Microstructure and Mechanical Properties of TiN/TiCN/TiC Multilayer Thin Films Deposited by Magnetron Sputtering

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Abstract:

Enhancement of mechanical properties by using TiN/TiCN/TiC multilayer thin films deposited on commercially pure cast Titanium (CP-Ti), Ti6Al4V and silicon (Si) substrates via magnetron sputtering technique was investigated in this study. The structural, chemical and mechanical properties of the coatings were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), nanoindentation and scratch test. Results of the XRD analysis showed reflections corresponded to FCC (1 1 1) cubic and polycrystalline structure for TiN/TiCN/TiC films. XPS analysis revealed formation of titanium nitride, titanium carbonitride and titanium carbide in the coatings. According to SEM images, the coatings demonstrated dense cross-sectional morphology and columnar structure as well as good adhesion to the substrate with a thickness of 1.77 µm deposited on silicon (1 0 0). Scratch and nanoindentation test results showed the best mechanical behavior for the coated Ti6Al4V substrate material with the 19.96 GPa hardness and 25 N critical load values, because of its higher hardness and toughness of substrate in compared to Cp-Ti substrate.

Keywords: Magnetron sputtering; TiN/TiCN/TiC film; Cp-Ti; Ti6Al4V; Adhesion; Scratch; Nanoindentation doi:10.20944/preprints201807.0160.v1

1. Introduction

Titanium and its alloys because of their low density and elastic modulus, high corrosion resistance, biocompatibility and long fatigue life are widely used in spacecraft, automotive, dentistry, orthopedic field and medical industry [1, 2]. Various deposition techniques such as chemical vapor deposition (CVD) [3], plasma enhanced chemical vapor deposition (PECVD) [4], magnetron sputtering [5], and thermal spraying [6, 7] have been used to deposition of TiCN coatings.

Hard coatings such as TiN, CrN, ZrN, WC, WC–Co, WC–Ni, ZrCN and TiCN coatings as a first generation of single layer played an important role due to their higher hardness and toughness and also lower friction coefficient compared to high-speed steel and cemented carbide [8]. TiCN and ZrCN coatings are known as protective coating materials which have specifically been used because of their high melting point, extreme hardness, and high thermal conductivity [9, 10].

TiN films are commercially important due to their high hardness, high thermal, chemical stability and wear resistance [11-13]. As a hard ceramic material, TiN films usually are deposited on Titanium, steel and aluminum substrate materials. The TiN coatings are useful in some applications such as cutting tools and load bearing parts [14]. TiCN films also exhibits excellent wear resistance, high hardness and good corrosion resistance. These properties along with non-cytotoxic character make TiCN films ideal for biomedical applications [15].TiN/TiCN multilayer coatings are expected to show higher hardness and wear resistance in compared with TiN and TiCN thin films. Su and Kao [16] showed that TiN/TiCN multilayer thin films have excellent mechanical properties, superior chemical stability, good wear and corrosion resistance. The aim of this work is to investigate microstructure and mechanical properties of TiN/TiCN/TiC multilayer thin films deposited on silicon CP-Ti and Ti6Al4V substrates by magnetron sputtering technique.

2. Experimental Details

CP-Ti (grade 4) and Ti6Al4V (grade 5) with 0.02 μm surface roughness were used as substrate materials. These samples were cut in 25×25×3 dimensions by using abrasive water jet method. Chemical composition of samples is given in Table 1. Samples were ultrasonically cleaned with acetone and ethanol, respectively. TiN/TiCN/TiC multilayered films were deposited on silicon (1 0 0), CP-Ti and Ti6Al4V substrates by using a DC closed field unbalanced magnetron sputtering system produced by Teer Coatings Ltd (plasmag-550). The placement of magnetrons and targets in coating device is given in Figure 1.

Two Titanium targets with 10 cm of diameter and a purity at 99.9% for both targets have been used for synthesize of the films. The sputtering gas was a mixture of Ar and N_2. The C_2H_2 was used to prepare the carbon content of the coatings. The deposition was carried out at a bias voltage

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of -60 V, a target current of 6 A and a distance from substrate to target of 90 mm. Following putting samples into chamber, the chamber was pumped down to a base pressure of 2.5×10^{-3} tor. Afterwards, substrate materials were cleaned by ion bombardments for 20 min to remove oxide layers and surface contaminations. Before deposition of the TiN/TiCN/TiC multilayer film, Ti interlayer film was grown for 5 min, which could be beneficial to good adhesion properties [17]. Experimental parameters of TiN/TiCN/TiC coating are shown in table 2.

