

Chemical vapour deposition of diamond on stainless steel: the effect of Ni–diamond composite coated buffer layer

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Received 11 June 1997; accepted 10 December 1997

Abstract

Diamond films were grown on nickel and nickel–diamond composite coated stainless steel substrates using microwave plasma chemical vapour deposition (MPCVD). X-ray diffraction (XRD), scanning electron microscopy and Raman spectroscopy studies give clear evidence for the growth of diamond on buffer layered substrates. XRD results further suggest that after CVD treatment the interface nickel ($a=3.522 \text{ \AA}$) shows an increase in the lattice constant ($a=3.563 \text{ \AA}$). The unit cell expansion can be attributed to the formation of the Ni–C solid solution phase. The new unit cell parameter of Ni match closely with diamond ($a=3.566 \text{ \AA}$). In addition, the embedded diamond particles assist in faster nucleation and growth of the diamond crystallites on composite coated substrates. © 1998 Elsevier Science S.A.

Keywords: CVD; Composite; Diamond; Diffusion

1. Introduction

Extreme mechanical, thermal and electronic properties of diamond make it a technologically important material for both tribological and electronic applications. An obviously attractive application of the chemical vapour deposited (CVD) diamond films would be the direct deposition of diamond on steel resulting in hard wear resistant tools. However, direct deposition of the CVD diamond on steel substrates [1,2] has so far resulted in poor quality films. Catalytic effect of Fe and the high solubility of carbon into it, results in a highly unsuitable base for CVD diamond growth. A number of attempts [3–8] have been made to develop good quality films using suitable buffer layers prior to diamond deposition. For example, Tsai et al. [9] developed a three-step process on metal substrates where diamond cannot grow directly with good adhesion. Shih et al. [10] have used electrodes Ni plating as a buffer layer to grow diamond on tool steel. Fayer et al. [11] reported good-adherence of diamond film on stainless steel (SS) with a buffer layer of chromium nitride prior to diamond deposition. In

this paper, we report the growth of high quality diamond film on commercial SS substrate using Ni–diamond composite coating on SS prior to CVD. The Ni layer suppresses the Fe diffusion on the growing surface and the diamond particles embedded in the Ni matrix act as nucleation centers.

2. Experimental details

Diamond films were grown using a multi-step process on commercial SS substrates. The major constituents of the substrate are Fe, Si, Ni, Cr and C. Deposition of the diamond coatings was carried out on the substrates, with a strike Ni layer (0.5–1 μm thick) followed by a composite Ni-diamond coating (18–20 μm thick). Composite coating was done by suspension of diamond particles in a Watts type electroplating bath. The size distribution of the suspended diamond particles in the electroplating solution was 8–20 μm . The area coverage of the diamond particles, estimated by scanning electron microscopy (SEM), was 40–45%. Composite coated substrates were annealed at 900 °C in H_2 -plasma. The CVD was carried out in microwave plasma CVD chamber whose details are described elsewhere, [12]. A micro-

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wave generator (2.45 GHz, 0–700 W) was used to generate the plasma of input gas mixture of H_2 and CH_4 . Substrates were kept on a graphite holder and its temperature was maintained at 925 °C. The flow rates of the gases were measured using mass flow controllers. For a comparison, bare Ni (12–15 μm thick) coated SS substrates were subjected to CVD for different deposition times while keeping the CH_4/H_2 ratio constant. All the films were characterized by XRD, SEM and Raman spectroscopy to investigate, respectively, the crystallinity, the surface morphology and the non-diamond impurity content. Energy dispersive X-ray (EDX) analysis was used to determine other elemental impurities in the films.

3. Results and discussion

Fig. 1a shows the SEM micrograph of the Ni-diamond composite coated SS substrate. Diamond particles embedded in the Ni matrix are irregular in shape. Fig. 1b shows the surface morphology of the diamond grown on composite coated substrate. The initially irregular shaped particles are converted to regular cuboctahedron shapes. In Fig. 1c the micrograph of

a typical continuous diamond film grown on the composite coated substrate is shown. Area coverage of the diamond particles was increased by 65–70% in order to get the continuous films in a shorter time. Crystallinity is further improved with a initial Ni layer (discussed later) prior to composite coatings (Fig. 1d).

