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COMPARISON OF PROPERTIES OF TiN/TiCN AND PLASMA NITRIDING/TiCN FILMS DEPOSITED ON THE TOOL STEEL BY PULSED DC- PACVD

S. M. M. Shafiei[1], M. Divandari[1], S. M. A. Boutorabi[1, 2] and R. Naghizadeh[1]
* *shafiei@iust.ac.ir*
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[1] School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.
[2] Center of Excellence for High Strength Alloys Technology (CEHSAT), Tehran, Iran.

Abstract: *In this work, TiN/TiCN & PN/TiCN multilayer films were deposited by plasma- assisted chemical vapour deposition (PACVD). Plasma nitriding (PN) and TiN intermediate layer prior to coating leads to appropriate hardness gradient and it can greatly improve the mechanical properties of the coating. The composition, crystalline structure and phase of the films were investigated by X-ray diffraction. Atomic force microscopy and scanning electron microscopy were employed to observe the morphology and structure of the films. The TiCN layer exhibited a columnar structure. The adhesion force between the film and the tool steel substrate was 30.8 MPa for TiN/TiCN and 25.4 MPa for PN/TiCN film determined by pull off tests. The hardness of TiN/TiCN film was 12.75 GPa while it was 5.4 GPa for PN/TiCN film, respectively. The improvement of the adhesion in TiN/TiCN was attributed to a less gradient hardness configuration. In addition, the mean friction coefficients of the films were about 0.2 for TiN/TiCN and 0.3 for PN/TiCN film determined by nanoindentation tests.*

Keywords: *PACVD; TiCN; TiN; Plasma nitriding; Multilayer*

1. INTRODUCTION

Surface modification using hard films as a surface engineering process has long been proven to be an outstandingly successful way. Multilayer structure hard films have recently drawn wide attention of researchers who attempted to improve the properties of the multilayer films in comparison with the traditional single layer films [1-4]. In comparison with the earlier developed TiN, TiCN and TiC coatings, the binary coatings often combine the individual advantages of these coatings and have high hardness, wear resistance, low friction coefficient and good adhesion to substrate. The binary coatings can be conveniently deposited on a substrate through a plasma assisted chemical vapour deposition (PACVD) process [5]. Among various multilayer hard films, the films containing Ti compounds (TiN/TiCN, TiN/TiC and Ti/TiN) have most frequently been investigated in the past decades [6-8].

Furthermore, the coatings can be mechanically supported by adding a nitriding step before deposition. By using sputter-cleaning and plasma nitriding (PN) process, the surface and subsurface are modified, allowing an appropriate hardness gradient between the surface zone of the substrate and the subsequent coating [9, 10].

The aim of this work is to investigate the characteristics of TiN/TiCN & PN/TiCN multilayer films, and it compares TiN and PN as an intermediate layers. Also, as it is expected that the films combine the advantages of single layer films.

2. EXPERIMETAL DETAILS

TiCN coatings with compositional gradients were deposited on a X4Cr5MoWSiV hot-work tool steel substrate using a PACVD coating system equipped with a voltage-controlled pulse generator.

During coating, process parameters such as gas flow ratio, wall temperature, voltage duration of pulse-on and pulse-off time and total pressure were monitored. H2, Ar, N2 and CH4 gases and TiCl4 vapor were used as process gases for coating deposition. Total pressure was kept at 2 mbar and substrate temperature was controlled at 470°C to avoid exceeding the tempering temperature of the hot-work tool steel. Plasma

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nitriding was used as pre-treatment to decrease hardness gradient between substrate and coating [17,18]. The processing parameters for deposition are listed in Table 1. The N2/CH4 gas flow ratio was defined CH4 / (CH4+N2). The crystalline structure of the coatings was determined by grazing incidence X-ray diffraction (GIXRD) using CuKα radiation (λ = 0.154056 nm). The full-width at half-maximum (FWHM) of the Bragg peaks is used to approximate crystallite size based on the Scherrer formula [8]:

$$D = {(0.9\lambda)}/{(\beta.\cos\theta)} \quad (1)$$

Where D is crystallite size, β is the FWHM of the Bragg peak, and θ is the Bragg reflection angle. The film morphology studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The adhesion properties of the coatings were evaluated using a pull off test. Five pull off tests were performed for each sample and an average value of the critical loads obtained. Hardness, elastic modulus and friction coefficients of films were determined by nano indentation test.