Table 1. Chemical composition of CP-Ti and Ti6Al4V substrate materials (wt. %)

Substrates	Ti	V	Fe	Al	Sn	Cu
Ti6Al4V	89.8	3.78	0.03	6.31	0.05	0.01
CP- Ti	99.8	0.05	0.09	0.005	0.099	0.01

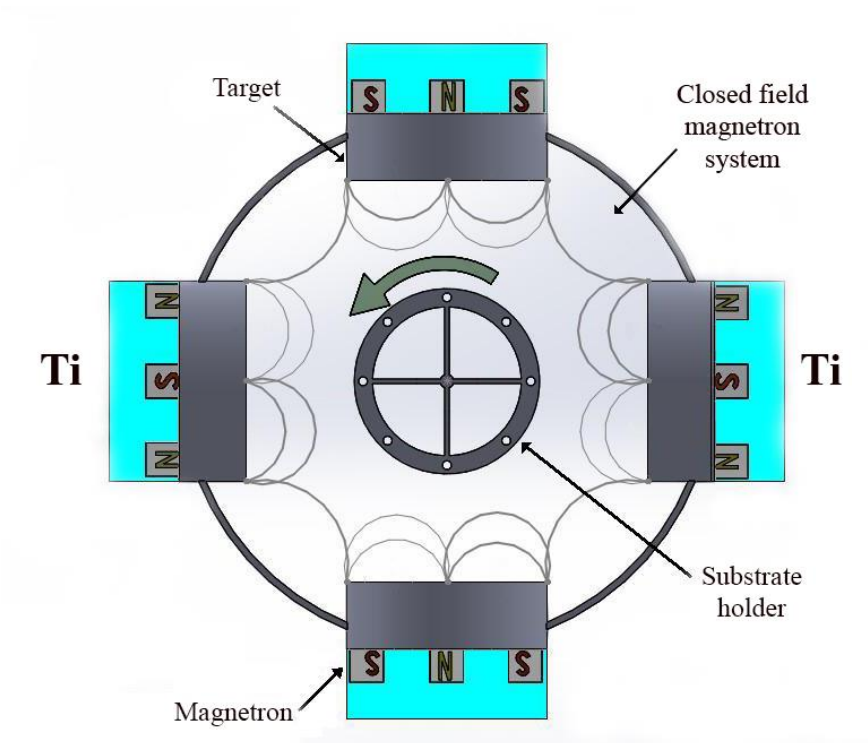

Figure 1. The placement of magnetrons inside the PLASMAG-550 device

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Table 2. The TiN/TiCN/TiC multilayer thin film obtained by variation of N_2 and CH_4 flow rate.

Ar flow rate (%)	N_2 flow rate (%)	C_2H_2 flow rate (%)	Ti target current (A)	Work time (min)	Phase
100	0	0	0	20	Ion cleaning
100	0	0	6	5	Ti
40	60	0	6	10	TiN
25	5	70	6	10	TiCN
25	5→50	70→25	6	35	TiCN (gradual)
75	0	25	6	15	TiC

Surfaces morphology and cross-section of the multilayer TiN/TiCN/TiC thin films deposited on CP-Ti, Ti6Al4V and silicon substrates were observed by Quanta 250 FEG model scanning electron microscope. Surface structure and fractured crystalline structure of the film was investigated by using the GNR X-Ray Explorer diffractometer with CuKα radiation (λ=1.5406 Å) at an incident angle from 20 to 60. The chemical composition of various compounds of the coating surface and subsurface was performed by XPS (PHI-5000 versaprobe) with monochromatized Al Kα X-ray source at pass energy of 58.75 eV. In order to obtain insight into the chemical states of the film, the XPS Ti2p, N1s and C1s core-level spectroscopy of the film were examined at pass energy of 187.85 eV and samples were sputtered by argon to remove the probable contaminations and or oxidations from the film surfaces.

The adhesion force of the TiN/TiCN/TiC film was measured by means of scratch test. The test was conducted by CSM Revetest Scratch Tester in dry atmosphere condition with a progressive load sliding between 0-30 N over the coating surfaces using Rockwell-C indenter tip with radius of 0.2 mm. The loading rate and track length were 100 N/min and 3 mm, respectively. Instron hardness tester was used to measure the nano-hardness values of TiN/TiCN/TiC films deposited on the surface of CP-Ti and Ti6Al4V substrates. The applied load was 10 mN, a loading time of 15 s, waiting time of 10 s, discharging time of 15 s and thermal sliding time of 45 s.