XRD pattern of the composite coated substrate before and after CVD are shown in Fig. 2. As can be seen from the figure, before CVD both Ni and diamond peaks are present. After CVD, diamond (111), (220) and (311) peaks cannot be distinguished due to the overlap with the Ni peaks, as the latter reflections are shifted towards the lower 2θ position. This is well supported by the shift of the Ni (200) peak where no diamond peak appears. Shifting of the Ni peaks gives an indication for Ni lattice expansion. This might be caused by the diffusion of the carbon from the gas phase resulting in the formation of Ni–C solid solution. This conjecture is confirmed on the bare Ni-coated SS substrates (without diamond inclusions) subjected to CVD for different times. The XRD patterns (Fig. 3) show the shifting of all the Ni peaks towards lower 2θ positions after CVD. It can be seen from Table 1 that the lattice expansion increases with time and approaches saturation beyond 10 h. Based on this information [13] carbon

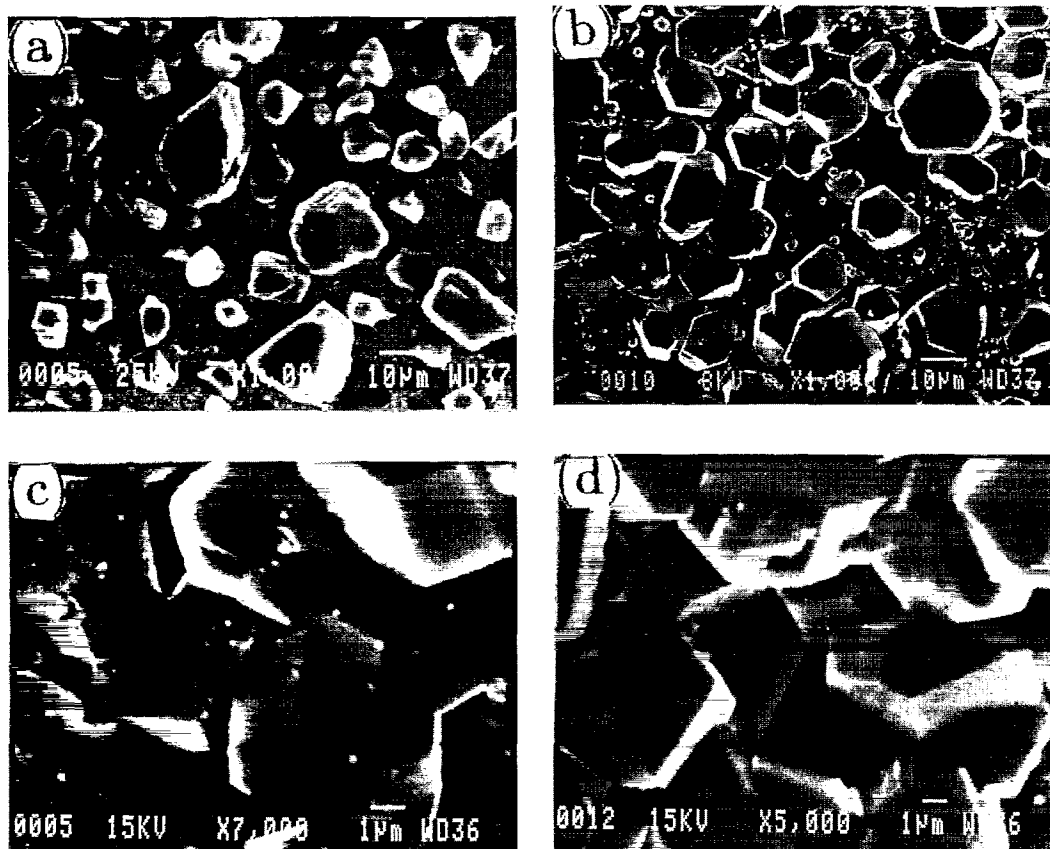


Fig. 1. SEM of: (a) Ni-diamond composite coated SS substrate, (b) CVD diamond grown on composite coated substrate; (c) continuous diamond film grown on composite coated substrate; and (d) continuous diamond film on the Ni/Ni-diamond composite coated substrate.