Table 1. PACVD parameters.

Parameters	Value
Pulsed voltage	650 V
Duty cycle	33%
Temperature	470°C
PACVD time	120 min
$CH_4/(CH_4+N_2)$ flow ratio	50%
Total pressure	2 mbar
TiN coating temperature	470°C
TiN coating time	120 min
nitriding time	120 min
nitriding temperature	470°C

3. RESULTS AND DISCUSSION

Fig.1 illustrates the GIXRD patterns of the TiCN coatings deposited at 470 ºC with PN and TiN as the intermediate films. The (200) plane is revealed to be the preferred structure. Fig.1b shows that by using TiN intermediate layer, the (111) plane is thermodynamically stable relative to the (200) plane and the broad peak of the (200) plane in Fig.1b indicates that the crystallite size decreases which is led to increasing of the specific surface of TiCN. This implies that the film structure is denser because the plane (111) orientation is the dense packed plane.

The residual stresses of the samples were determined by X-ray measurements. The surface residual stresses of TiCN layers are -20.74 MPa with TiN coating and -23.42 MPa with PN treatment prior. The residual stress values decrease with TiN intermediate coating. Which is ascribed to coincidence of lattice is more. Also films deposited with PN treatment prior are more crystallite.

Fig. 2 shows the topography and cross-sectional morphology of the TiCN coating under SEM. Also it shows clearly that the TiN/TiCN coatings are free of columnar structure, and have a denser and finer microstructure than plasma nitriding/TiCN coatings, so they have better wear-resistance and corrosion resistance [14]. The close-up view of the surface exhibited a cauliflower-like pattern (Fig.2b). It doesn't seem to be a result of crystallization by epitaxial growth that is a typical mechanism of many coatings. On the cross section of TiN/TiCN coating (Fig.2b), the microstructure over a thickness of 5.75 μm contained no pores, voids or microcracks unlike PN/TiCN coating. It seemed that the TiN/TiCN coating was formed through the piling up of crystallites in scale of nanometers (≤ 100 nm), which was different from the typical columnar crystalline structures of PN/TiCN coating. It is likely that during the PACVD deposition, columnar growth of TiCN was being led to the formation of nano-columnar structural characteristics.

Fig. 2 illustrates typical cross-sections view of the coated samples, which obviously indicates the deposition of a uniform TiN/TiCN film. The