3. Results and Discussion

3.1. Microstructure and Composition Examination

The XRD pattern of TiN/TiCN/TiC multilayers film deposited on silicon (1 0 0) is given in Figure 2. XRD pattern indicated that the coating was consisted of FCC (1 1 1) cubic and polycrystalline structure of TiN-TiCN-TiC phase corresponding to the (1 1 1), (1 0 0), (1 0 1) and (2 0 0) planes

[18]. Tendency of XRD peak was observed for (1 1 1) plane which could be verified by the highest intensity belongs to TiN (1 1 1) or TiCN (1 1 1) planes [19].

XPS was used to determine chemical composition of the film's surface and depth profiling. As a results, Figure 3(a). showed that Ti2p had two evidential peaks located at 455 and 460.8 eV, respectively associated to Ti 2p3/2 and Ti 2p1/2. At the same time, a dominant N1s peak can be seen at the 397.5 eV position. XPS spectra of Ti2p, N1S and C1s of the film are shown in Figure 3(b). Ti2p at binding energy of 455 and 461 eV was observed for TiCN confirmed by the C1s peak at 285 eV and N1s peak at 397 eV. XPS result of TiC uppermost layer of the film are given in Figure 3(c). Ti2p XPS peaks were consisted of two doublets (Ti 2p3/2 and Ti 2p1/2) at the binding energy of 459.1 eV and 465 eV, respectively. The C1s spectrum showed a peak at the position of 286.1 eV [20]. As mentioned earlier, it was found that titanium nitride (TiN), titanium carbonitride (TiCN) and titanium carbide (TiC) are mainly formed in the coating.

SEM was used to examine the changes in the surfaces and fractured cross-section of the coatings. As seen in Figure 4. both coated substrates were demonstrated the structural properties of dense, compact and fine-grain so that there was no significant difference when compared from the way of structure viewpoint. Cross-section SEM images of TiN/TiCN/TiC deposited on silicon (Figure 5) showed that the coatings had dense and columnar structure and thickness of film reached about 1.77µm.

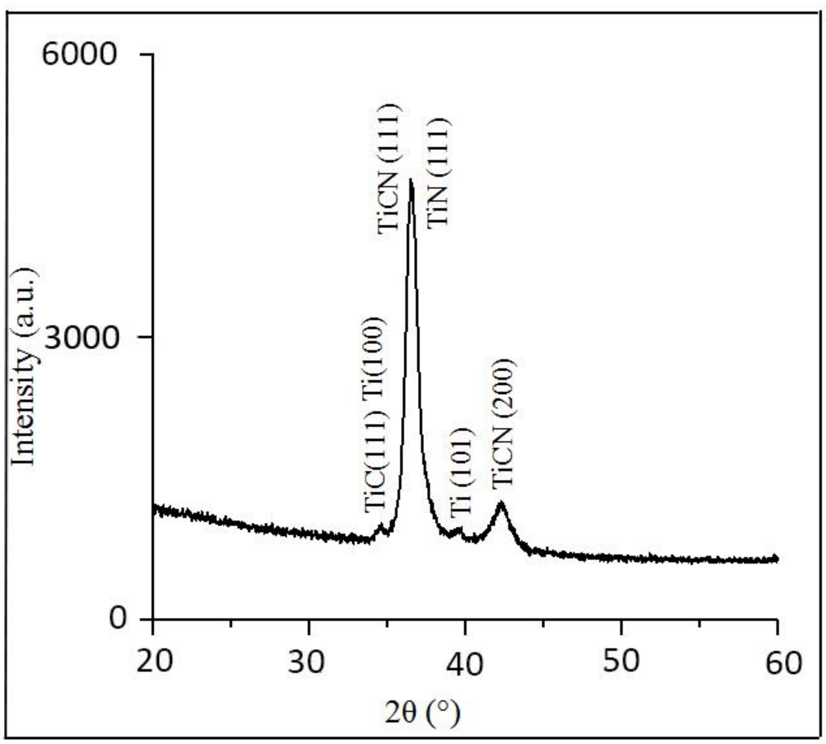

Figure 2. The XRD spectrums of the TiN/TiCN/TiC films deposited on the silicon surface

