

Hot-Filament Chemical Vapor Deposition of Polycrystalline Diamond Coatings to Interlayered Steel

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Zr-based nitride and carbide coatings have been deposited on high-speed steel by the cathodic arc method. Hot-filament chemical vapor deposition (CVD) has been used to deposit diamond films onto a treated steel surface. The films deposited by CVD were characterized using scanning electron microscopy, x-ray diffraction, and Raman spectroscopy to determine the surface morphology, roughness, crystal structure, and bonding characteristics.

Keywords chemical vapor deposition, diamond, HSS steel, interlayers

1. Introduction

Due to its wide range of exceptional properties, diamond is an ideal material for a range of tooling applications. The chemical vapor deposition (CVD) of diamond on technologically important substrates such as steels and WC-Co is critical because the carbon species forming the film diffuses into steel or into the cemented carbide binder phase. This causes a deterioration of the mechanical properties of the substrate, and the diamond films deposited have poor adhesion due to the interfacial sp^2 carbon formation catalyzed by transition metals with a partially filled 3d shell (e.g., Fe, Co, and Ni). A simple way of overcoming this problem is to deposit an interlayer between the substrate and the proposed diamond film.

Diamond-like carbon (DLC) has successfully been deposited on steel using graded layers in the following sequence of steps:



This approach was used with a technology known as *closed-field, unbalanced magnetron sputtering*, which was developed by Teer et al. (Ref 1) The deposited films displayed a low coefficient of friction, good adhesion, and low wear rates. Polycrystalline diamond has relatively large crystallites and, therefore, is better suited for abrasive application using dental burs. Therefore, in this study a similar approach was investigated for the diamond films created by CVD, which are harder than DLC films. The major advantages of CVD compared with sputtering include excellent uniformity, reproducibility, high

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throughput and/or productivity, good adhesion, excellent control, and the ability to coat complex shapes of large sizes. Various approaches have been undertaken to produce interlayer systems that can serve as a good host to diamond and steel. Zr-based nitride/carbide and a TiNSi_3N_4 nanocomposite have been studied to investigate the behavior of these interlayers on steel as an addition to surface pretreatment.

2. Experimental

The substrates used were M2 high-speed steel. The sample dimensions were $10 \times 10 \times 1.0$ mm high-speed steel cut from a block. The high-speed steel contained 0.85 wt.% C. The samples were then polished to a $2 \mu\text{m}$ surface roughness. After polishing, the samples were cleaned ultrasonically in acetone for 5 min. A dual ion beam source was then used to deposit a $0.2 \mu\text{m}$ nanocomposite of TiN-SiN_x interlayers onto steel. In this system, atoms were sputtered by one ion beam while a second ion beam was used for energy assistance. A schematic representation is shown in Fig. 1.

The ion beam approach has the advantages of providing

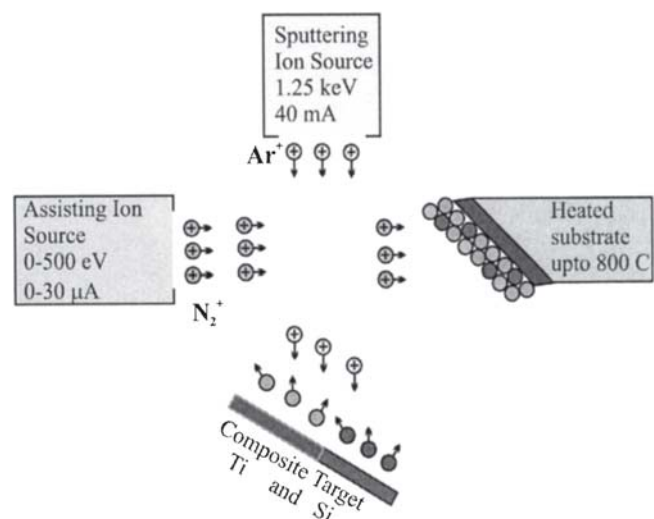


Fig. 1 Schematic of an ion beam system (Ref 2)