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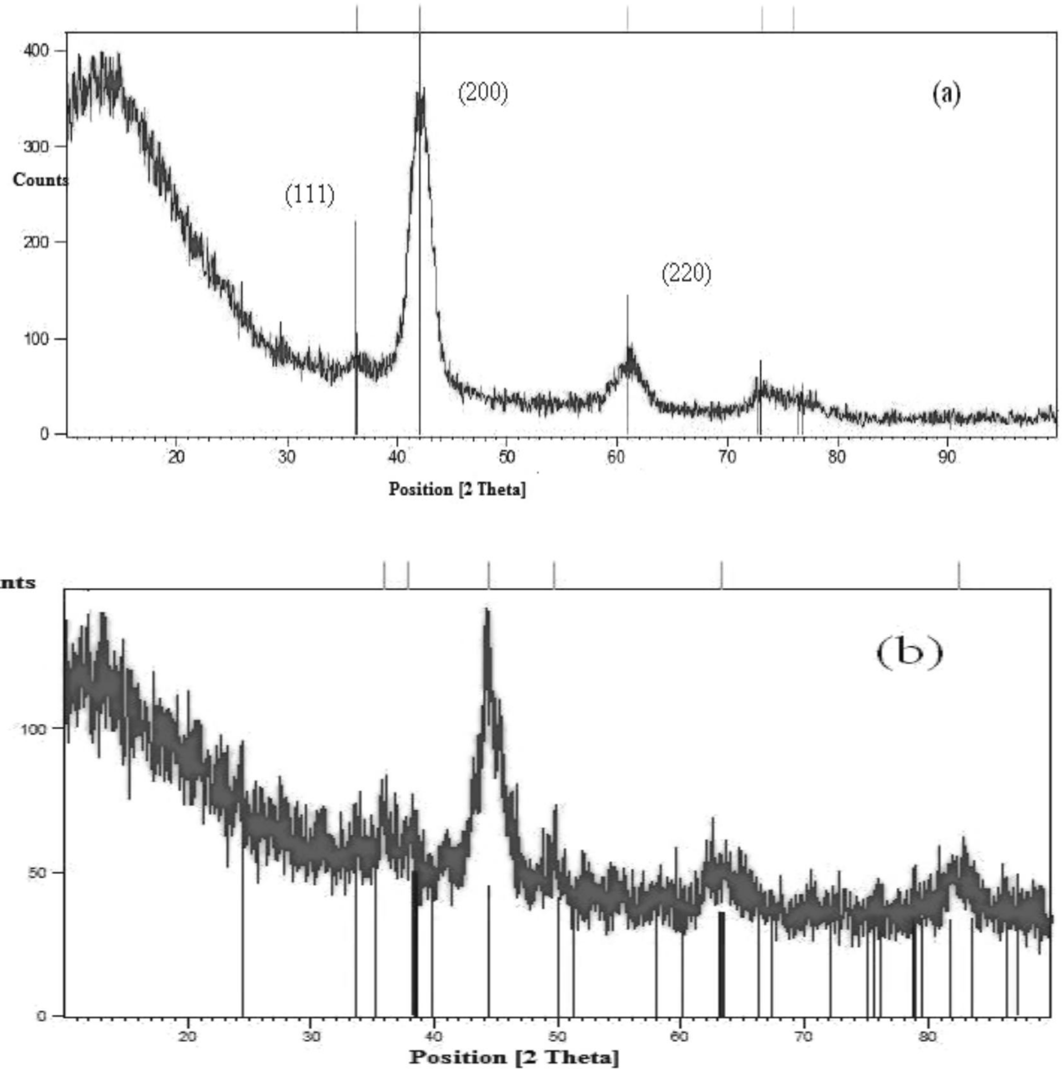

Fig. 1. GIXRD patterns acquired from the TiCN coatings a) PN+TiCN, b) TiN+TiCN.

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substrate –film interface for TiN/TiCN film is observed to be quite smooth and free of cracks and pores after deposition, which supposes a suitable adherence to the substrate as in shown Fig.3.

AFM was carried out quantitatively to study the surface morphology of the PN/TiCN & TiN/TiCN multilayer film. Figure 4 shows a representative 3 μm ×3 μm AFM image of the final surface after deposition of the multilayer. The root-mean-square (RMS) roughness of the final surface TiCN layer are about 120 nm PN/TiCN and 99.4 nm TiN/TiCN multilayer films by means of statistical analysis. In general, it can be observed that the size of the features and the roughness increase as the multilayer is completed [11]. According to Quir´os et al [12], increasing of roughness could be due to more sputtering time in TiN/TiCN deposition led to more assisting ions and significant damage. Figure 5 shows roughness of coating increased by increasing crystallite size.