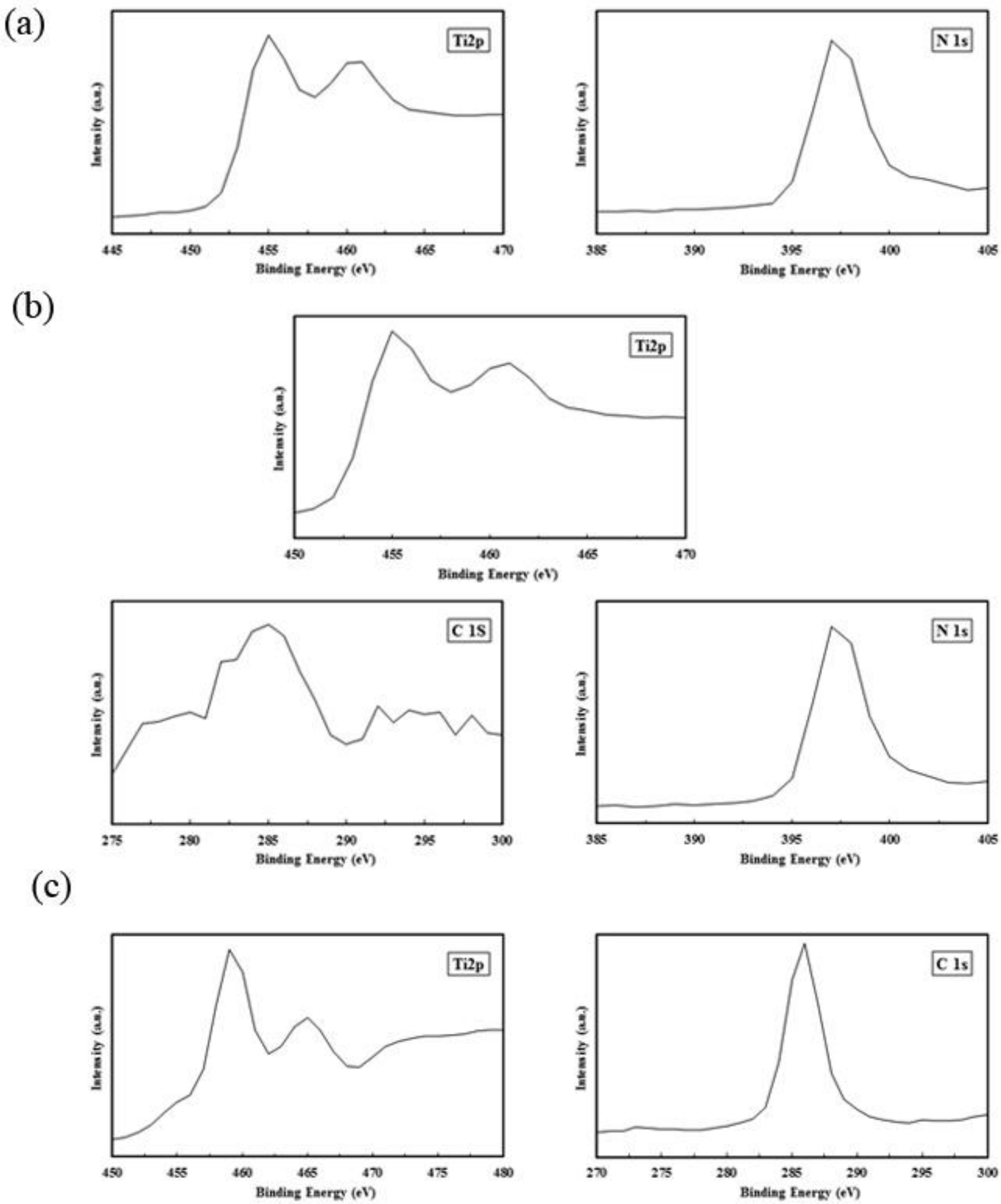

Figure 3. XPS spectra of TiN/TiCN/TiC multilayer film; **(a)** TiN, **(b)** TiCN, and **(c)** TiC

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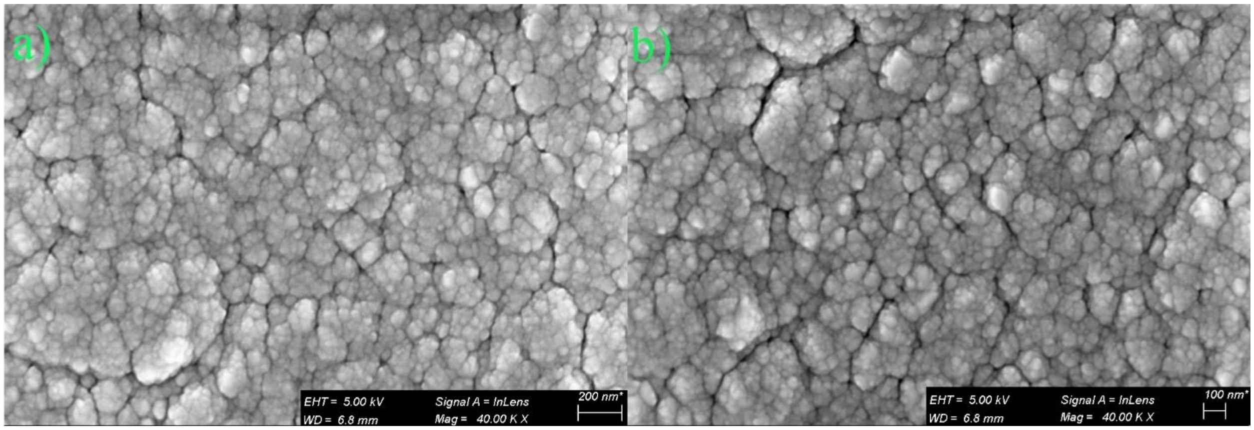