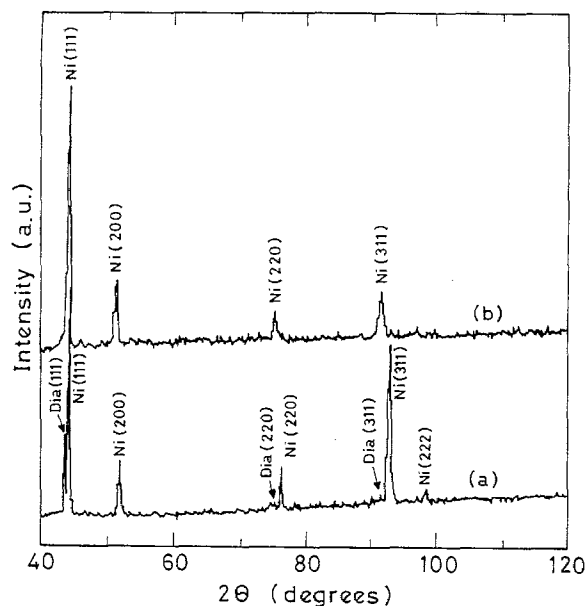


Fig. 2. XRD pattern of the composite coated substrates: (a) before and (b) after CVD.

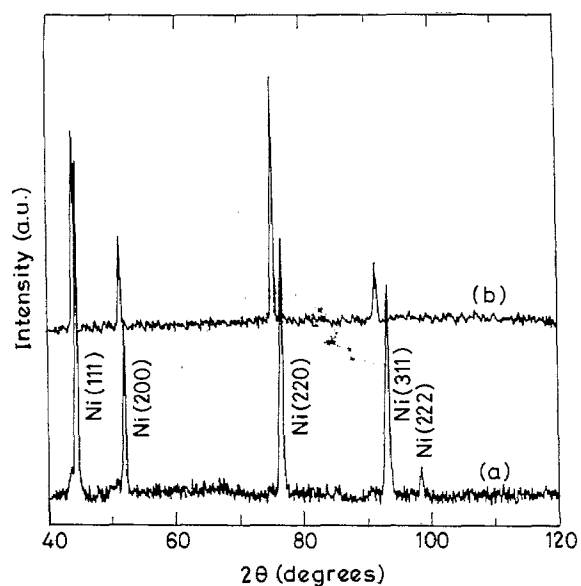


Fig. 3. XRD pattern of the bare Ni coated substrates: (a) before and (b) after CVD with 0.3% CH₄ for 10 h.

concentration in the Ni–C solid solution was found (with 10% error) to be a maximum of 4 wt.%. Diamond nucleation is not seen on bare Ni coated substrates in spite of their exposure to 0.3% CH₄ in balance H₂ for 10 h (Fig. 4a). This may be due to the carbon dissolution in Ni resulting in insufficient concentration of the carbon precursors in the gas phase. It naturally follows that if the substrates are exposed to a higher CH₄ concentration the carbon dissolution may saturate relatively quickly and sufficient concentration of the precursors will be available for the nucleation of diamond. In conformity with this assumption we find that diamond nucleates in just 2 h when the CH₄ percentage in the gas mixture is increased to above 1% in balance H₂ (Fig. 4b).

Fig. 5a shows the Raman spectrum of the CVD

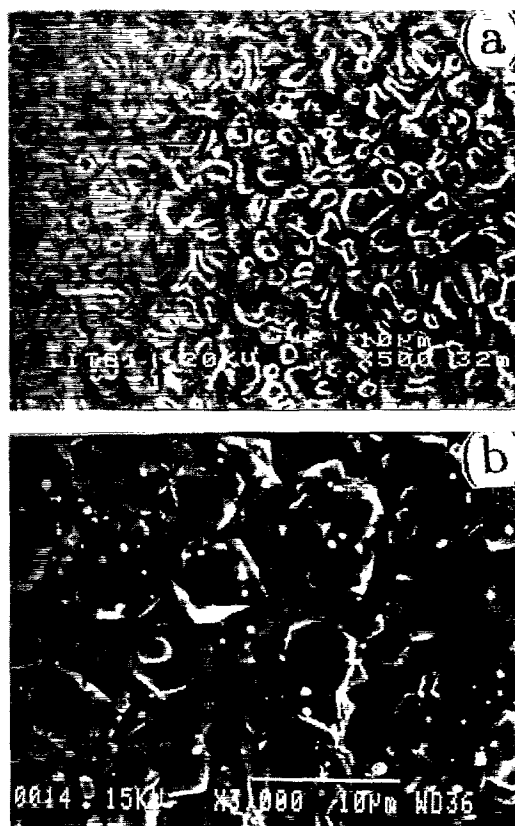


Fig. 4. SEM of: (a) bare Ni coated substrate after CVD with 0.3% CH₄ for 10 h and (b) CVD diamond grown on bare Ni coated substrate with 1.6% CH₄ for 2 h.