Fig. 6 shows the hardness of TiCN films measured by nano-indentation. Clear mechanical improvements can be observed. The hardness of TiN/TiCN film was 12.75 GPa while it was 5.4

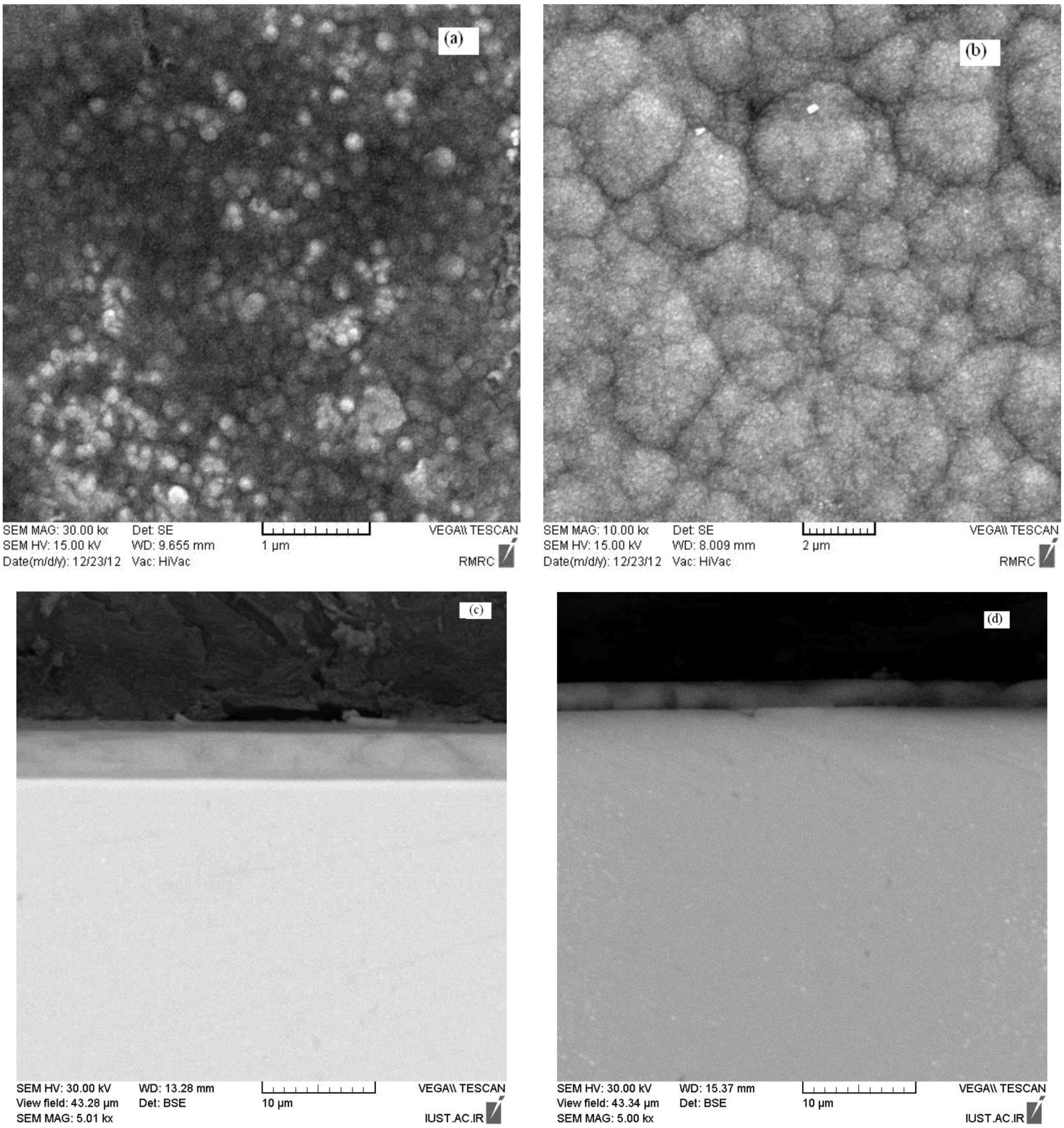

Fig. 2. SEM micrographs of the TiCN coating, a, c) TiN/TiCN, b, d) PN/TiCN.