Figure 4. SEM images of TiN/TiCN/TiC coatings; **(a)** CP-Ti substrate, and **(b)** Ti6Al4V substrate

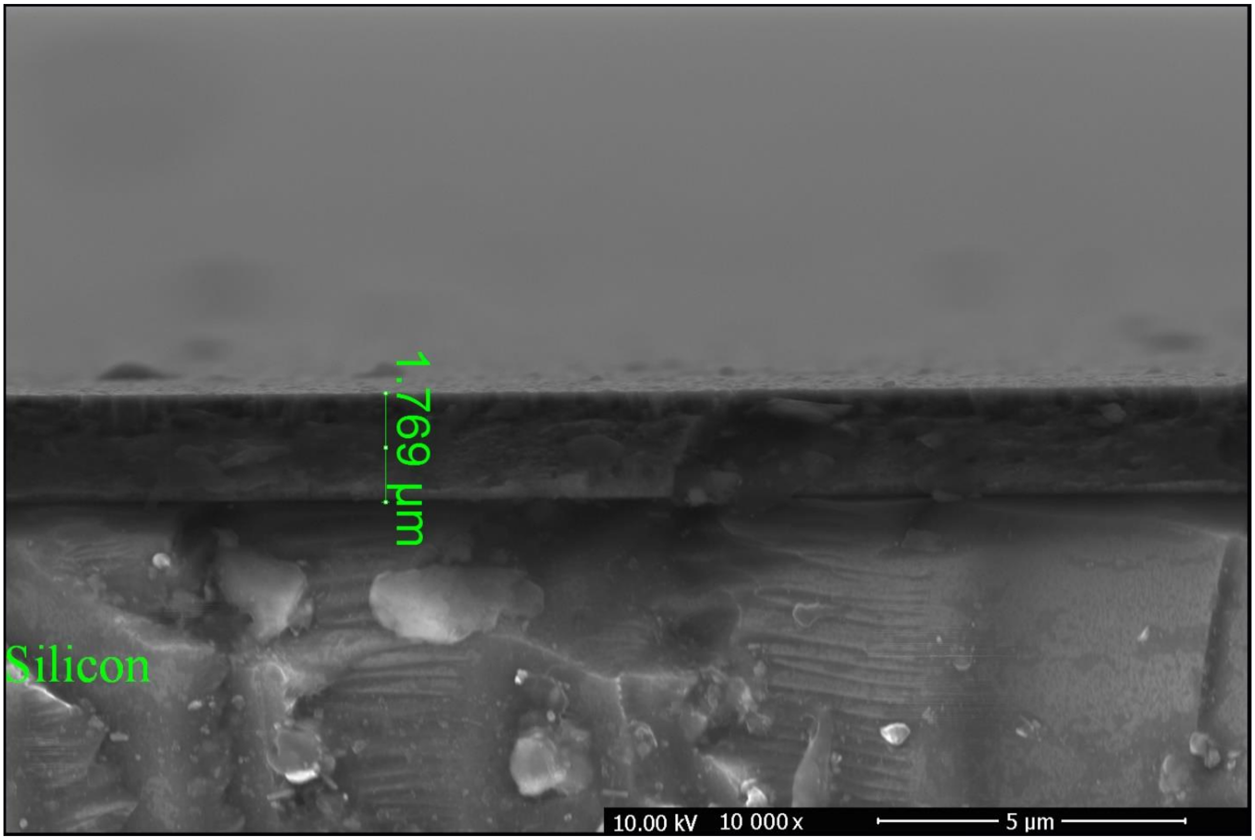

Figure 5. Cross-section SEM images of the silicon substrate

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3.2. Mechanical Properties

3.2.1. Scratch Test:

Adhesion test of TiN/TiCN/TiC film deposited on CP-Ti and Ti6Al4V substrates via magnetron sputtering were carried out by the scratch test. The value changes chart of coated CP-Ti and Ti6Al4V substrates of friction force, coefficient of friction and normal force obtained from the scratch test are given in Figure 6. At the coated CP-Ti substrate, when the load value reached to 6N, initial small cohesive fractures (Lc_1) began to show and followed up to 14N. These cohesive cracks widely formed on coating surface and present ductile fracture. First adhesive fractures occurred at 14N (Lc_2), where coating started to separate from the substrate in the form of brittle fracture. At the coated Ti6Al4V substrate, there was not any remarkable cracks on the film surface up to 10N. The significant cohesive cracks in the coating was occurred at 10N load (Lc_1). When the load increased, the slightly adhesive cracks came into sight at 17N (Lc_2).

