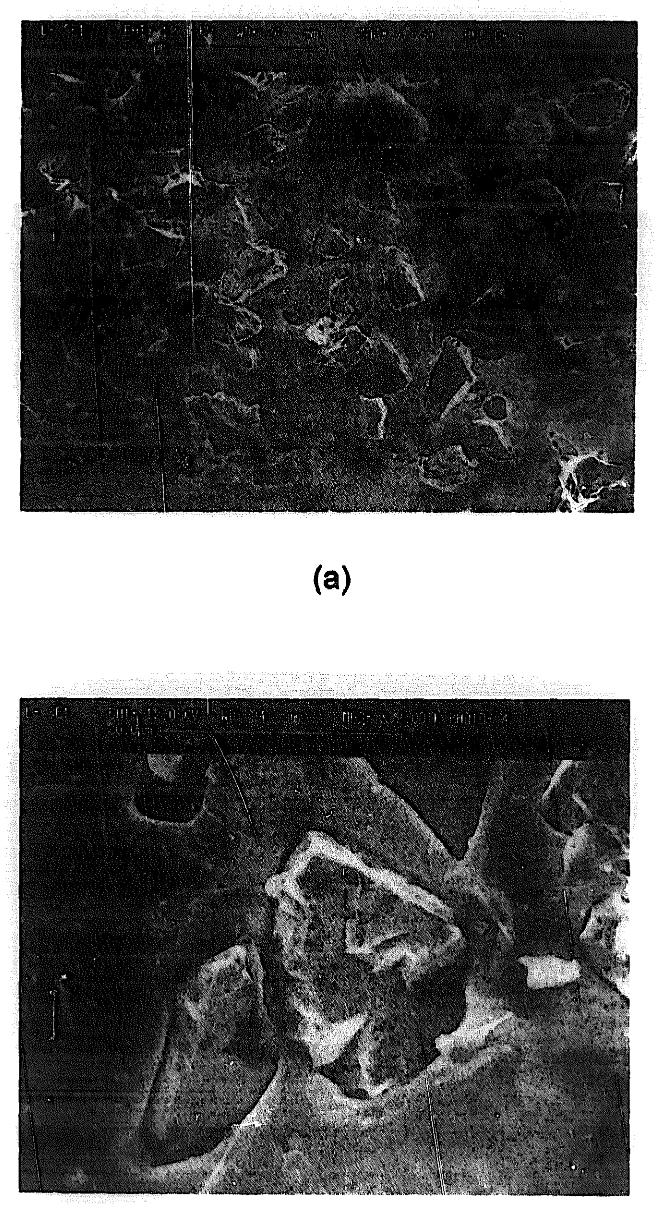
Diamond films were then deposited on the electroplated substrate by a 5 kW microwave plasma enhanced chemical vapor deposition system with hydrogen and methane as the source gases. The typical deposition conditions were: $CH_4/H_2 = 18/300$ (sccm); 2.5 kW microwave power; 70 torr total pressure; 880 °C substrate temperature; as well as 3 or 6 h deposition time.

The film morphologies, residual stress and crystal quality were characterized by SEM, Raman and cathodoluminescence (CL) spectroscopy, and XRD. In order to increase the resolution of non-diamond content in the films, an He–Ne laser ($\lambda = 633$ nm) was used in Raman spectroscopy. The adhesion of the films was evaluated by SEM examining the retentivity of diamond grits on the fractured surface resulting from cutting the diamond coated tools with a low speed diamond saw at a cutting speed of 150 m min^{-1}. The possible diffusion bonding at the interface was examined by SEM line scanning.

