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Finestructures study of the diamond/titanium interface by transmission electron microscopy

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HIGHLIGHTS

- The diamond/Ti6Al4V interfacial finestructures have been investigated by HRTEM.
- A thin layer composed of many crystalline $TiC_{1-x}O_x$ nanoparticles is first identified.
- The $TiC_{1-x}O_x$ phase has a similar structure to cubic TiC.
- In $TiC_{1-x}O_x$, C atoms and O atoms randomly occupy the vacancies of C in TiC.
- The $TiC_{1-x}O_x$ layer maintains the thickness of 20–30 nm as increasing deposition time.

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ABSTRACT

It is well known that a TiC layer can be formed and should act as a buffer layer in diamond films deposited on Ti alloy. Through our cross-sectional investigation in HRTEM, a thin layer (20–30 nm) was first identified between the outermost diamond film and the inner reactive TiC layer adjacent to the substrate. This layer consists of numerous crystalline nanoparticles with grain sizes of 5–20 nm. Through electron nanodiffraction patterns combined with EDS and EELS analysis, these nanoparticles can be identified as a $TiC_{1-x}O_x$ phase with a similar structure to cubic TiC. Besides, C atoms and O atoms in $TiC_{1-x}O_x$ randomly occupy the vacancies of C in TiC. The thickness of this $TiC_{1-x}O_x$ layer does not change significantly with increasing deposition time, and the diamond phase directly nucleates and grows on it.

1. Introduction

Diamond films have attracted considerable scientific and industrial interests because of their excellent properties such as extreme hardness, stiffness and wear/corrosion resistance. Considerable efforts have been made to produce CVD diamond films on Ti alloy substrates to improve their surface properties [1–4], as the poor friction behavior and weak wear resistance limit the extended applications of titanium and its alloys. A key issue in the synthesis of diamond onto metallic substrates is the formation of intermediate layers at the diamond film/substrate interface. Titanium can easily react with C to form stable carbides, and the carbide (TiC) layer grown between titanium substrate and diamond film has been already sufficiently studied in previous studies [5–8]. However, the other phases and their relative locations inside the reaction layer are still not clear. Detailed investigations of the interfacial structure are very important because the adhesion properties of diamond deposited on Ti alloy are strongly dependent on the interface.

Up to now, some detailed structural investigations of the diamond/titanium interface were achieved by X-ray photoelectron spectroscopy (XPS). Perry et al. [9] identified the presence of amorphous titanium oxide on the fractured Ti/diamond interfaces. But the surface contamination caused by the adsorption of oxygen could not be avoided [10] after the interfacial fracture. Therefore, it was difficult to say whether the oxide was originally formed

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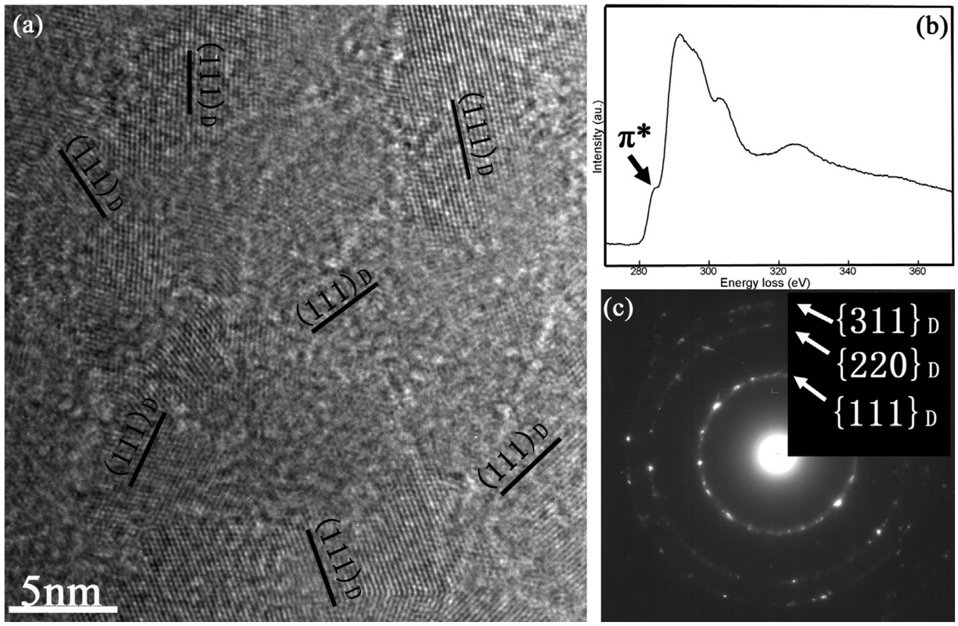

