



Strain-induced ordered structure of titanium carbide during depositing diamond on Ti alloy substrate

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ABSTRACT

During the deposition of diamond films on Ti alloy substrates, titanium carbide is a common precipitated phase, preferentially formed at the interfacial region. However, in this case, the precipitation of an ordered structure of titanium carbide has not been reported. In our work, a long periodic ordered structure of TiC has been observed at the deposited diamond film/Ti alloy interface by high resolution transmission electron microscopy (HRTEM). The long periodic ordered structure is identified as 6H-type. The formation mechanism is revealed by comparative studies on the different structures of TiC precipitated under different diamond deposition conditions in terms of deposition time, atmosphere and temperature. A large number of carbon vacancies in the interfacial precipitated TiC phase are verified through electron energy loss spectroscopy (EELS) quantification analysis. However, an ordered arrangement of these carbon vacancies occurs only when the interfacial stress is large enough to induce the precipitation of 6H-type TiC. The supplementary analysis by X-ray diffraction (XRD) further confirms that additional diffraction peaks presented in the XRD patterns are corresponding to the precipitation of 6H-type TiC.

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1. Introduction

The structure of titanium carbide has been extensively investigated in the past due to its wide applications in technology and industry [1]. A well-known cubic face-centered lattice of NaCl-type structure (space group $Fm-3m$) is the basic structure of titanium carbide. Furthermore, depending on the levels of ordered arrangement of vacancies in the carbon sublattice under certain conditions, titanium carbide may exhibit non-stoichiometry (represented as TiC_x) and various ordered structures would be formed. Recently, these kinds of non-stoichiometric titanium carbide have demonstrated functional properties in hydrogen storage [2–4], and the related studies on the structure-property relationships of TiC_x -materials gains increasing scientific interest.

Since the early 1970's, the structures of the non-stoichiometric TiC_x formed due to carbon vacancies ordering have been studied by many techniques, such as X-ray diffraction, neutron diffraction and electron diffraction [5–13]. Several phases have been identified which are strongly associated with the specific arrangement of the carbon vacancies. When the carbon vacancies are randomly distributed, the structure of TiC_x remains a cubic NaCl-type structure, with the $Fm-3m$ space group. When the carbon vacancies are orderly distributed, two ordered

phases can be formed in titanium carbide. One is a trigonal ordered structure, with the $R-3m$ space group, and the other is a cubic ordered structure, with the $Fd-3m$ space group [12,13].

In most cases, the non-stoichiometric TiC_x samples used for structure study were obtained by reactive sintering of appropriate powder mixtures of $TiC_{1.0}$ and titanium metal in vacuum or in a pure argon atmosphere. Then a following key step of post annealing treatment in the temperature region of 770 K–1070 K for a certain period of time was indispensable for the ordered arrangement of carbon vacancies in these samples [2,9,14]. That is because the activation of the migration of carbon vacancies needs a high temperature because of the diffusion barrier of 3.46 eV [15], whereas a long-range order of the carbon vacancies is more favorable in thermodynamics. Besides, Xiang et al. [16] reported that the ordered carbon vacancies can be realized by high-energy ball milling of Ti powders in toluene, when they synthesized the non-stoichiometric TiC_x sample through spark plasma sintering method.

Apart from the ordered structures induced by the ordered arrangement of carbon vacancies, Dzhabaladze et al. [17] reported the ordered structure of titanium carbide caused by microplastic deformation. In their work, a 6H-type of titanium carbide was formed on the surface layers during grinding and polishing of titanium carbide. They suggested that the creation of packing defects and their ordering by microplastic deformation were the formation mechanism for the 6H-type ordered structure of titanium carbide.

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Table 1

The deposition information of samples with diamond films deposited on Ti alloy substrates.

Samples	Deposition temperature	Deposition gas	Diamond film thickness
#1	750 °C	1% CH ₄ /H ₂	~2 μm
#2	500 °C	100% CH ₄	~2 μm
#3	500 °C	100% CH ₄	~7.5 μm

During chemical vapor deposition of diamond films on pure Ti or Ti alloys, a titanium carbide intermediate layer is preferentially formed between the diamond films and the substrate, which plays an important role in enhancing diamond nucleation density and interfacial adhesion. However, the ordered structure of such titanium carbide has not been thoroughly studied so far [18–23]. In the literature, little research focused on the structure of these interfacial titanium carbides, especially its connection with the deposition parameters. In our work, the ordered structure of titanium carbide precipitated at the diamond film/Ti alloy substrate interface is observed. High resolution transmission electron microscopy (HRTEM) is employed to investigate these different precipitated types of titanium carbide. We found that, depending on the specific deposition parameters in terms of deposition time, atmosphere and temperature, the TiC that precipitates at the interfacial region has different structures. In addition to the NaCl-type TiC, 6H-type ordered structure of TiC is identified. Especially, a large number of carbon vacancies are identified in the interfacial precipitated TiC by EELS quantification. The comparative studies on the samples prepared under different deposition parameters reveal that the precipitation of interfacial ordered TiC is closely associated with the interfacial stress which leads to the ordered arrangement of carbon vacancies. Furthermore, the precipitated mechanism of the ordered structure of titanium carbide is clarified.