3. Results and discussion

3.1. Diamond film growth and film quality

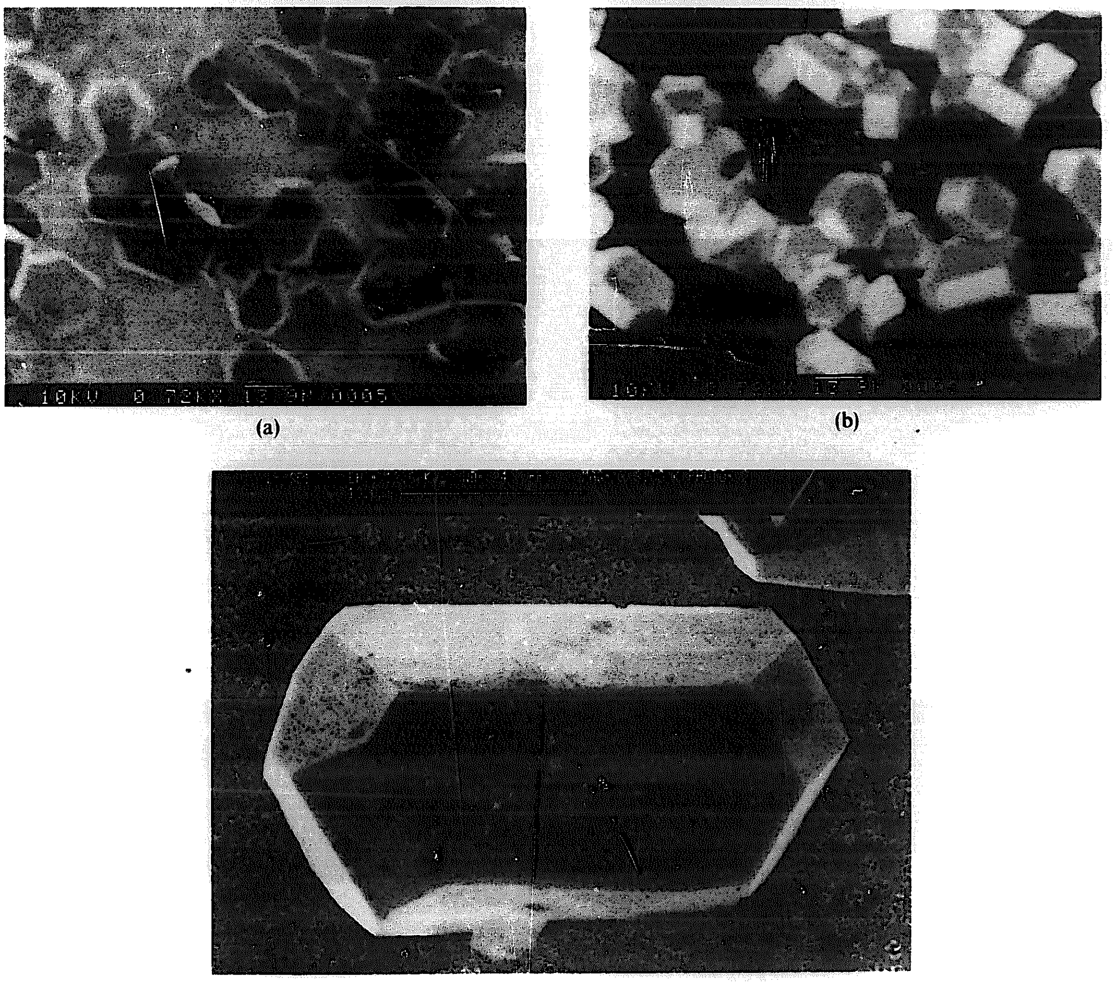
From a C–Ni binary phase diagram, it is known that the maximum solubility of carbon in nickel is about 0.55% C at 1316 °C, and carbon exsolution from C–Ni system produces graphite. Therefore, Ni was falsely believed for a long time to deter diamond nucleation. Recently, it was found that the solubility of the gaseous carbon species in metal can be greatly enhanced in the presence of plasma to form liquid metal–carbon–hydrogen alloys at diamond deposition temperatures [14,15]. It is expected that the exsolution of carbon as diamond could occur under appropriate conditions, and it could be facilitated by the presence of isostructural phases as seeds or substrate for diamond nucleation and growth. Another factor favoring diamond nucleation on Ni film is that the lattice constant of nickel ($a = 0.352$ nm) is close to that of diamond ($a = 0.356$ nm) [15–18]. Therefore, diamonds appear to readily precipitate from these liquid metal–carbon alloys containing atomic hydrogen and deposit on the Ni interlayer. Furthermore, the micro-diamonds in this process can act as effective seeds to further enhance the diamond nucleation and crystal quality. In summary, the substrate, electroplated with a layer of nickel mixed with micro-diamonds, can provide favorable surface conditions for diamond nucleation and growth. The morphology for the nickel-plated substrate before diamond film deposition is shown in Fig. 1. Fig. 1b is a higher magnification of Fig. 1a, showing the blunted edges and gaps at the interfaces between the diamond particles and nickel matrix. It implies a strong interaction between them. The original diamond seeds are irregular in shape, as also shown in Fig. 1. However, the diamond crystals become more regular in shape with sharper edges and faceted planes



