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RESEARCH ARTICLE

Investigation of Mechanical Properties of TiN/TiCN/TiC Multilayer Thin Films Coated on Ti6Al4V Substrate

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HIGHLIGHTS

- > By the application of TiN/TiCN/TiC multilayer thin films, the mechanical properties of Ti6Al4V substrate, such as nano-hardness and scratch resistance, was significantly improved.
- > Nano-hardness of coated Ti6Al4V substrate material increased from 4.81 GPa to 19.96 GPa.
- > Scratch test showed that the critical load of the coating was found about 26 N.
- > Thickness of coating reached to 3.065 μm deposited on Ti6Al4V substrate.

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ABSTRACT

This study addresses the improvement of hardness and scratch resistance provided by TiN/TiCN/TiC multilayer thin films on Ti6Al4V and Silicon (Si) substrates using magnetron sputtering. X-ray diffraction (XRD), scanning electron microscopy (SEM), and nano-indentation and scratch tests have been carried out in order to characterize the film layer in terms of structural, chemical, and mechanical properties. The cubic and polycrystalline structure of TiN/TiCN/TiC film deposited on Si was confirmed by the XRD analysis. SEM cross-sectional images revealed that the coating has dense and columnar structure with a thickness of 3.065 μm and had formed a good adhesion to the substrate. Hardness and critical load values of the coated Ti6Al4V substrate, as obtained from the scratch and nano-indentation test, were 19.96 GPa and 26 N, respectively.

Contents

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1. Introduction

By the virtue of their low density, high corrosion resistance, biocompatibility and long fatigue life, titanium and alloys have a broad application in many industries, such as spacecraft, automotive, dentistry, orthopedics and medical [1–4]. Chemical vapor deposition (CVD) [5], Plasma enhanced chemical vapor deposition (PECVD) [6], thermal spraying [7, 8] and magnetron sputtering [9] are a few to name among the techniques and methods that are used to obtain enhanced surface properties.

In comparison to high-speed steel and cementide carbide, first generation of single layer hard coatings, e.g. TiN, TiC, CrN, ZrN, NbN, TiCN, ZrCN, WC, WC–Co and WC–Ni have an important place in respective industries for having a relatively higher hardness and toughness as well as lower friction coefficient. TiN, TiC and TiCN films are widely preferred particularly in cutting tools, load bearings [10], tribological applications [11] as they exhibit an excellent wear resistance, and high hardness and in and biomedical field [12] for their good corrosion resistance and biocompatibility [13–18].

Multilayer coatings, on the other hand, such as TiN/TiCN, outperform the single layer films, TiN and TiCN, in the aspects of mechanical properties such as higher hardness, wear and corrosion resistance [19]. The present study is also aimed at characterizing the microstructure and mechanical properties of TiN/TiCN/TiC multilayer thin films coated on Ti6Al4V substrate using magnetron sputtering.

2. Materials and Methods

Table 1 Chemical composition of Ti6Al4V samples provided by supplier.

Element (%)	Ti6Al4V
Ti	89.8
Si	< 0.0100
Mn	0.0114
Cr	< 0.0100
Mo	< 0.0100
Al	6.31
Cu	< 0.0100
Fe	0.0329
V	3.78
Zr	< 0.0100
Sn	< 0.0500
Nb	0.0342

25×25×3 mm samples cut from grade 5 Ti6Al4V using abrasive water jet were used as substrate material. Chemical composition of samples, as provided by the supplier, is given in Table 1. TiN/TiCN/TiC multilayered films were deposited on Ti6Al4V substrates by using a DC Closed Field Unbalanced Magnetron Sputtering System (CFUBMS) manufactured by Teer Coatings Ltd. Detailed deposition parameters and further details about the sputtering device can be found in our previous study [20].

For the analysis of the chemical composition of the coating layer, a Si substrate, which does not give any diffraction peaks and hence does not interfere with the XRD spectrum, was also coated using the same coating procedure. The Si sample was only used for the XRD analysis of the coating layer.

