International Journal of Science and Research Archive, 2020, 01(02), 022–031

International Journal of Science and Research Archive

Cross Ref DOI: 10.30574/ijsra

Journal homepage: https://www.ijsra.net/

(RESEARCH ARTICLE)

Microstructural effects of the substrate on adhesion strength and mechanical properties of TiN Thin Films

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Publication history: Received on 25 November 2020; revised on 05 December 2020; accepted on 07 December 2020

Article DOI: https://doi.org/10.30574/ijsra.2020.1.2.0037

Abstract

Microstructure of base material plays an important role in adhesion strength and mechanical properties of Titanium Nitride (TiN) coating especially to increase the lifecycle of parts when in practical use. Present study covers the influence of grain size/microstructure of plain carbon steel (tailored via heat treatment) on TiN thin films deposited by physical vapor deposition (PVD) technique. Strong effect of grain size (microstructure) on adhesion strength of TiN thin films on annealed, normalized and quenched substrates have been observed. Mechanical characterization of TiN films e.g. Elastic modulus (E), Hardness (H_v), Stiffness (S) etc. have been studied via nano-indentation technique. TiN thin films failure investigation has been performed with Micro scratch testing under progressive load. Film exfoliation under critical loads has been corroborated via scanning electron microscopy (SEM). The results showed that TiN films deposited on fine microstructure substrate possess excellent mechanical properties and good adhesion strength as compared to coarser microstructure substrate. Insights of this study might be helpful in designing engineered thin films on optimized microstructures.

Keywords: TiN; PVD; Nano-indentation; SEM/EDS; Micro-scratch

1. Introduction

TiN thin films are well known for their excellent mechanical properties i.e. high hardness (H), elastic modulus (E), good wear resistance and low frictional coefficient (Fc). These characteristics make TiN an excellent candidate as protective and functional coating to increase the lifecycle of machining tools [1] or act as an oxidation barrier in semiconductor (SMD) devices [2]. In recent past, many efforts have been made to improve the adhesion and wear properties of TiN films for their effective application [3-5].

Y.-G. Kim et al [6] studied Si3N4 (ceramic) substrate provided with TiN, PVD (Physical Vapour Deposition) coating. Authors used orthodox ceramic manufacturing method to prepare substrate and studied effect of microstructural grain size on adhesion strength of TiN coating. K.D. Bakoglidis et al [7] studied adhesion of Carbon Nitride coating on steel substrate (AISI-52100). Authors have investigated the effect of low-temperature metal pre-treatments in order to improve the adhesion of CNx film on steel substrates, which is critical for tribological applications. In turn, Vera et al [8] studied steel substrate (AISI 8620) with TiN PVD deposition, in order to evaluate the friction coefficient and wear rate at room temperature conditions. Authors found that the TiN coating offered good wear resistance performance F. F Komarov et al [9] investigated TiN coating on AISI 304 steel substrate and studied micro hardness and wear properties. Song-sheng LIN et al [10] studied effect of surface roughness on adhesion strength of TiN on stainless steel. It is worthwhile to note that strong adhesion is the key to achieve high performance TiN coating.

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A number of parameters have been found which influence adhesion strength of TiN coating with substrate in Physical Vapor Deposition (PVD) system. PVD process always results in excellent adherence of coating and provides uniform thickness. Typical coating thickness obtained from PVD process about is 3-5 µm. Typical characteristics of PVD coatings mainly depend upon substrate hardness, coating thickness, internal stresses and microstructure (particularly grain size) of substrate etc. [11-13]. Microstructure/grain size of substrate can be controlled by heat treatment process, which involves controlled heating and cooling in solid state which results in controlled microstructure of the material, ensuring the optimal properties [14].

Owing to controllability of its microstructure and formability, plain carbon steel is used in wear plates or liners, which finds many applications in machines or components including shredders, casting equipment, mill & lining equipment etc. [15]. Owing to well established relation of TiN thin films adhesion strength with mechanical properties e.g. elastic modulus, Hardness, stiffness and wear properties [16] it would be imperative to study TiN films on carbon steel, its coating adhesion and tribological properties.

