Ultrathin W—Al Dual Interlayer Approach to Depositing Smooth and Adherent Nanocrystalline Diamond Films on Stainless Steel

LETTER

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ABSTRACT The adherence of diamond coated on steel is commonly low and needs to be strengthened with thick intermediate layers. In this paper, a nanoscale W—Al dual metal interlayer has been applied on SS304 substrates to facilitate deposition of continuous, adherent and smooth diamond thin films. During the microwave plasma-enhanced chemical vapor deposition process, the Al inner layer 30 nm thick diffuses into steel surface inhibiting carbon diffusion and graphitization. The W outer layer 20 nm thick is transformed into W carbides, both preventing carbon diffusion and enhancing diamond nucleation. The diamond films synthesized are of high purity and have smooth surfaces and dense structures. Indentation and shear deformation tests indicate high delaminating tolerance of the diamond films.

KEYWORDS: diamond thin film • chemical vapor deposition • steel • adhesion • interlayer

INTRODUCTION

Coating of high-quality diamond thin films on steel substrates has been an attractive research topic because this combines the individual advantages of diamond surface coatings, which are superhard, chemically inert, and wear resistant, with the low cost of steel cores that possess superior mechanical/ physical performances but easily fail prematurely from corrosion-wear surface attack. Despite the huge industrial potentials, practical applications of this technique have been restricted because of difficulties in achieving densely structured and properly adhering diamond coatings on steels, primarily by the transition metal-catalyzed preferential formation of thick graphite prior to diamond nucleation and growth that leads to serious spontaneous spallation of diamond film after CVD fabrication (1–4). The most common method to solve the adhesion problem is using additional intermediate layers to prevent carbon diffusion and graphitization (5, 6). Ideal interlayer materials should offer high diamond nucleation density, matching thermal expansion coefficient, and enhanced interfacial adhesion (7, 8). However, diamond nucleation density/rates on the intermediate layer materials currently in use are not sufficiently high (9), and the involving multi-interfacial adhesion issues (substrate/interlayer, interfacial reaction layer, interlayer/diamond film) for thick interlayer (several micrometers and higher) need to be strengthened (10–12). Ultrathin single interlayer is also associated with problems like insufficient barrier effect for obtaining high-purity diamond (13, 14). Recent findings have indicated that elemental Al has a unique effect on inhibiting graphitization of carbon on transition metals (15–17), whereas the strong carbide-forming element, W, can greatly enhance diamond nucleation, leading to improved surface smoothness (18–20). In this paper, we report on the feasibility of using an ultrathin Al—W dual interlayer for diamond coating on grade 304 stainless steel, a substrate known to be difficult to coat.

EXPERIMENTAL SECTION

The substrate material used for diamond coating was commercial austenitic stainless steel grade 304. The substrates were machined into specimens of 10 mm × 10 mm × 1 mm in size and mechanically polished with 600 # SiC sandpaper, and finally ultrasonically cleaned in acetone and dried for use by flowing N_2. W—Al dual metal interlayer was prepared on SS304 by an ion beam assisted sputtering system. An Al target of 99.99% purity was first sputtered by an Ar ion beam for 1 h, then shifted to a W target of 99.99% purity for 0.5 h sputtering. The entire thickness of the W—Al dual interlayer was about 50 nm, as determined by a profile meter. For comparison, a single W or Al interlayer with a similar thickness 50 nm was also coated

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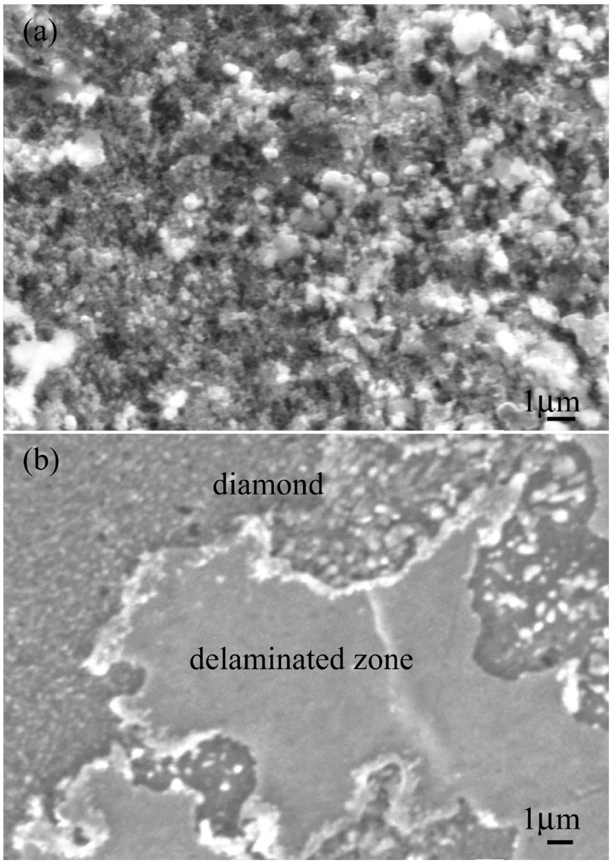