A Quanta 250 FEG was employed to take cross-sectional SEM images from TiN/TiCN/TiC the multilayer thin films deposited on Ti6Al4V and Si substrates whereas the crystalline structure was examined using a GNR X-Ray Explorer diffractometer at CuKα radiation (λ=1.5406 Å) with a Bragg-Brentano configuration (θ/2θ) in the scan range of from 20° to 90° at of 2°/min scan speed.

The adhesion and scratch resistance of TiN/TiCN/TiC film was examined with a CSM Revetest Scratch Tester sliding over the coating surface with a progressive load ranging between 0-30 N using Rockwell-C indenter tip with a radius of 0.2 mm in a dry atmosphere condition. The loading rate and track length were 100 N/min and 3 mm, respectively. Instron hardness test, details of which is given in Table 2, was carried out measure the nano-hardness of the surface of the thin film deposited on the Ti6Al4V substrate.

Table 2 Instron hardness test details

Property	Value
Applied load	10 mN
Loading time	15 s
Waiting time	10 s
Discharging time	15 s
Thermal sliding time	45 s.

3. Results and discussion

3.1. Examination of microstructure and composition

As can be seen in Fig. 1, the XRD spectrum of TiN/TiCN/TiC multilayer film deposited on Si, all peaks that relate to the (111), (220) and (222) plane of the cubic TiCN phases, (111) and (200) planes of the TiC phases and TiN (311) phase are present in TiN/TiCN/TiC multilayer coating. The Ti interlayer, applied to improve the adhesion between the coating and the substrate [14, 21, 22], can also been seen in the corresponding peak of (101) plane.

The most dominant peak in the XRD spectrum belongs to the TiCN (1 1 1) phase which indicates good crystallization which could result in improved tribological and mechanical properties of the film. On the other hand, TiC (111) phase, which has high hardness and good resistance properties, was also observed [23–25].

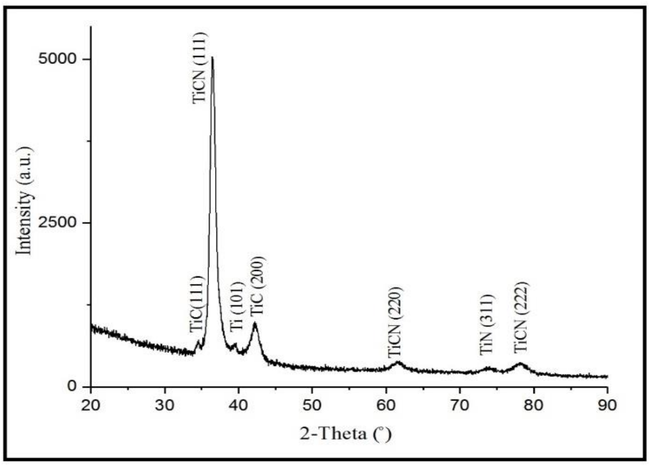

Figure 1 XRD spectrum of the TiN/TiCN/TiC film deposited on Si.

Seen in Fig. 2 is a cross-sectional SEM image from the TiN/TiCN/TiC film deposited on Ti6Al4V within the scope of this study. On order to get a clear view of the cross-section of the films, coated substrates were given a brittle behavior by being frozen in liquid nitrogen and then fractured instantaneously whereafter they were rinsed with ethanol. The film thickness, as measured on the SEM image, was 3.065 µm. The film-substrate interface was observed to be quite smooth with no apparent delamination.

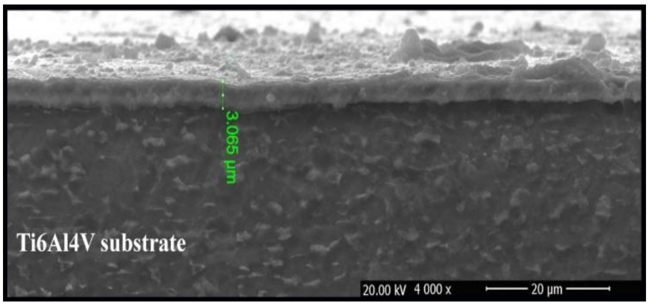

Figure 2 SEM cross-sectional images of TiN/TiCN/TiC films deposited on Ti6Al4V substrate.

