

Nucleation and Growth Microstructural Study of Ti Films on 304 SS Substrates

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Coating of steel surfaces with titanium films has been studied with the objective to protect them against corrosion, and to create an intermediate film for CVD diamond and TiN film deposition. In this work, the nucleation, growth mechanisms and microstructural formation of the titanium films deposited on 304 stainless steel (304 SS) substrate are presented and discussed. The titanium films of variable thickness were obtained by vapour phase deposition produced by electron beam. The surfaces of these samples were observed by scanning electron microscopy. The cross sections of these samples were observed by using an atomic force microscope. The Ti film-304 SS interfaces were analyzed by X-ray diffraction. The results showed that titanium films have a columnar growth. The Ti film-304 SS interface had a residual compression stress at room temperature due to the inter-diffusion process.

Keywords: *Ti film nucleation and growth, microstructural study, electron beam*

1. Introduction

Steel materials with modified surfaces are widely used in a large variety of important technological applications including cutting tools, machine components and molding dies, where their surfaces can be submitted to physical and/or chemical erosion¹⁻³. Therefore, adequate coatings that are well bonded on steel surfaces are desirable in such applications to enhance the mechanical performance and to increase the lifetime against abrasion and corrosion. As a consequence of surface smoothness, hardness and chemical inertness, the use of diamond polycrystalline films as protective coatings for steel materials is highly desirable and technologically relevant. However, nucleation of the diamond phase is extremely difficult on these material surfaces mainly because of the high diffusivity of carbon ions into steel substrates at temperature used to obtain CVD diamonds, which consumes the carbon species needed for nucleation of diamond phase⁴⁻⁷. In order to enhance nucleation density, the growth of polycrystalline diamond films and the adhesion of these coatings on steel, the creation of a carbon diffusion barrier near or on the surface of the substrate is required. This barrier can be obtained by using an intermediary layer of a material that has a low diffusion coefficient for carbon, such as a thin deposited

film or a surface modified by ion implantation^{1,4,8-10}. On the other hand, polycrystalline CVD diamond films have a good adhesion on titanium surfaces^{7,9,11-14}.

Titanium nitride (TiN) has been widely employed in cutting tools to extend their working life and in decorations for its golden color. As a protective coating, TiN layers have been studied extensively^{15,16}. TiN films have been particularly attractive due to their potential applications ranging from hard and corrosion-resistant films to diffusion barrier layers in advanced integrated-circuit devices¹⁷. Studies on the TiN properties have solved significant problems, such as the reduction of the usefulness of the TiN films for corrosion-resistant films and for diffusion barriers in the films¹⁵⁻¹⁸. However, the adherence of TiN films on steel substrate is not well known yet. Nowadays, many studies are focused on the deposition of adherent diamond coatings and TiN films on steel materials to improve their wear and corrosion resistance^{4-7,9,10,16,19}.

The purpose of this research work is to investigate the titanium film evolution and Ti film-304 SS substrate interface during the coating processing. The adherence of titanium films on steel substrate has been demonstrating good adherence results²⁰. The variations of the topographic and

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structural phase have been investigated using a scanning electron microscopy (SEM), an atomic force microscope (AFM) and an X-ray diffraction (XRD). The titanium films were deposited by electron beam device.

2. Experimental details

In preparation for titanium nucleation and growth, 304 SS substrates of 15 mm diameter and 3 mm thick were mechanically ground with abrasive papers, polished with 1 μm alumina, and ultrasonically cleaned in an acetone bath before being put in the evaporation chamber.