(a)

(b)

Fig. 1. Typical SEM morphologies: (a) after nickel and micro-diamonds electroplating; and (b) the high magnification of (a).



(a) (b)

(c)

Fig. 2. Typical morphologies of diamond crystals after 3 h deposition: (a) SEM morphology; (b) CL image of (a); and (c) the high magnification of one of the diamond crystals in (a).

after 3 h diamond deposition. The average crystal size is 25 μm, as shown in Figs. 2a and b for typical SEM and CL morphologies, respectively, of diamond for this process. Fig. 2c is a magnification of one of the crystals in Fig. 2a, showing a clear and obvious crystalline shape, facet, apex and hill. Fig. 3a shows an SEM morphology of the diamond films and Fig. 3b is a higher magnification of Fig. 3a. Like Fig. 2, the crystals with clear, obvious and sharper edges as well as faceted planes are observed. The diamond films for this process are signified by a small percentage of non-diamond carbon content in the films, as indicated by four narrow XRD diamond peaks and a narrow Raman peak around 1332.5 cm^{-1} and no significant peak around 1560 cm^{-1}. Fig. 4 presents the typical Raman spectra with a peak at 1331.0 cm^{-1} and FWHM of 4.7 cm^{-1}, indicating a good diamond crystal quality.

3.2. *Film adhesion*

In order to evaluate adhesion of diamond films on the substrate for the present process, the retentivity of diamond grits in the Ni interlayer for the diamond coated tool steels and the commercial electroformed diamond tools were compared by examining the fracture surface from cutting the specimens with a low speed diamond saw, as shown in Figs. 5 and 6, respectively, where Fig. 5b is a CL image of Fig. 5a. Fig. 6 shows a poor retentivity for the electroformed tool, i.e. an obvious gap between the diamond grit and Ni matrix. In contrast, the diamond crystals in Fig. 5 for this process are uniformly embedded in a nickel matrix to form good mechanical interlocking by recessing part of the diamond crystals below the shear plane. In other words, a better retentivity of diamond grits after cutting for the diamond coated tools of the present process can be achieved. It also indicates that the films for this process can withstand temperature change during the cutting test.

As for interfacial diffusion, Fig. 7 shows the corresponding Ni, Cr, and Fe line scanning at the interface of diamond grit and the nickel layer for the present process. It shows that Cr and Fe from the steel substrate are effectively diffused into the nickel layer, suggesting