FIGURE 1. SEM images of diamond film grown for 4 h on (a) blank and (b) 50 nm W interlayered SS304 steel substrates.

on steel substrates. The interlayered steel was scratched for 90 s with diamond powder suspension to enhance diamond nucleation. Deposition of diamond was conducted in a 2.45 GHz microwave plasma assisted CVD system (Plasmionique) using H_2 and 1 vol % CH_4 at a total feed rate of 100 sccm, a working pressure of 30 Torr, and substrate temperature approximately 680 °C (4). The morphology and structure were characterized by scanning electron microscopy (SEM, 20 kV, JSM 840 A), micro-Raman (Renishaw 2000, Ar laser wavelength 514 nm), atomic force microscopy (AFM) using a PicoSPM instrument (Molecular Imaging, Tempe, AZ), and glancing incidence X-ray diffraction (GIXRD) employing a Rigaku Geigerflex 2173 rotating anode instrument. A synchrotron near edge extended X-ray absorption fine structure spectroscopy (NEXAFS) was measured on the spherical grating monochromator beamline at the Canadian Light Source (CLS), University of Saskatchewan, to characterize the electronic structure and chemical bonding of the diamond films synthesized. The diamond film adhesion properties were evaluated by Rowell C indentation test using a load as high as 1470 N and mechanical bending deformation test on a cutting machine (2, 14).

RESULTS

Direct coating of highly adherent diamond thin films on SS304 substrates is technologically impossible due to the preferential formation of loose graphite intermediate layer on the steel surface, as illustrated in Figure 1a. The surface reaction products are primarily a graphitic carbon matrix embedded with sparsely distributed diamond particles. Only after a long incubation period does diamond film formation commence on the top of the loose graphite soot, inducing spontaneous delamination of diamond films after deposition. Use of a single Al interlayer can facilitate diamond nucleation and ahdesion, but can not guarantee a smooth and uniform diamond film. In addition, the diamond films produced with a single W interlayer of similar thickness tend to delaminate locally (Figure 1b). However, the use of a W−Al duel interlayer has markedly improved the diamond growth process.

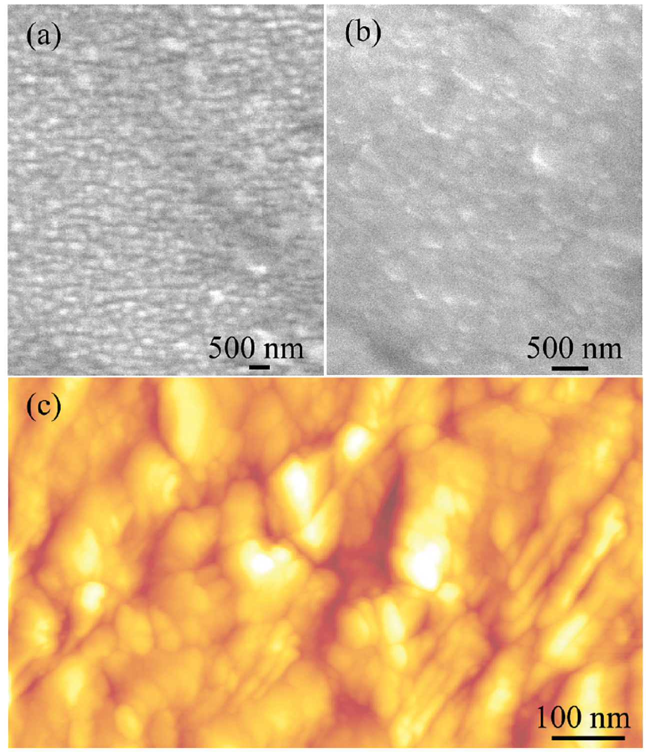

FIGURE 2. (a, b) SEM and (c) AFM images of diamond thin film grown for (a) 4 and (b, c) 7 h on 50 nm W−Al interlayered steel substrate.