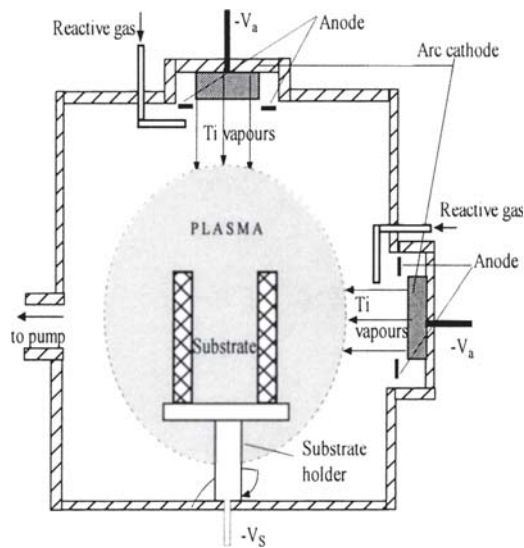


Fig. 2 Schematic of a PVD-arc deposition system

excellent control of deposition parameters, removing residual gases and other contaminants from the substrate by the ion bombardment, transferring additional energy to the surface, and depositing atoms that give more surface mobility. This allows the atoms to move to different sites, producing denser and better-bonded films and allowing the film stress to change, usually from tensile to compressive (Ref 2). The Zr-based nitride and carbide coatings were deposited using a reactive-cathodic arc method. The films were all of 10 μm thickness and were deposited at 250 $^{\circ}\text{C}$. A schematic of the deposition system is shown in Fig. 2. The system has two cathodic arc evaporators equipped with a Zr target. Nitride and carbide coatings were deposited only in N_2 and C_2H_2 atmospheres, respectively. The base pressure in the system was 5×10^{-4} Pa, and the deposition pressure was maintained between 6×10^{-2} and 8×10^{-1} Pa.

Preliminary experiments have shown that the highest microhardness values for the films were obtained for a substrate bias (V_s) of about -200 V and a cathodic arc current (I_a) of 110 A for Zr. Before deposition, the samples were ultrasonically cleaned with trichloroethylene and mounted on a rotating holder inside the deposition chamber. Prior to deposition, the samples were sputtered via Zr ion bombardment (1 kV for 5 min). The nanocomposite layers were deposited at 400 $^{\circ}\text{C}$. These interlayers were prepared according to the deposition parameters listed in Table 1 and were characterized by Rutherford backscattering. Prior to diamond deposition, several substrates were ultrasonically treated for 10 min with a 0.25 μm diamond powder suspension. This treatment, usually referred to as *seeding*, enhances diamond nucleation either by implanting tiny diamond fragments into the substrate surface, on which diamond can subsequently grow during CVD (Ref 3), or by creating suitable defects at the substrate surface, which favors the heterogeneous nucleation of diamond from the gas phase (Ref 3, 4). Diamond depositions were carried out using the hot-filament CVD reactor, which has been described previously (Ref 5). In Table 2, the diamond deposition parameters are reported. After the CVD process, the ramp-down procedure lasted around 20 min, and was used to compensate for the thermal expansion and stress exerted on the diamond and steel interface, and to minimize any delamination in going from the deposition temperature to room temperature.

Table 1 Nanocomposite TiN/SiN_x deposition conditions

Target	Ti/Si
Base pressure	$2.7 \cdot 10^{-6}$ Torr
Reactive gas	N_2
Sputtering gas	Ar
Temperature	400 $^{\circ}\text{C}$
Beam energy	600 eV
Si content, at. %	8.7
Ti-to-Si-to-N ratio	$\text{Ti}_{0.38}\text{Si}_{0.087}\text{N}_{0.533}$
Ion-to-atom ratio	1:1
Deposition time	120 min

Table 2 Chemical vapor deposition parameters

CH_4/H_2 volume ratio	1.0%
Gas pressure	4.8 kPa
Flow rate	300 sccm
Filament/substrate distance	8 mm
Filament temperature	2150–2200 $^{\circ}\text{C}$
Substrate temperature	650–700 $^{\circ}\text{C}$
Deposition time	4 h