Deposition of titanium film on 304 SS substrate was carried out by electron beam evaporation device. The films were deposited at an incident angle of approximately 87° . The vapour source subtended an angular spread of 3° due to the substrate-source separation of 42 cm and the melt diameters of approximately 2 cm. The accelerating voltage and the electron beam current were 4keV and 150 mA, respectively. After the samples chamber was evacuated to 6.75×10^{-7} Torr, the deposition was done at a substrate temperature of 200°C by using a halogen lamp. The polished substrates were heated at 200°C for 5 min in vacuum to remove adsorption gases on the surfaces before deposition. During titanium nucleation and growth, the base pressure was hold at less than $(1.5\text{-}2.25) \times 10^{-6}$ Torr. Under these conditions, the substrate temperature was about 200°C , which was reached without additional heating. The deposition temperature was measured by a thermocouple, embedded 1.0 mm below the deposition surface. A quartz crystal thickness monitor (CTM) was used to maintain a nominal deposition rate of 2 \AA/s . Due to the substrate location and orientation, the film growth rate normal to the substrates surface was approximately 1 \AA/s that was recorded by the CTM. This electron beam provided a controlled stepper motor that rotated the substrates. To evaluate the nucleation and the growth of titanium films on 304 SS substrate, titanium was deposited on three growth thickness: 0.5 μm , 1.5 μm and 3.0 μm . In order to obtain samples of the films at incremental stages of growth, the deposition was periodically paused, the substrates were allowed to cool slowly to room temperature and then the system was vented with dry N_2 , and portions of the substrates removed for later analysis.

The surface morphology of the deposited films were investigated by scanning electron microscopy (SEM), JEOL model JSM-5310a, attached to an energy dispersive spectrometry (EDS). The study of the crystalline structure of the samples before and after titanium films deposition was obtained by X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation 40 kV / 20 mA. Using the wavelength of $\text{Cu K}\alpha$ the 2θ interval was chosen from 30° up to 90° with a step size of 0.02° . The cross-section of the Ti film-304 SS substrate system was observed by atomic force microscopy.



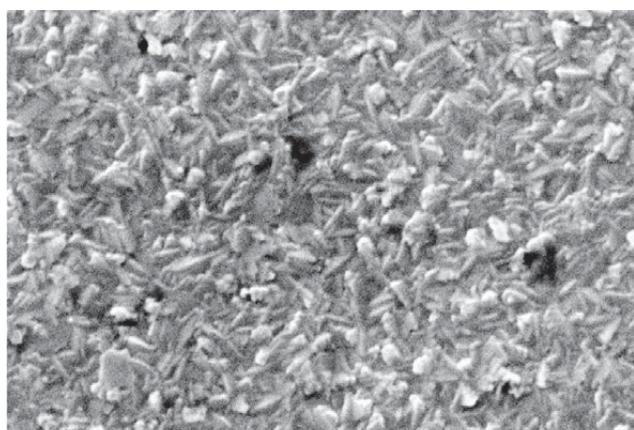
EHT=20.00 KV 300 nm I-I Mag= 35.00 K X 14:03 3-Jul-2002
WD = 8 mm Detector = SeI INPE/LIT

(a)



EHT=20.00 KV 300 nm I-I Mag= 35.00 K X 14:52 26-Jun-2002
WD = 6 mm Detector = SeI INPE/LIT

(b)



EHT=20.00 KV 300 nm I-I Mag= 35.00 K X 14:25 26-Jun-2002
WD = 6 mm Detector = SeI INPE/LIT

(c)

Figure 1. Surface morphology of the nucleation and growth titanium films on 304 SS substrates with different deposition thickness: a) 0.5 μm ; b) 1.5 μm ; c) 3.0 μm .

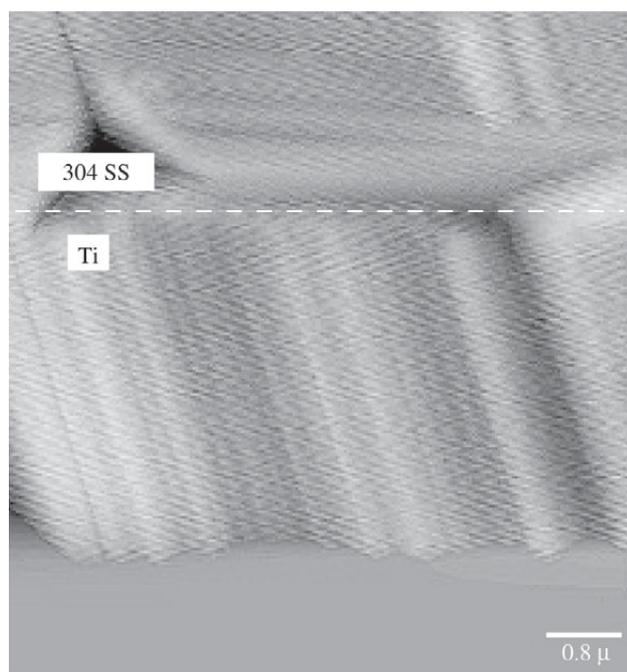


Figure 2. An AFM image of the cross-section observation of the microstructure of titanium film deposited on 304 SS substrate by electron beam evaporation indicating a columnar growth.