Previous studies have reported that the critical load values of TiCN coatings under different growth conditions were in the range from 6N to 45N [21]. SEM images of scratching test of CP-Ti and Ti6Al4V samples are given in Figure 7. When the SEM images were examined it was seen that due to the tensile stress on the coating surface, first cohesive cracks were started in the vertical direction of the scratch path and defined as Lc_1 critical load [22]. With increasing the normal load value, the coating being separated from the substrate material and causes adhesive fractures [23]. The critical load values of TiN/TiCN/TiC coating deposited on CP-Ti substrate were 6N and 14N, respectively (Figure 6a). The Ti6Al4V substrate with 10N and 17N critical loads indicated better scratch properties (higher hardness and strength values) in compared with CP-Ti substrate (Figure 6b). The reason for this result is that the critical load can be influenced by the properties of the substrate material because the coated hard and high-toughness substrates shows higher critical loads [24]. Critical load results were also confirmed by SEM images of scratch tracks (Figure 7).

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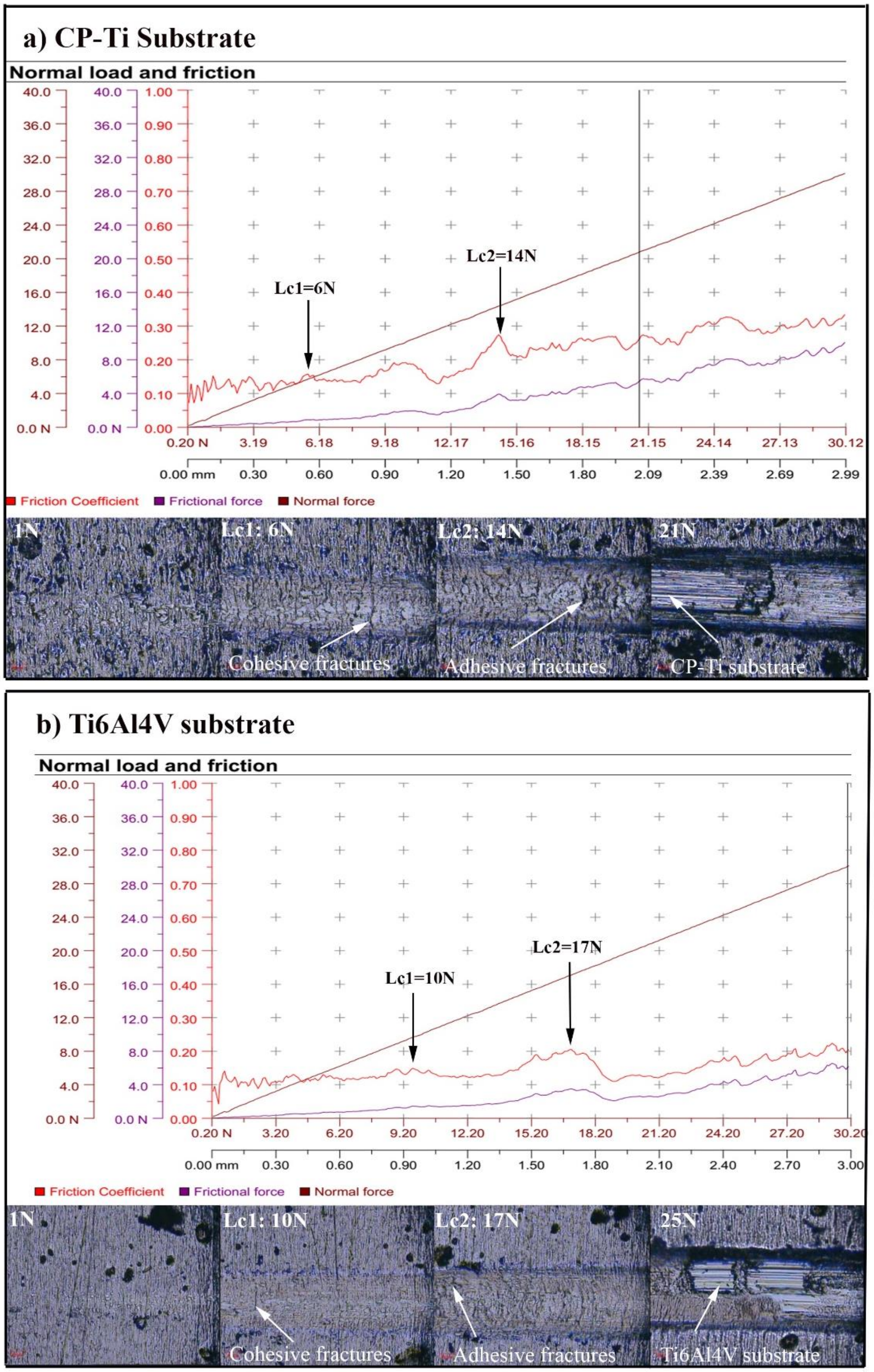