GPa for plasma nitriding/TiCN film, respectively (according to results of AFM) because TiN/TiCN multilayer was denser. However the elastic modulus values remain very low, from 40 GPa for PN/TiCN to 90 GPa for TiN /TiCN film that these are values typically found for diamond like carbon (DLC) coatings [13]. However, the highly rounded curves of the unloading stage of the indentation cycle may disqualify the Oliver and Pharr procedure for modulus determination [14]. When the coatings have experienced sufficient ion bombardment during the deposition (in form of high energy, high dose or low deposition rate, or all together) their mechanical properties (such as hardness) are improved, revealing strong bonding of the elements and dense structures [15].

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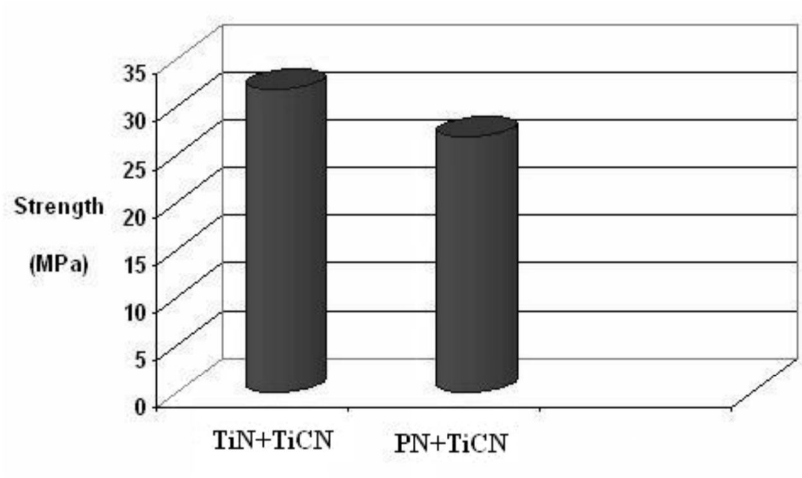