Table 1
Unit cell expansion of Ni after CVD (0.3% CH₄) on Ni coated SS at different times

Time (h)	Before CVD <i>a</i> (Å)	<i>V</i> (Å ³)	After CVD <i>a</i> (Å)	<i>V</i> (Å ³)	Volume change (%)	Carbon conc. (wt.%)
2	3.517(2)	43.52(7)	3.532(1)	44.06(3)	1.24	1.2
4	3.522(1)	43.69(3)	3.563(1)	45.22(5)	3.50	3.7
7	3.518(1)	43.55(4)	3.575(4)	45.70(2)	4.95	4.7
10	3.516(1)	43.46(5)	3.574(2)	45.67(8)	5.09	4.6

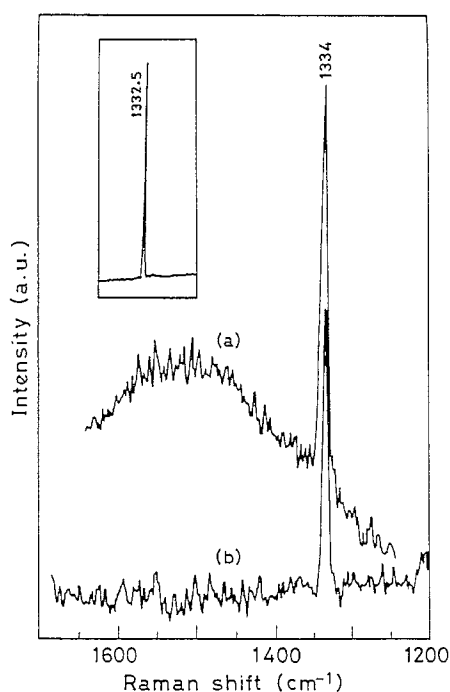


Fig. 5. Raman spectra of the CVD diamond grown on: (a) composite coated substrates and (b) Ni/Ni–diamond composite coated substrates. The inset shows the typical Raman spectrum of composite coated substrate before CVD.

diamond deposited on Ni–diamond composite coated SS substrate while the inset shows the typical Raman spectrum of the Ni–diamond composite coated substrate before CVD. A sharp peak at 1334 cm^{-1} corresponds to the good crystalline diamond. The broad band at around 1500 cm^{-1} indicates the non-diamond carbon present in the film. There is no distinct graphitic peak at 1580 cm^{-1} in any of the films grown on either Ni or Ni–diamond composite coated substrates. This may be suppressed due to the post annealing treatment of the substrates in the hydrogen atmosphere [14]. EDX results from the composite coated substrates show that small amounts of Fe impurities are still present on the surface after CVD. The diamond particles which are trapped at the early stage of the composite electrodeposition will be very close to the SS substrate. At the time of CVD Fe may segregate to the surface through the diamond–Ni interfaces. This may be the reason for the observed Fe on the surface which may be one of the main causes for the non-diamond formation. However, Fe diffusion was reduced by depositing a 12–15 μm bare Ni layer prior to Ni–diamond coating. In addition, it improves the quality of the CVD diamond significantly. Fig. 1d shows the micrograph of a continuous film grown on the SS/Ni/Ni–diamond composite coating. Crystallinity of the diamond grains is significantly improved. Fig. 5b shows the Raman spectrum of a diamond film grown on the SS/Ni/Ni–diamond substrate. The intensity of

the non-diamond band is considerably reduced in support of our conjecture. Further EDX analysis shows that the concentration of Fe impurities has reduced greatly on the surface of these samples.

4. Conclusions

In summary, the following conclusions are drawn from the present work:

- Good quality diamond films are produced by CVD on Ni–diamond composite buffer layered SS. The embedded diamond particles assist faster nucleations and growth of the diamond films.
- A Ni layer deposition prior to composite coating reduces the Fe diffusion considerably and improves the quality of the films greatly.
- The formation of Ni–C solid solution decreases the lattice mismatching during CVD. This is important for the growth of epitaxial diamond films on single crystal Ni substrate.

Acknowledgement

We are grateful to Mr S. Chakrovorty of Grauer and Weil (India) Ltd and Dr M. K. Totlani of Bhabha Atomic Research Centre for fruitful suggestions on Ni and Ni–diamond composite coatings. We acknowledge the financial support of the Board of Research in Nuclear Sciences (Department of Atomic Energy, India).

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