Figure 2 shows the surface morphologies of diamond grown on SS304 precoated with a 50 nm thick W−Al interlayer. The diamond exhibits a high nucleation density rate and after 4 h deposition (Figure 2a), tiny diamond particles have coalesced and covered the whole surface of steel substrate. After 7 h (Figure 2b), a continuous diamond film forms and exhibits much denser structures while no local spallation occurs. A closer observation by AFM (Figure 2c) shows the average sizes of the diamond crystallites are primarily in the range of several tens to hundred of nanometers, and a root-mean-square surface roughness of the film is determined to be 16.5 nm over a 2 μm × 2 μm AFM scan area. The smooth surface and densely packed structure of the diamond films are very useful for tribological applications considering their low friction coefficient.

Figure 3 shows the Raman spectrum, synchrotron C k-edge NEXAFS spectrum recorded in total electron yield (TEY), and GIXRD patterns of the diamond film grown on W−Al interlayered steel, respectively. Only one diamond

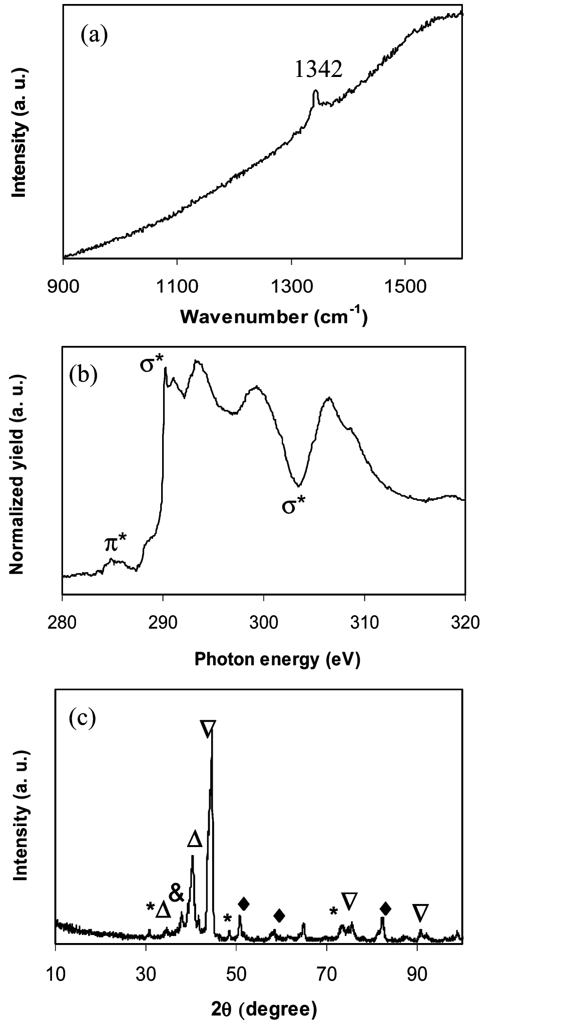

FIGURE 3. (a) Raman spectrum, (b) TEY NEXAFS spectrum, and (c) GIXRD patterns (▽ Diamond, ◆ Fe_3Al_5, Δ W, * WC, & W_2C) of diamond film grown for 7 h on 50 nm W−Al interlayered steel substrate.