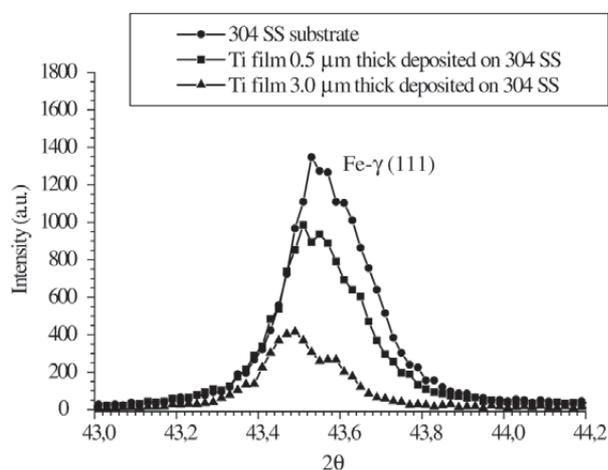


Figure 3. XRD patterns for the 304 SS surface without film and titanium films deposited with 0.5 μm and 3.0 μm thick by electron beam on 304 SS substrate.

3. Results and discussion

Figure 1a, b and c shows the surface morphology of the titanium nucleation and the growth with different deposition thickness from 0.5 μm to 3.0 μm . Results showed that after approximately 0.5 μm thick, it can not be observed titanium nucleus on 304 SS substrate as shown in Fig. 1a. Titanium nucleation started on 304 SS substrate after depo-

sition for about 1.5 μm thick as shown in Fig. 1b. After approximately 3 μm thick, it can be observed that many titanium crystal clusters were observed on the surface. This shows a heterogeneous microstructure formed by several crystal sizes. As can be seen in Fig. 2, in the cross-section of the Ti film-304 SS system, the Ti film has a columnar growth. These microstructures differences between the film surface and its cross-section result in different mechanical behavior.

XRD peaks from the Fe- γ phase (111), (200) and (220) of the 304 SS substrate without film and Ti film-304 SS substrate systems are observed. A detailed analysis of X-ray diffractograms of 304 SS surface without film and titanium films grown with 0.5 μm and 3.0 μm thick on 304 SS surface shows some differences in the peak positions and the peak intensity. This can be seen in Fig. 3, where the Fe- γ (111) peaks for the 304 SS substrate and Ti film-304 SS systems are presented. It can be observed that with the increase of the deposition thickness, the peak of Fe- γ (111) decrease in 2θ indicating the diffusion of titanium atoms into the 304 SS substrate. The shifting in the peak positions reveals the presence of stress in the modified 304 SS surface by titanium film. As shown in²⁰, this stress state is a result of the atomic solid solution presents at the Ti film-304 SS substrate interface.

4. Conclusions

The titanium films deposited on stainless steel substrates have been studied as intermediate layer for the TiN and diamond films grown in steel materials. Only after deposition for about 1.5 μm thickness titanium nucleation started on 304 SS substrate surface. The X-ray diffraction results showed that titanium films grown on the 304 SS substrate by using the electron beam device revealed the presence of stress. This was related to the compression stress due to atomic solid solution presents at the interface²⁰. This residual compression stress is formed as a result of the inter-diffusion process, that is, Ti atoms are present in the steel microstructure and Fe, Cr and Ni atoms are present in the Ti film.

These results suggest that a titanium film growth on a stainless steel substrate by using the electron beam evaporation device has potential applications as interlayer to promote better adherence of TiN and diamond films on steel materials.

Acknowledgements

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