2. Material and Methods

The materials used in this study were diamond-coated Ti6Al4V alloy substrates after treatment by microwave plasma enhanced chemical vapor deposition (MPCVD). Diamond film deposition was conducted in a 2.45 GHz microwave plasma enhanced CVD system (Plasmionique) at a working pressure of 30 Torr. A thermocouple mounted underneath a stainless steel substrate holder was used to measure the temperature. The deposition conditions studied were the deposition atmosphere, the temperature and the time, as listed in Table 1. Under all circumstances, a TiC intermediate layer preferentially precipitated at the interfacial region between the diamond film and the Ti6Al4V substrate, and the fine structure of this TiC layer will be thoroughly investigated.

The general morphologies of the deposited samples were observed by scanning electron microscope (SEM). A Rigaku X-ray diffraction (XRD) with Cu K $\alpha_{1,2}$ radiation was used for x-ray analysis. Cross-

sectional specimens for TEM observations were prepared by conventional method, i.e., by cutting, gluing, and grinding with silicon carbide paper, then dimpling to about 15 μm, and finally ion-milling by Ar⁺ from both sides until some perforation occurred. A Tecnai G2 F20 transmission electron microscope was used at 200 kV for electron diffraction analysis and high-resolution transmission electron microscopy (HRTEM) observation. A Tecnai G2 F30 transmission electron microscope, equipped with a postcolumn Gatan imaging filter (GIF 2000), was used for chemical composition analysis. The microscope was operated with an electron acceleration voltage of 300 kV, a convergence angle of 5 mrad and a collection angle of 11 mrad. The probe size for electron energy loss spectroscopy (EELS) was approximately 5 nm. The Gatan Digital Micrograph software was used for the quantitative analysis of EELS data.

3. Results and Discussion

In the plasma activated CH₄-H₂ atmosphere, a relatively high carbon potential exists and due to the strong reactivity of elemental titanium with carbon, a titanium carbide intermediate layer can form preferentially on the alloy surface. This in-situ formed carbide layer plays an important role in the diamond nucleation density and interfacial adhesion. Fig. 1 shows general SEM images of such double-layered coating structure, which indicates that the delamination of the diamond film from the substrate may occur either at the diamond-carbide interface or at the carbide-substrate interface.

A unique TiC structure is observed during the study of the titanium carbide layer precipitated along diamond film/Ti alloy interface when the diamond film is deposited with 1% CH₄/H₂ mixture gas at about 750 °C, as shown in Fig. 2. In the following discussion, this sample is labeled as #1 sample. Fig. 2a is a typical morphology of TiC layer precipitated at the interfacial region, with the diamond film thickness being about 2 μm. The precipitated TiC layer presents an elongated morphology along the interface. The corresponding selected-area electron diffraction (SAED) pattern taken from the TiC layer is presented in Fig. 2b. Besides the regularly strong white spots belonging to the [1–10] zone axis of cubic TiC, additional reflection spots are observed. These additional weak spots locate at the positions of n/6 (where n is an integer) of the (111)_{TiC} diffraction. The corresponding HRTEM image of the TiC layer is shown in Fig. 2c, viewed along the [1–10] zone axis of cubic TiC. There are apparent elongated defects identified in the HRTEM image, whose elongated direction is consistent with the elongated direction of the TiC layer. In the direction perpendicular to these elongated defects, as marked by the white arrow in Fig. 2c, a long period ordered structure appears. The width of the long period ordered structure is about 1.49 nm, which contains six (111)-plane of the cubic TiC, indicating that the long period ordered structure of TiC is 6H-type. This 6H-type TiC precipitated in the interfacial region during the

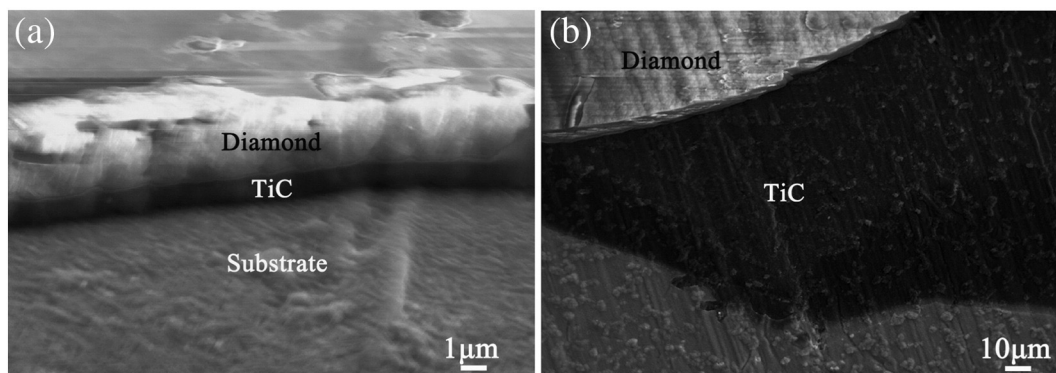


Fig. 1. Cross-sectional (a) and surface (b) SEM images of diamond films deposited on Ti alloy substrates, showing the formation of an intermediate layer of TiC.

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