Figure 6. Friction force, coefficient of friction, normal force values graph and optic microscope images of **(a)** CP-Ti and **(b)** Ti6Al4V substrates

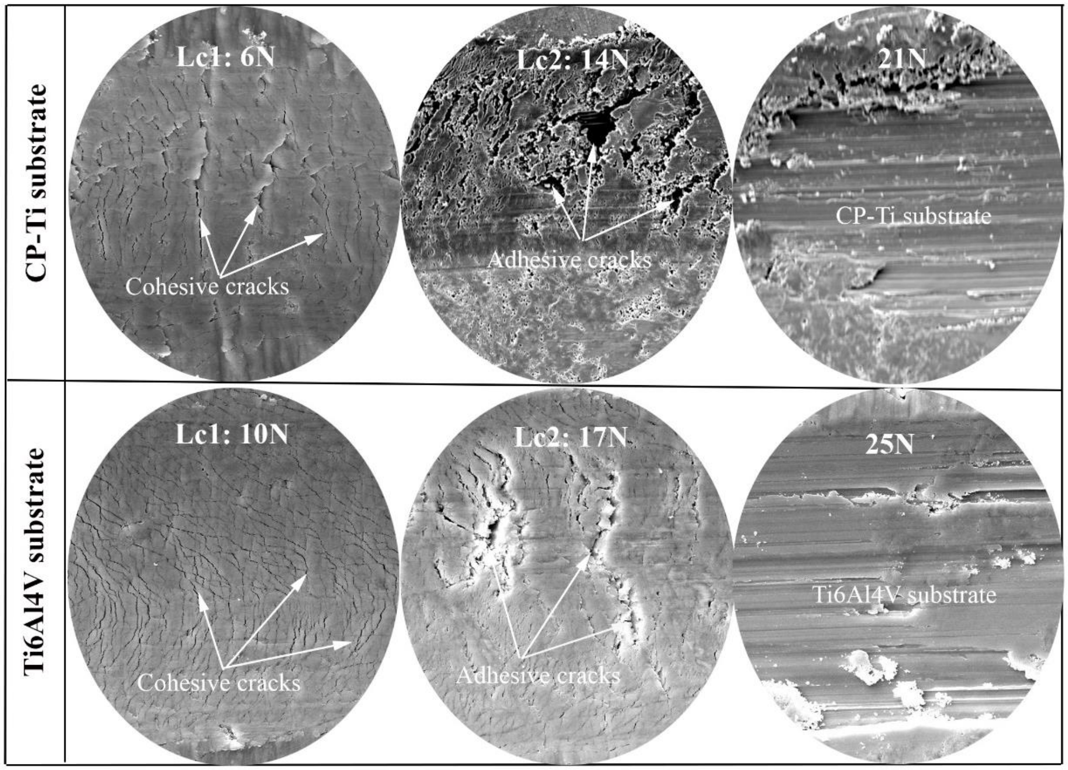

Figure 7. SEM images of scratch tracks of CP-Ti and Ti6Al4V substrates

. 3.2.2. Nano-Hardness Measurements

Figure 8. gives a typical loading-unloading indentation curves of TiN/TiCN/TiC film coated on Cp-Ti and Ti6Al4V substrate materials. The initial loading part was involved of an elastic-plastic displacement while the unloading section released the elastic energy. Table 3 presents the result of nanoindentation and elastic modulus measurements for coated and uncoated substrates of TiN/TiCN/TiC multilayer films. The mean values of hardness and elastic modulus of the films deposited on Cp-Ti substrates were 19.96 GPa and 162.81 GPa and on Ti6Al4V substrates were 19.96 GPa and 162.81 GPa, respectively. These values are the average of 5 measurements taken on each sample. The highest hardness of the multilayer film,19.96 GPa, was obtained in coated Ti6Al4V substrate. Some authors have been reported hardness of TiN, TiCN and TiN/TiCN multilayer film with thickness of 0.5-6 μm which are about 8.2 GPa to 27.3 GPa [3, 25-27].