3. Experimental Results and Discussions

Figure 3 shows scanning electron microscopy (SEM) images of the as-deposited nanocomposite interlayer that was grown on a steel substrate. The deposition temperature used was 400 $^{\circ}\text{C}$. A very thin layer was deposited after only 120 min. Patches of uncoated regions were evident from the SEM micrographs. The film was discontinuous, and it is, therefore, necessary to deposit for longer times to obtain any appreciable nucleation for a continuous layer. The crystallites were of variable sizes, with the mean being approximately 200 nm. Figure 4(a) shows the nanocomposite sample subjected to CVD without surface treatments, and Fig. 4(b) shows a pretreated sample surface with diamond suspension with an average grit particle size of 0.25 μm . Even though the magnifications on the SEM micrographs are different, qualitatively one can conclude that nucleation is poor with isolated diamond crystals being evident. The crystals ranged from 0.5 to 4 μm in size. Some of these crystals were on the interlayer, and others were on the substrate without the interlayer. It is possible that diamond is also nucleating on impurities in the substrate. Further investigations are required to confirm and understand this observation. Clearly, with pretreatment, there appears to be an enhancement in the nucleation of diamond. In this micrograph, the crystallite density is much higher and the sizes of the crystallite have a larger range, from 0.5 to ~ 7 μm . It can be concluded that pretreatment enhances nucleation as expected. It is possible that diamond nucleated on the surface defects, where diamond particles were possibly embedded. Even though diamond nucleation was very noticeable, diamond growth was nonuniform and the film discontinuous. More detailed investigations are required to understand these effects.

The investigations were extended to Zr-based interlayers, namely, ZrN and ZrC deposited with the reactive cathodic arc (RCA) technique at 250 $^{\circ}\text{C}$. Figure 5 shows the SEM micrographs of a ZrN coating deposited on the HSS steel by the RCA technique. The morphology of the as-prepared ZrN coating showed a low surface density of crystallites with a size not

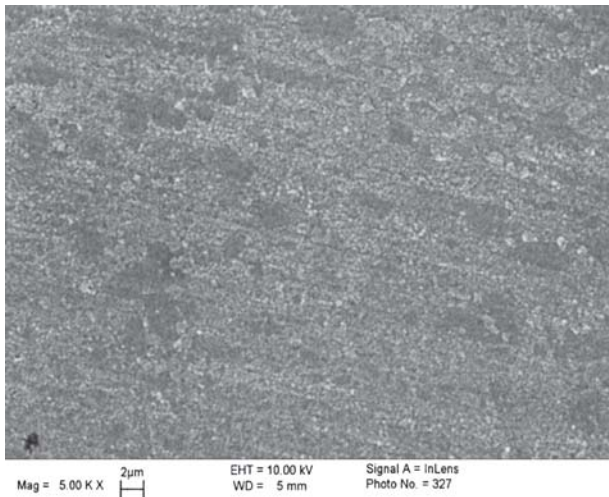


Fig. 3 As-deposited nanocomposite interlayer

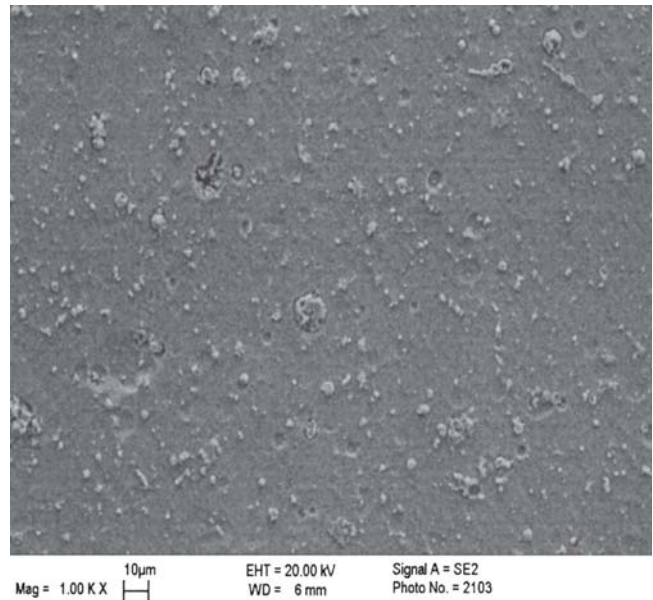
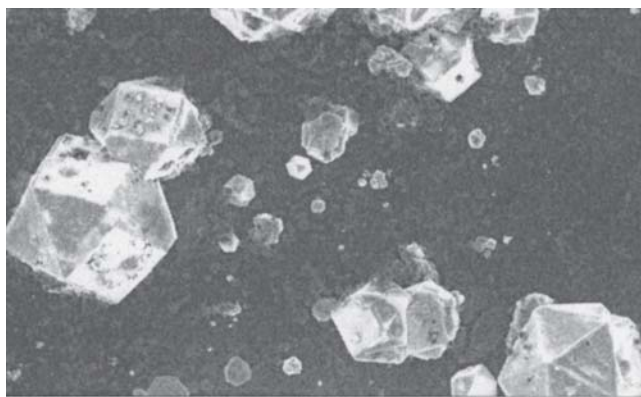
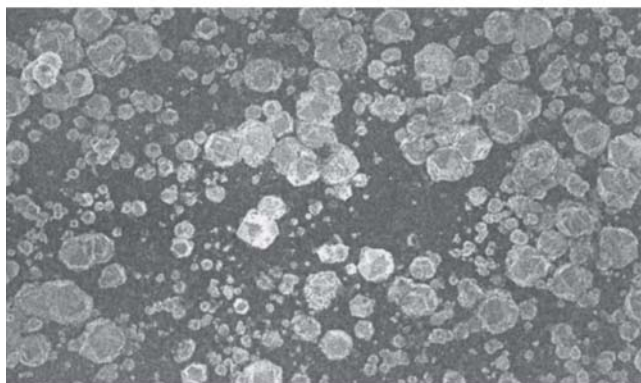