Fig. 3. the adhesion strength of TiCN coatings for different multilayer

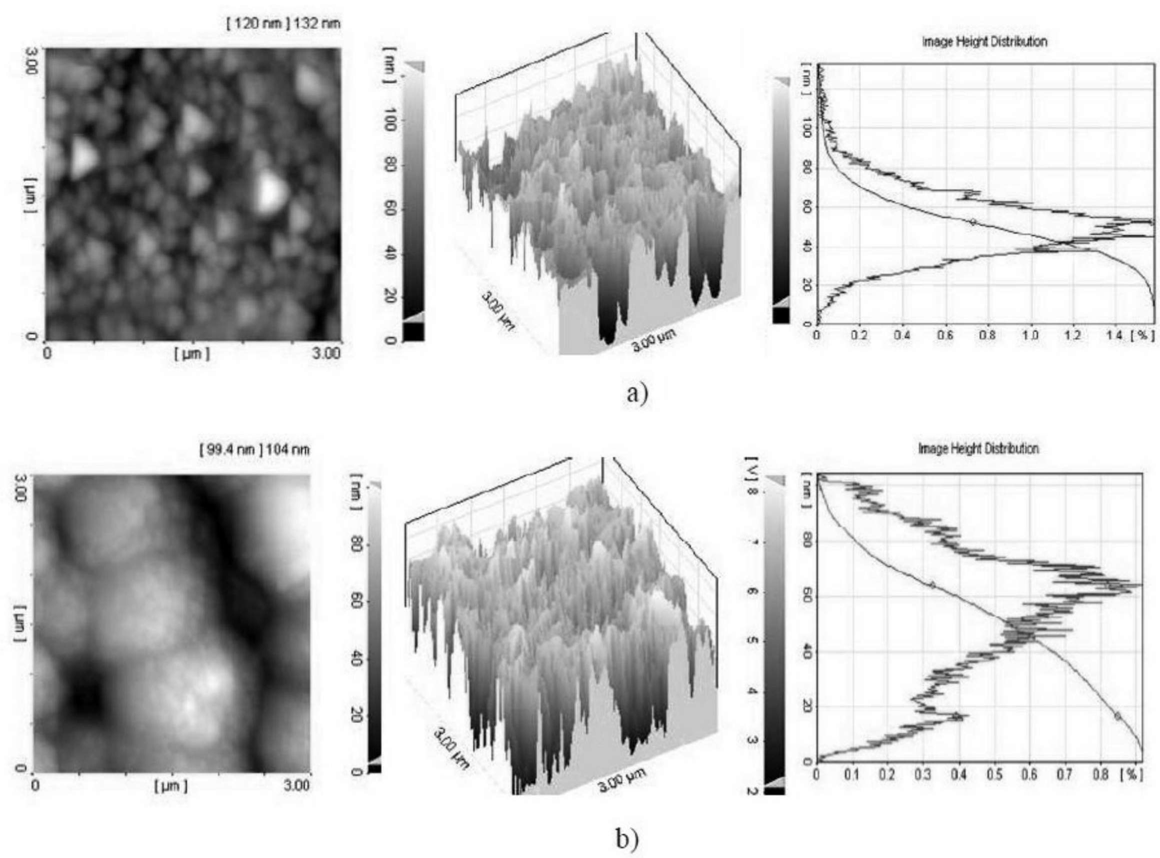

Fig.4. AFM topographic images of coatings from the multilayer: (a) PN/TiCN, (b) TiN/TiCN.

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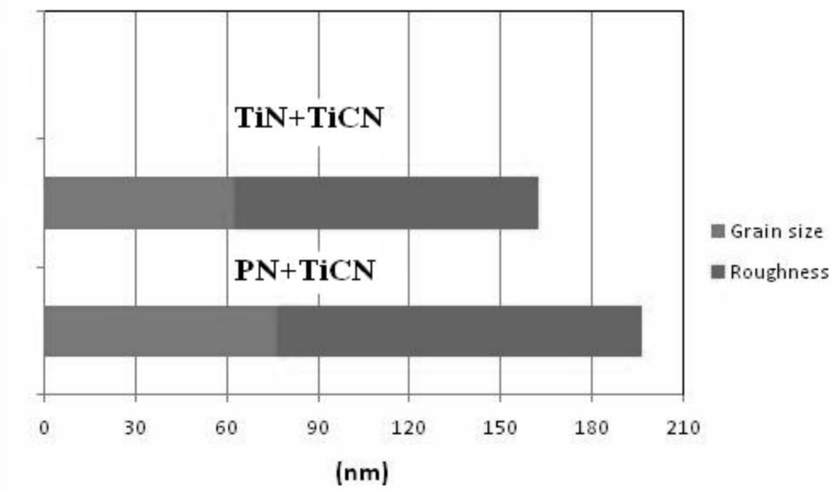

Fig.5. relation between grain sizes with roughness.

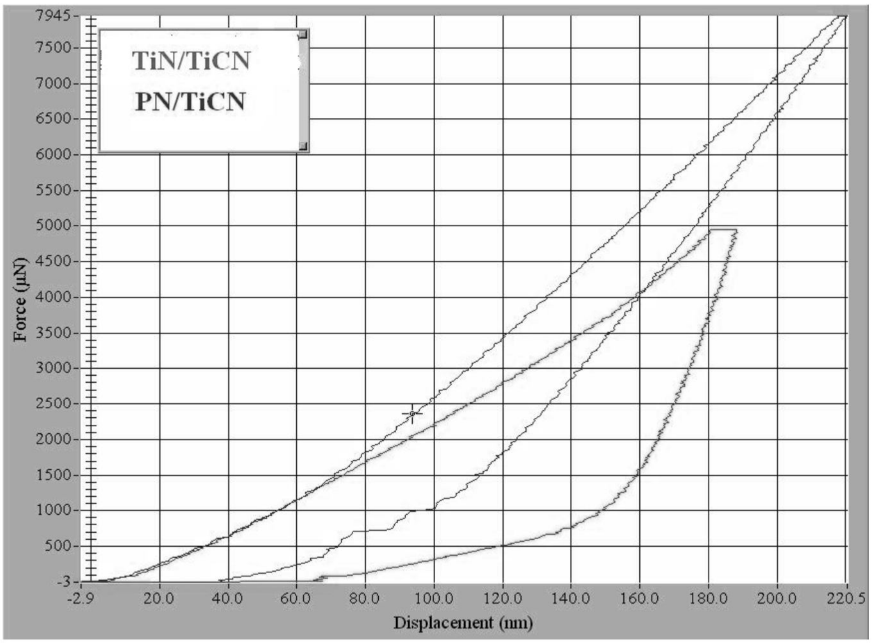

Fig.6. load-displacement curves.