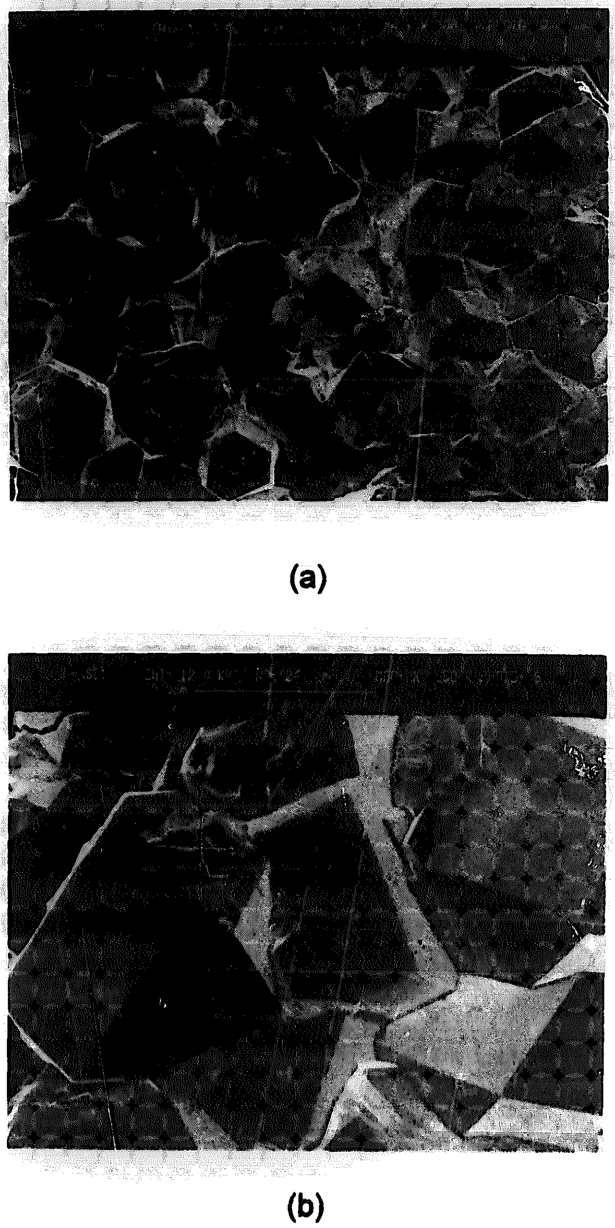


Fig. 3. Typical SEM morphologies of diamond films on the nickel electroplated steel substrate after 6 h deposition: (a) low magnification; and (b) high magnification.

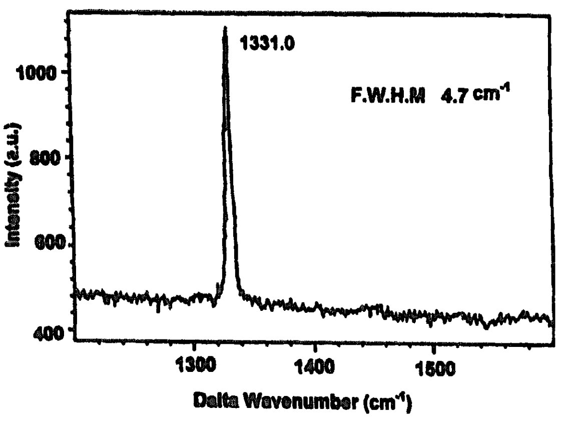


Fig. 4. Typical Raman spectra of diamond films for this process.

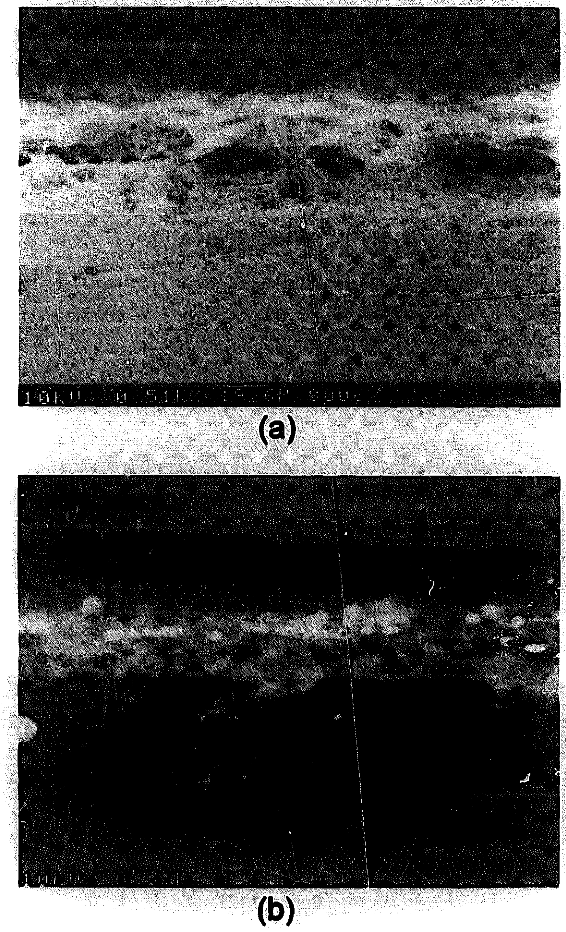


Fig. 5. Typical fracture surface of the diamond -coated tool steel for the present process: (a) SEM micrograph; and (b) CL image.