Fig. 5 As-deposited ZrN interlayer



(a)



(b)

Fig. 4 (a) Nanocomposite interlayer without surface treatment. (b) Nanocomposite interlayer with surface treatment

exceeding a few micrometers. In addition, the surface shows pits of various dimensions. A cleaner ZrN coating can be deposited using a filtered cathodic arc; however, this was not done due to constraints in deposition facilities. These films were then pretreated with a diamond suspension, as mentioned earlier, and then CVD was used to deposit the diamond films. After a 3 h CVD treatment, a diamond film of approximately

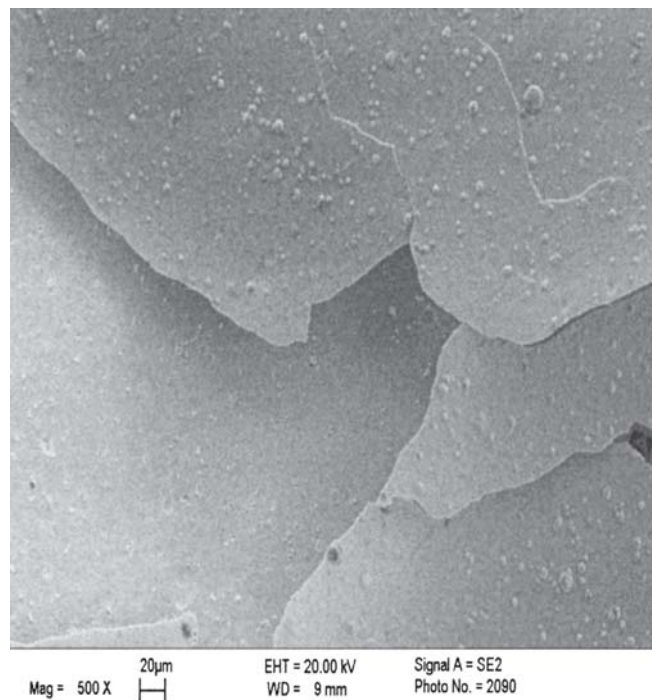


Fig. 6 Diamond film delamination on ZrN

1.5 μm thickness, which had a rough surface, was deposited. The continuous diamond film underwent spontaneous delamination during cooling to room temperature, as shown in Fig. 6. This is probably due to differences in the thermal expansion coefficient. The detailed structure of the ZrN was investigated using x-ray diffraction (XRD) to elucidate structure changes. Figure 7 shows the XRD patterns of the as-deposited ZrN interlayer and after 3 h of CVD at slightly different temperatures (620 and 650 $^{\circ}\text{C}$). The pattern of the interlayer before CVD deposition showed peaks that were attributable to the ZrN phase and very small amounts of metallic Zr, probably embedded in the ZrN globules.