As can be seen in the SEM image, given in Figure 3(a), showing the surface morphology of TiN/TiCN/TiC coatings deposited on Ti6Al4V, the surface is of a dense, homogeneous, and granular morphology. Figure 3(b) shows cross-sectional image of TiN/TiCN/TiC films deposited on Si substrate where the film thickness reached about 1.77µm. When the layers of the coating are examined closely, TiCN layer has a dense structure with a thickness of 1.07 µm while TiN and TiC layers exhibit columnar structures with a thickness of 200 nm and 500 nm, respectively.

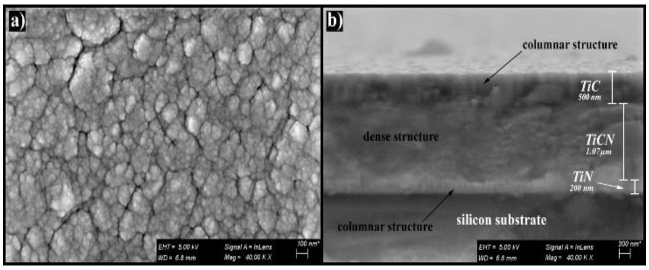

Figure 3 SEM images of (a) surface morphology, and (b) fracture cross-section of the TiN/TiCN/TiC coating

3.2. Mechanical properties

3.2.1. Scratch test

The graph showing the value changes of friction force, friction coefficient, and normal force and optic microscope images obtained from the scratch test are given in Fig. 4 for coated Ti6Al4V substrate. Up to 10 N, no remarkable crack was observed on coated Ti6Al4V substrate surface. Significant cohesive cracks occurred at 10 N (Lc1). Slight adhesive cracks became apparent at 17 N (Lc2) and when the load reached 26 N (Lc3) the coating was observed to have scuffed off.

Examining Fig. 5 which shows the SEM images belonging to the scratch test of coated Ti6Al4V samples, it can be seen that first cohesive cracks occurred in scratch path of a vertical direction at Lc1 [26]. At Lc2, the film started to separate from the substrate and therefore adhesive fractures occurred [27] and finally at Lc3 the coating totally scuffed off the substrate surface. The values of the critical loads may vary depending on the properties of the substrate materials and film thickness, for instance, coatings on softer substrates tend to fail relatively earlier in comparison to those on harder substrates. Furthermore, the film thickness has strong effect on the properties and performance of coating during the test, i.e. the more the thickness the greater the scratch resistance to delamination due to the lower stress concentration in the interface, likewise a greater load is required to remove the coating as a greater load is supported by the coating [28, 29].

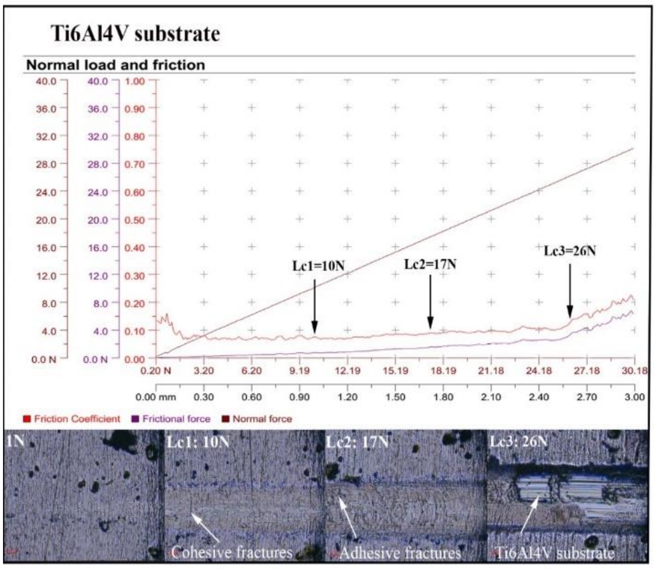

Figure 4 Frictional force, friction coefficient, normal force values graph and optic microscope images of Ti6Al4V.