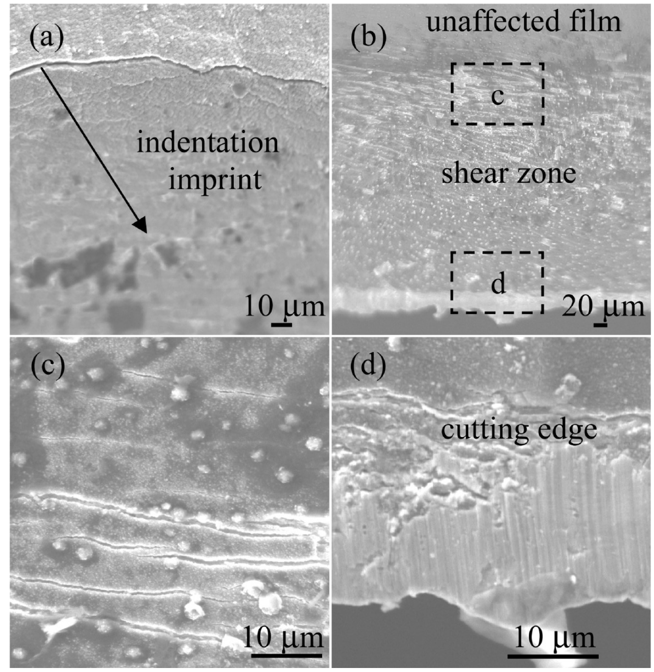

FIGURE 4. SEM surface images of diamond grown for 7 h on 50 nm W−Al interlayered steel: (a) after 1470 N Rockwell C indentation test; (b) general view after cutting of diamond-coated steel sheet; (c) magnified view of shear deformation zone; and (d) magnified view of cutting edge. No significant film spallation occurs after applying above high mechanical loads.

characteristic peak centered at 1342 cm^{-1} appears in the spectrum (Figure 3a) along with high background intensity caused by fluorescence. The upward shift of the peak position from standard diamond at 1332 cm^{-1}, is attributed to a compressive stress accumulation in the film, and it is a sign of good adhesion of the film to the substrate (21). In fact, once the diamond film delaminates from the substrate, the diamond peak measured from the free-standing films is located at 1332 cm^{-1} again because of stress release after debonding.

The significant broadening of the peak can be caused by both the compressive stress and the refinement of the diamond grain size in a nanoscale, while the absence of any obvious graphitic peaks indicates the high purity of the diamond film synthesized. This is further confirmed by carbon K-edge synchrotron NEXAFS spectrum (Figure 3b). The spectrum demonstrates a sharp absorption edge at 289.7 eV and a huge dip at 303.2 eV, corresponding to featured σ bonding of pure diamond. The nondiamond carbon peak at 285.8 eV associated with sp^2-structured π bonding is very weak in the spectrum. The XRD result in Figure 3c reveals that besides the dominant diamond, Fe−Al intermetallics and W carbide phases also emerge. This means that during the CVD process, the Al interlayer has diffused inward and formed FeAl compounds near the surface of steel, while W is partially carburized and diamond should have grown on the W carbide layers. The bonding ability of the diamond film to the steel is evaluated by Rockwell C indentation test with a high load of 1470 N (Figure 4a). No obvious delamination or cracking of the diamond films is observed around the imprint. The diamond film-coated steel plate is also sheared with a metal cutting machine. An approximately 21° bending deformation of substrate occurs along the cutting edges (Figure 4b), and the diamond film coated is accordingly subjected to a huge shear stress. Even so, no large area film spallation is induced. Although lateral cracks appear within the film in the shear zone (Figure 4c), the diamond film still sticks well to the substrate at the cutting edge (Figure 4d). These results confirm that the diamond film coated on steel possesses high adhesion strength.

DISCUSSION

These results indicate that the application of an Al and W dual interlayer, even with an ultrathin total thickness, has markedly enhanced diamond nucleation, adhesion, and surface quality. On the one hand, the beneficial role Al plays is closely associated with its diffusion into the steel and forms an Al-rich surface layer (22). The catalytic effect of iron favoring graphite formation can be greatly inhibited after Al modification, as has been verified from a series of related work (15−17). Due to the effective prevention of detrimental graphite formation at diamond film-steel interface, adhesion

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ability of diamond films to steel substrate is improved. On the other hand, W and carbon have a strong affinity and the top surface of W can be quickly carburized upon exposure to CVD atmosphere. As diffusivity of carbon in W carbides and metals is very low (23), transport of carbon through the carbide layer is insignificant and carbon is primarily accumulated on the carbide surface, facilitating carbon supersaturation and diamond nucleation (19, 20, 24). The enhanced diamond nucleation density and formation of thin W carbide transition layer provide higher contact area and chemical bonding between the diamond film and interlayer. As a result, the interface adhesion and surface smoothness are both greatly improved. It should be noted that for a single metal, W or Al, such an ultrathin interlayer can produce only discontinuous and less adherent diamond films on steel.

CONCLUSION

In summary, a W−Al ultrathin interlayer combination with a total thickness of 50 nm has produced promising synergic effect on enhancing diamond nucleation, adhesion, and surface smoothness when grown on stainless steel substrates. These improvements can be attributed to the inward diffusion of Al to form Fe−Al compounds, inhibiting graphitization and substrate metal diffusion, whereas surface carburization of W facilitating diamond nucleation and providing stronger chemically bonded interfaces.

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