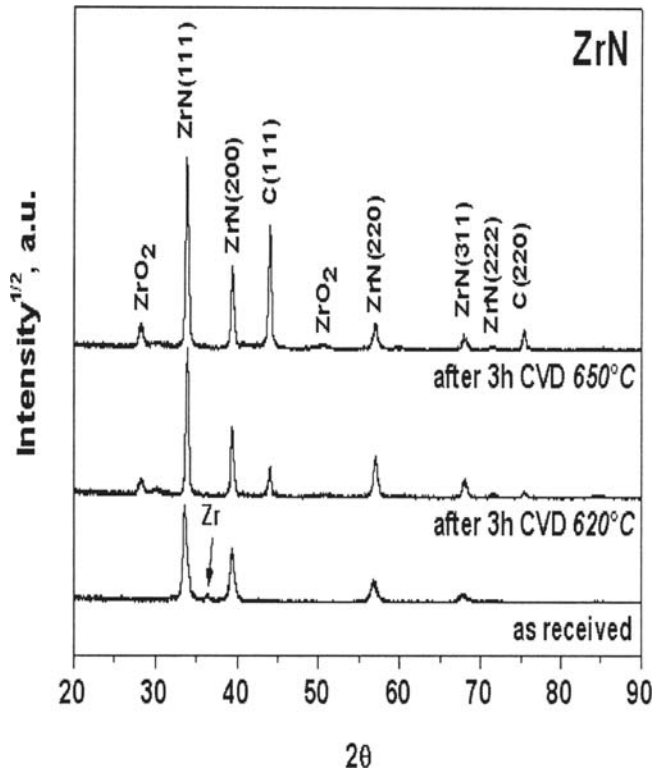


Fig. 7 XRD spectra of ZrN

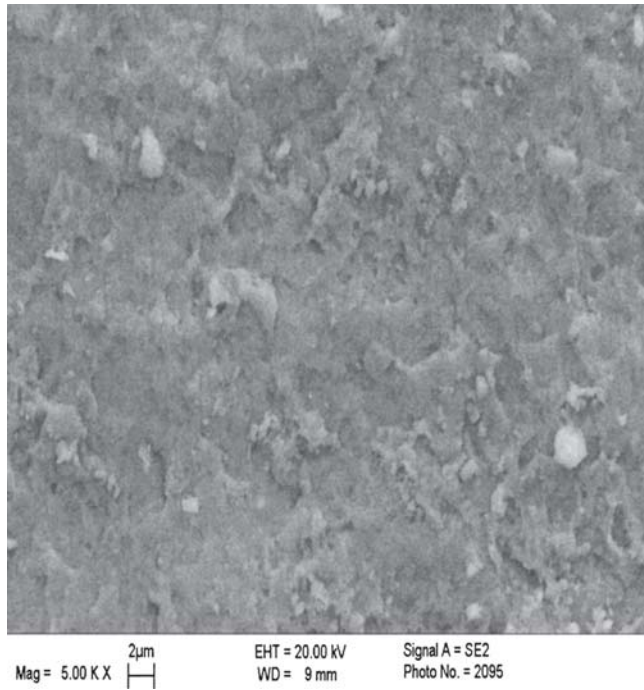


Fig. 8 As-deposited ZrC interlayer

After diamond deposition, the ZrN peaks became sharper due to the high CVD temperature, which induced an increase in ZrN crystallite size. Moreover, after 3 h of CVD, XRD patterns showed the presence of diamond peaks, the disappearance of metallic Zr, and the formation of small monoclinic zirconia (ZrO_2) islands, which were confirmed in repeated CVD experi-