Fig. 6. Typical fracture surface of the commercial electroformed diamond tools.

a good diffusion bonding between nickel layer and the steel substrate; and there is a layer within the Ni layer and closer to the diamond grit side, which shows the high possibility of forming liquid Ni–Fe–Cr–C–H alloys

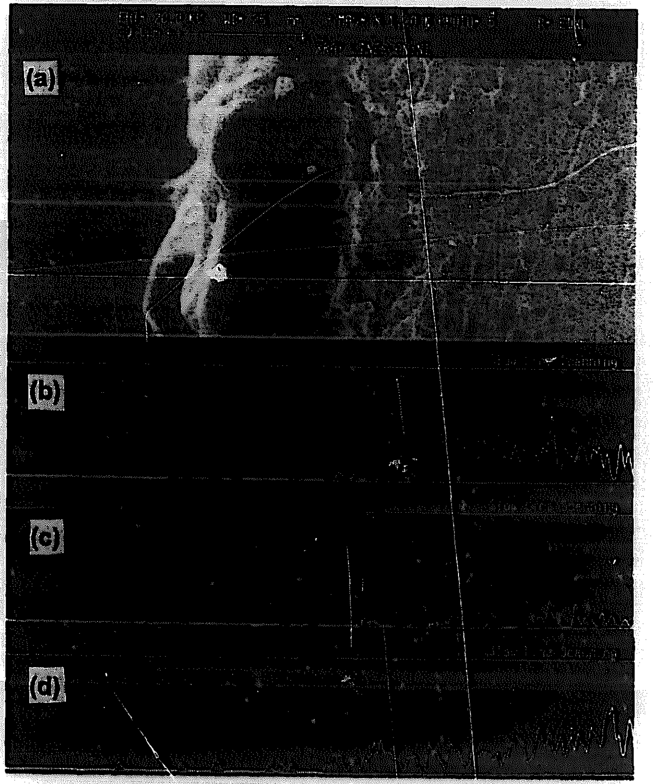


Fig. 7. Typical fracture surface of the diamond-coated tool steel for the present process and the corresponding element line scanning: (a) SEM micrograph; (b), (c) and (d) are Ni, Cr and Fe line scanning, respectively.

during diamond deposition. This is in agreement with the statement that metal–carbon–hydrogen alloys can greatly enhance nucleation density and retention force of diamond grits in nickel matrix.

The residual stress of the films was also measured by Raman shift techniques, a detailed description of the method has been published elsewhere [9]. The typical Raman peak at 1331 cm^{-1} in Fig. 4 is found to be slightly shifted to a lower frequency side of 1332.5 cm^{-1}, indicating a low tensile residual stress in the films. The average residual stress for this case is about 0.67 GPa, which is much smaller than other processes [9,12]. This is another factor favoring the suggestion that good adhesion is due to a smaller mismatch in lattice constant between Ni and diamond.

4. Conclusions

A process to utilize a liquid nickel diamond hydrogen alloy system has been successfully developed to obtain the diamond-coated tool steels with high diamond quality, low residual stress and good adhesion. The process can be successfully used to deposit diamond films on steel substrates for three reasons: (1) the nickel–carbon–hydrogen alloy system can effectively enhance diamond nucleation and growth, and form a high retention force; (2) the micro-diamonds are effective seed crystals for diamond nucleation and growth, and the diamond grits are effectively embedded into the nickel layer to form a good mechanical interlocking; and (3) the nickel plating can form a good diffusion bond with the steel substrate.

Acknowledgement

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