Fig. 1. (a) A cross-sectional HRTEM image of the diamond film formed on Ti6Al4V substrate, (b) the core-loss EELS spectra and (c) the SAED pattern of the film. All of these proved an ultrananocystalline diamond film was formed under pure CH_4 atmosphere.

during the deposition or not. Furthermore this was also contradictive to Vandenbulcke's result [11] that there was no oxygen in the whole interfacial region (also by XPS). Meanwhile, by using the reflection high-energy electron diffraction (RHEED) technique, Terranova et al. [12] analyzed the diamond/titanium interface and identified only a mix phase of titanium carbide/titanium hydride/graphite.

Transmission electron microscope (TEM) has the advantage of giving direct images about the interface. However, the TEM studies were very limited and most were only focused on the microstructures of the film [8,13], may be due to the difficulty of the preparation of the cross-sectional TEM samples. Therefore, detailed structural investigations of the diamond/titanium interface by TEM are very imperative. In this work, by the preparation of cross-sectional specimens for TEM observation, the finestructures of the interface between Ti alloy substrate and diamond film have been investigated in HRTEM combined with EDS and EELS analysis.

2. Experimental

The material used for this study was diamond films grown on Ti6Al4V alloy substrate by microwave plasma enhanced chemical vapor deposition (MPCVD), with extremely high methane concentration (100% CH_4) and at a moderate temperature of approximately 500 °C in our previous work [14]. The deposition time was 1.5 h, 3 h, 8 h and 15 h, respectively. Detailed deposition process was described elsewhere [14].

Cross-sectional specimens for TEM observations were prepared by conventional method, i.e., by cutting, gluing, then grinding with silicon carbide paper to about 15 μm, and finally ion-milling by Ar^+ from both sides until some perforation occurred. A Tecnai G^2 F30 transmission electron microscope, equipped with a high-angle angular-dark-field (HAADF) detector, X-ray energy-dispersive spectrometer (EDS) systems and a post-column Gatan imaging filter (GIF 2000), was used for electron diffraction analysis, high-resolution transmission electron microscopy (HRTEM) observation and chemical composition analysis.

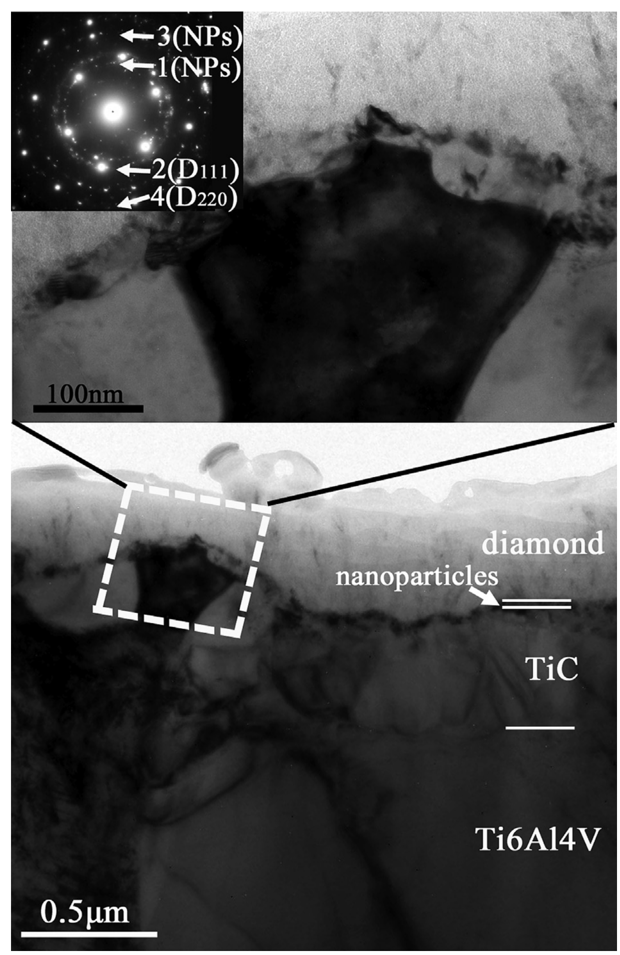

Fig. 2. Typical interfacial finestructures between Ti6Al4V substrate and diamond film (deposition for 3 h). The bright-filed (BF) image showing a thin layer composed of many nanoparticles exists between the diamond film and the TiC layer; the inset is the SAED pattern from the white square indicated interface, reveals that the nanoparticles are randomly oriented.