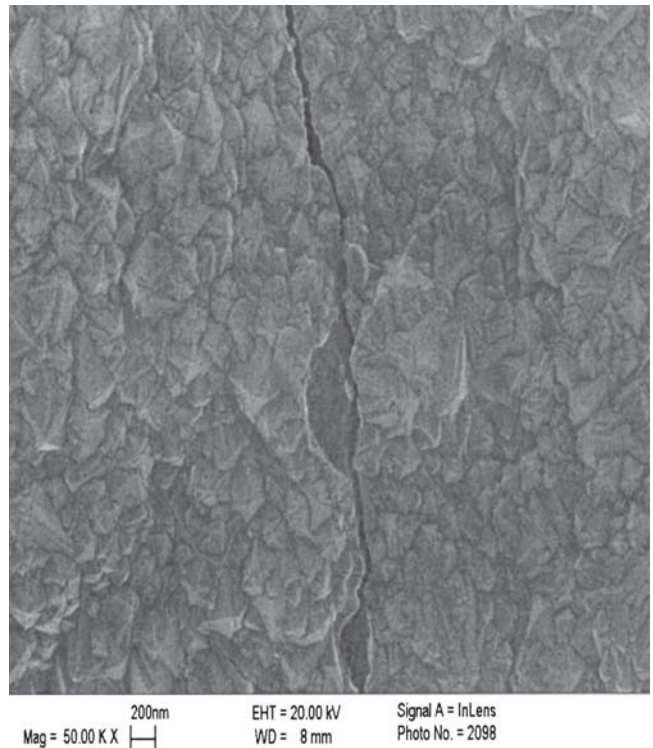


Fig. 9 Diamond film on ZrC

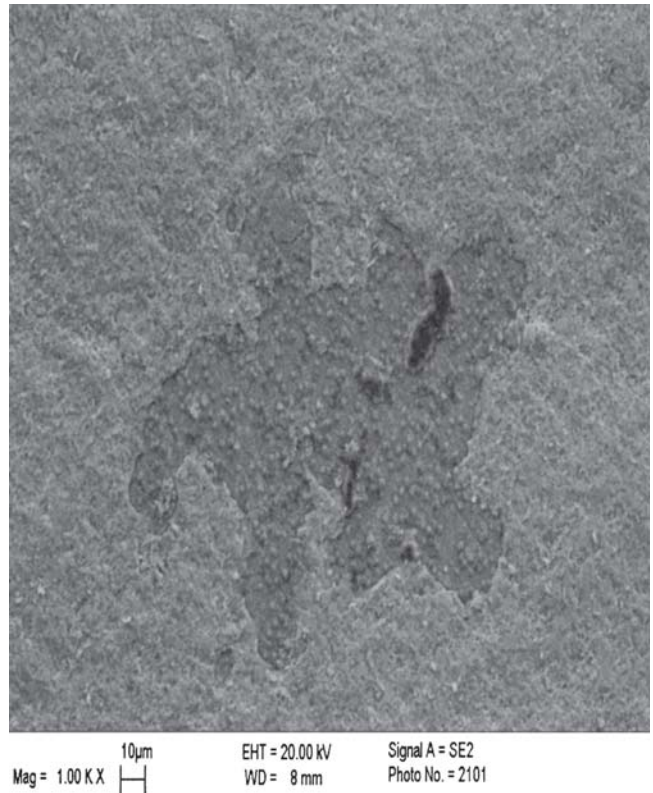


Fig. 10 Diamond film delamination after 3 h

ments using slightly different deposition temperatures. No ZrC peaks were detectable in the diffraction patterns after CVD. Therefore, ZrO_2 formation during CVD occurred by the oxi-

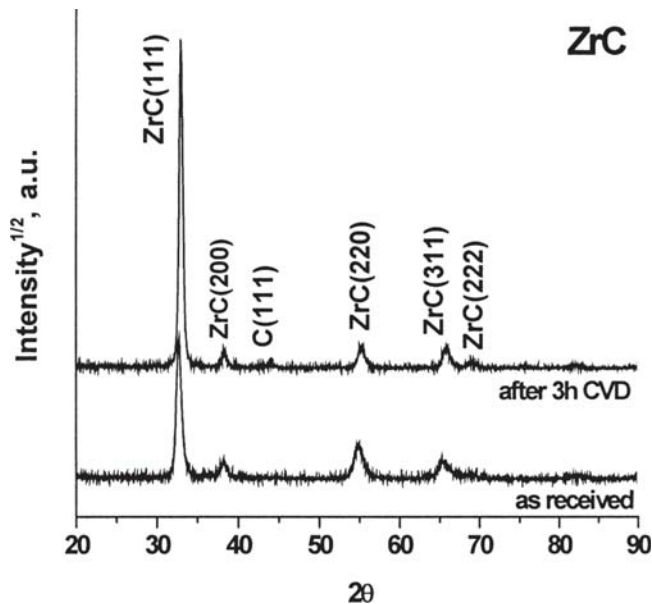


Fig. 11 XRD spectra of ZrC

duction of Zr in the CVD reactor. It was anticipated that the presence of carbide is expected to enhance the nucleation and growth of diamond. Figure 8 shows the SEM micrographs of ZrC film deposited on high-speed steel before diamond deposition and after 3 h of CVD (Fig. 9). After 3 h of deposition, the diamond film underwent spontaneous delamination and only a few small areas remained covered with diamond film, as shown in Fig. 10. The film in these areas was continuous, thus con-

firmed the effectiveness of seeding in promoting nucleation densities as large as those required to obtain a continuous diamond film. Figure 11 shows XRD patterns of the ZrC coating before and after diamond deposition. In the XRD pattern, before deposition only ZrC peaks were present. After 3 h of CVD, the ZrC peaks became slightly sharper, and a low-intensity diamond (111) peak was also detected.

4. Conclusions

The CVD temperatures were around 620 to 650 °C. The rise in temperature produced detrimental effects on the outcome of the films even when the ramp-down procedure was controlled to minimize such effects. The seeding procedure demonstrated that diamond film growth could be aided by the procedure. Further investigations are required to improve the adhesion of these films to the steel substrate.

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