In multilayer films, existing of hard substratum layers strengthens the structure and wear resistance of the coating. This increment is due to an increase in the average hardness of the coating[28] . In the present study we found that the hard TiCN layer of film could raise general hardness and stability of the TiN/TiCN/TiC coatings.

Multilayer films could improve mechanical properties of films like hardness in compared to every single-layered films. This improvement leads to high hardness and density and lower grain size, as observed in SEM images of Figure 4. It can be explained that high interface density of multilayered films leads to hinder dislocation movement and dislocation glide over the TiN, TiCN and TiC layers which could be justified by the differences in the elastic shear modulus of the individual layer materials [19].

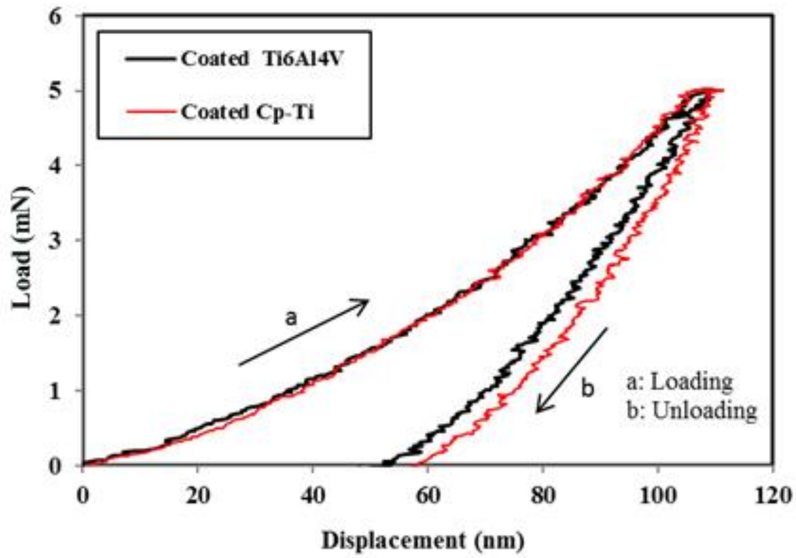

Figure 8. The typical loading-unloading curves of the TiN/TiCN/TiC multilayer film.

Table 3. Details of nanoindentation hardness measurements of TiN/TiCN/TiC coated and uncoated substrates

Samples	Nanoindentation Hardness (GPa)	Elastic modulus (GPa)
Coated Cp-Ti	19.75	162.81
Coated Ti6Al4V	19.96	175.87
Uncoated Cp-Ti	3.15	93.71
Uncoated Ti6Al4V	4.81	99.37

4. CONCLUSIONS:

The TiN/TiCN/TiC multilayered coatings were successfully deposited on silicon, CP-Ti and Ti6Al4V by CFUBMS method and thickness of film grown on silicon was 1.77 µm. According to the XRD and XPS spectrum of the TiN/TiCN/TiC coating, Ti, TiN, TiC and TiCN diffractions were detected in the coating. The most prominent crystallographic reflection in the coating was in the TiN (111) and TiCN (111) planes. The nano-hardness values of the coatings deposited on the surfaces of CP-Titanium and Ti6Al4V were measured as 19.75 GPa and 19.96 GPa, respectively. Regarding to nano-hardness results, although hardness of substrates was increased by applying coating, there was no significant difference between the hardness values due to the proximity of

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substrate materials' harnesses to each other. In this study, the critical load values from the scratch test of TiN/TiCN/TiC were determined as Lc_1 = 6N and Lc_2 = 14N for the coated Cp-Titanium substrate material and Lc_1 = 10N and Lc_2 = 17N for the coated Ti6Al4V surface. Scratch and nanoindentation tests showed that the coated Ti6Al4V substrate material with the 19.96 GPa hardness value and 25 N critical load value presented the best mechanical behavior due to higher hardness and toughness of substrate in compared to Cp-Ti substrate. With applying the coating of surface, the hardness of the coated materials was increased accompanied with achieving a high adhesion strength between the substrate and the coating

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Conflicts of Interest: The authors declare that they have no competing interests.

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