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A nanoscratching test can represent a qualitative evaluation of the tribological properties of the surface layer of the material. This method was mainly applied and described in detail by Hodzic et al. [16]. As the test proceeds, the normal and lateral displacement of the indenter tip and also the normal and lateral forces which are applied to the specimen, are simultaneously recorded. The coefficient of friction μ is defined as the ratio of the lateral force to the normal force (Fig.7). As can be seen in Fig.8, the coefficient of friction experiences minor fluctuations around 0.3 for PN/TiCN and 0.2 TiN/TiCN multilayers. The upward trend in the depth profile is due to the accumulation of the deformed material in front of the indenter tip. Deformed materials for TiN/ TiCN film is less than PN/TiCN layer because its hardness is

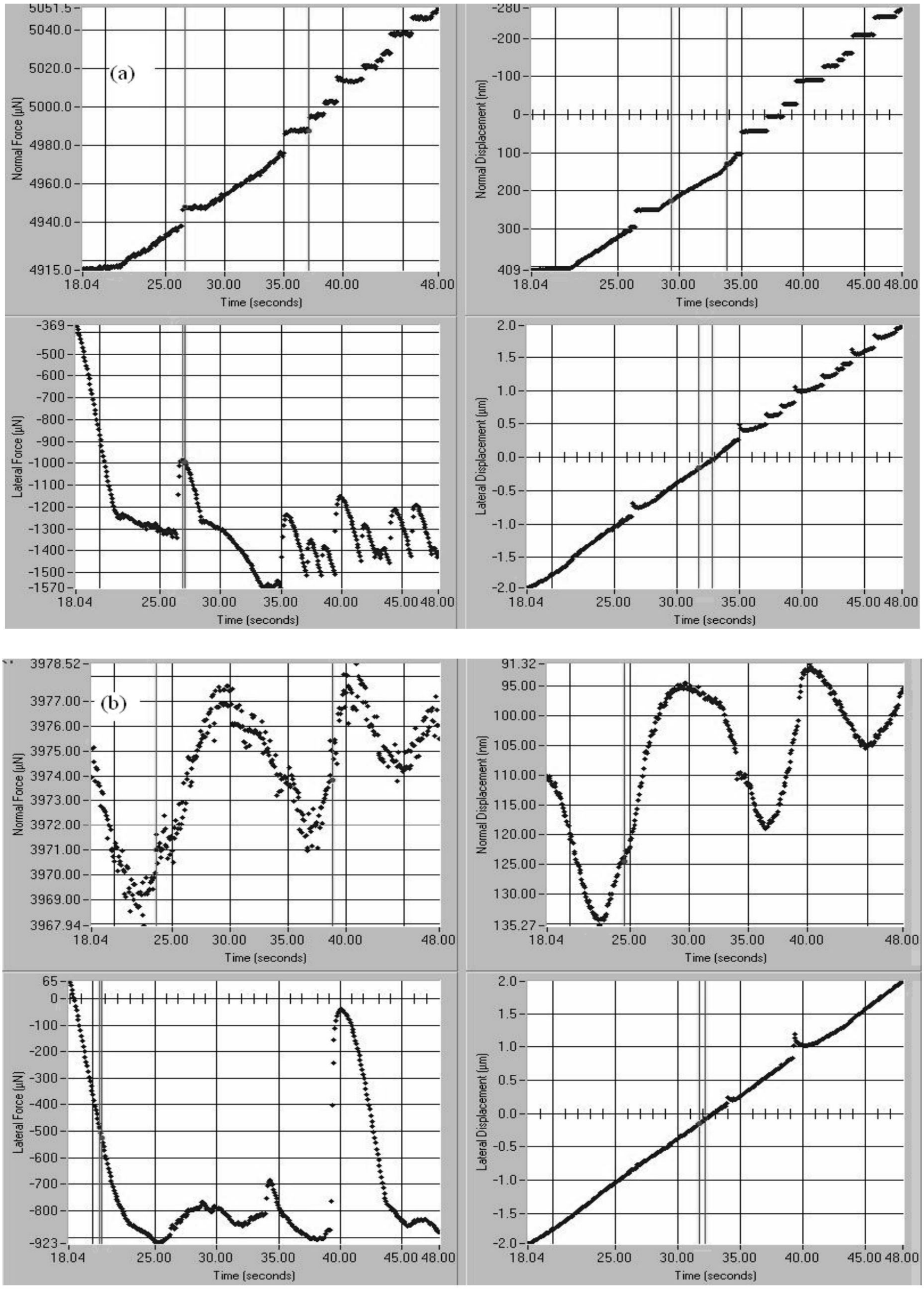

Fig.7. plots of the lateral, normal force vs. displacement upon scratching
a)PN+TiN, b)TiN+TiCN.

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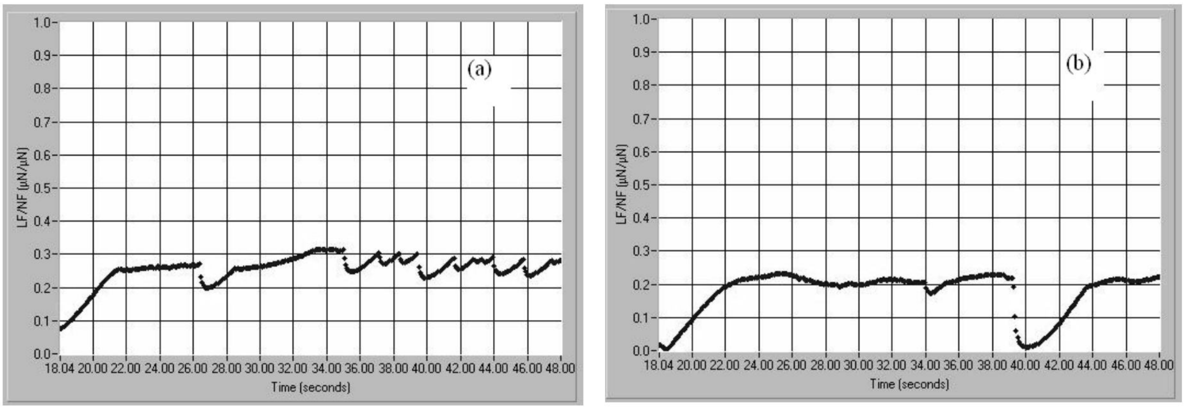

Fig.8. friction coefficient for different film a) PN/TiCN, b) TiN/TiCN.

lower. However, as presented in Fig.8, significant deviations in coefficient of friction occur during the scratching of the interface region.

4. CONCLUSIONS

In this work, plasma nitriding/TiCN and TiN/TiCN multilayers on AISI H12 substrate has been deposited by PACVD. We have evaluated the multi layers structure with respect to chemical composition, morphology, hardness and wear resistance. The major conclusions are the following:

1. TiN/TiCN film structure is denser because the plane (111) orientation is the densely packed plane.
2. SEM micrographs show clearly that the TiN/TiCN coatings on H12 steel are free of columnar structure, become denser, and have a finer microstructure than PN/TiCN coatings.
3. The root-mean-square (RMS) roughness of the final surface TiCN layer are about 120 nm in PN/TiCN and 99.4 nm in TiN/TiCN multilayer films.
4. The hardness of TiN/TiCN film was 12.75 GPa while it was 5.4 GPa for plasma nitriding/TiCN film, respectively. It was according to results of AFM, because TiN/TiCN multilayer was denser.

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