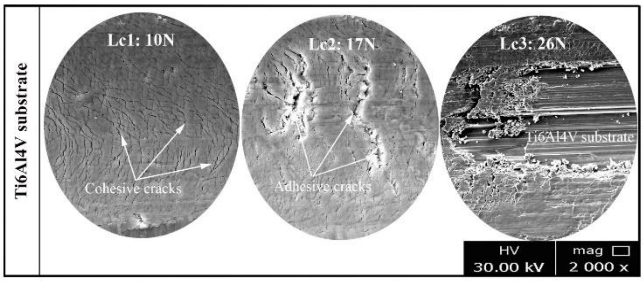

Figure 5 SEM images of scratch tracks of coated Ti6Al4V substrate.

3.2.2. Nano-Hardness measurements

Typical loading-unloading indentation curves for TiN/TiCN/TiC film on Ti6Al4V is shown in Fig. 6. Nano-indentation hardness and elastic modulus values for the bare substrate material and TiN/TiCN/TiC-coated samples are given in Table 2.

The effect of coating on the nano-indentation hardness is significant, with an improvement of approximately five folds.

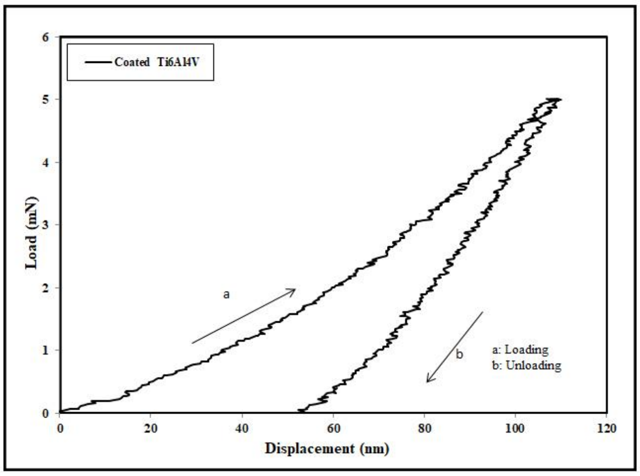

Figure 6 The typical loading-unloading curves of the TiN/TiCN/TiC multilayer film.

Table 3 Nano-indentation hardness and elastic modulus of Ti6Al4V before and after TiN/TiCN/TiC coating.

Samples	Nano-indentation Hardness (GPa)	Elastic modulus (GPa)
Uncoated Ti6Al4V	4.81	99.37
Coated Ti6Al4V	19.96	175.87

4. Conclusions

After the examination of TiN/TiCN/TiC multilayer film, successfully deposited on Si and Ti6Al4V using CFUBMS method, the following conclusions were reached:

The Si substrate, as expected, showed a weaker coating capability, due to that Si is a non-conductor/dielectric material and therefore it attracts less atoms that are sputtered from the target material during coating process, which leads to lesser deposition on the surface. As a confirmatory result the thickness of the coating on Si was measured to be 1.77 µm as low whereas on Ti6Al4V, a conductive substrate, it reached 3.065 µm.

The presence of Ti, TiN, TiC and TiCN on the surface of the coated Si samples were confirmed through the respective diffractions in the XRD spectrum.

Nano-hardness and scratch resistance values of coated Ti6Al4V obtained from the nano-indentation and scratch tests, when compared with the results we previously obtained from Cp-Ti substrate, indicate an apparent relation between the hardness of the substrate material and that of coated sample. Namely, properties of film are affected by the hardness of substrate materials. Hardness and scratch resistance values of coating showed that coating deposited on harder substrates can withstand greater loads compared to softer substrates.

The application of TiN/TiCN/TiC multilayer coating on Ti6Al4V substrate was found to have increased it nano-hardness from 4.81 GPa to 19.96 GPa. As for the scratch results, the critical load value (Lc3), which indicates the critical load where the coating is scuffed off the surface of the substrate, was determined as 26 N for TiN/TiCN/TiC-coated Ti6Al4V.

Conflict of Interest

The authors declare that they have no competing interests.

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