The aim of present work is to study the influence of microstructure/grain size difference of the substrate material on mechanical and adhesion characteristics of TiN coating on carbon steel.

2. Experimental work

In these experiments, the substrate used was AISI-1015 with dimensions of L= 50.8 mm, W= 25.4 mm, T=12.7 mm). A detailed chemical analysis of the substrate performed using optical emission spectrometer (OES) is reported in Table 1.

Table 1 Chemical Composition of substrate samples (AISI-1015)

Elements	**Fe**	**C**	**Mn**	**P**	**S**	**Si**	**Cu**	**Mo**
Wt %	Base	0.151	0.387	0.016	0.020	0.001	0.043	0.311

The substrate samples were heated at the rate of 5 ˚C/min till austenitic range in muffle furnace (SN-1700 Sinoder-Henan, China), soaked for 25-30 minutes at same temperature. The samples were further cooled at different rates to achieve different grain sizes. The heat-treated samples were prepared (grinded and polished) to 0.1µm grit paper according to ASTM standard and then etched in Nital (Nitric Acid & Ethanol) solution to reveal the microstructures. The TiN films were deposited onto the substrates via Physical vapor deposition (PVD) technique by using (PLATIT/π80®) system. Before coating, samples were cleaned by using ultrasonic bath and fixed on carrousel holders while rotation speed of carrousel around the vertical central axis was kept 15 rpm. During deposition, negative DC bias of -80 V was applied to the substrates under working pressure of 1.7 Pa in nitrogen gas atmosphere.

After deposition of coating, different characterization techniques were used. Microstructural analysis was carried out by using Image Analyzer optical microscope (LEICA DM4000M) at the magnification of 100X.

Calotest (VDI-3198) [17] was performed to measure coating thickness by using (KaloMax®-BAQ).A rotating ball of 30 mm diameter was pushed and rolled on to the film surface with a preselected load. Abrasive slurry was supplemented to the contact zone. Spherical depressions onto the film surface made by steel ball could clearly be seen in Fig.3. Resulted impressions were viewed under the optical microscope and highlighted (refer to red rings in fig. 3) at 20X magnification and values of X and Y were documented. Coating thickness is calculated by using the following relation and reported in Table 3:

$$R = \frac{X^2 - Y^2}{4.D.1000} \qquad \text{Eq. (1)}$$

Where R is coating thickness, X & Y are outer, inner diameter respectively and D is ball diameter (30 mm in this study).

Mechanical properties (i.e. elastic modulus (E_{IT}), hardness (H_{IT}) and Stiffness (S) etc.) of substrate and TiN films were assessed via nano indentation (NHT-CSM® instruments Switzerland) technique using 40mN load with a pause of 15 sec at the highest load. Three (03) indents were marked on each sample; average $H_{IT,}$ E_{IT} and S were calculated by employing Oliver and Pharr rule. Adhesion strength of TiN films on steel substrate was studied by micro scratch tester (MST/CSM Inc., Switzerland) using Rockwell indenter with diamond tip of 100 µm radius. Progressive type of loading was employed with starting load of 0.1N and final load of 20N with scratch speed of 1.50 mm/min. Scratch of “3 mm” were marked on each sample and analyzed under Nikon® (E Plan∞/0 EPI Series) microscope, adhesion strength was assessed through critical loads (Lc). The complete failure of the coating was determined by the signals of acoustic emission (A.E). All the samples were ultrasonically cleaned prior to indentation and scratch testing.

3. Results and discussion

Based on the experimental work carried out, following observations are made:

3.1. Microstructural Analysis

Fig. 1 (a, b & c) shows optical micrographs of annealed, normalized and quenched substrates respectively. It is pretty clear that heat treatment has influenced the morphology of substrate grain size i.e. annealed microstructure (with pearlite and ferrite) possess characteristic grain size, while normalized structure exhibited relatively finer grain size. However, the quenching resulted into needle like morphology of grains which is characteristic of martensitic formation.

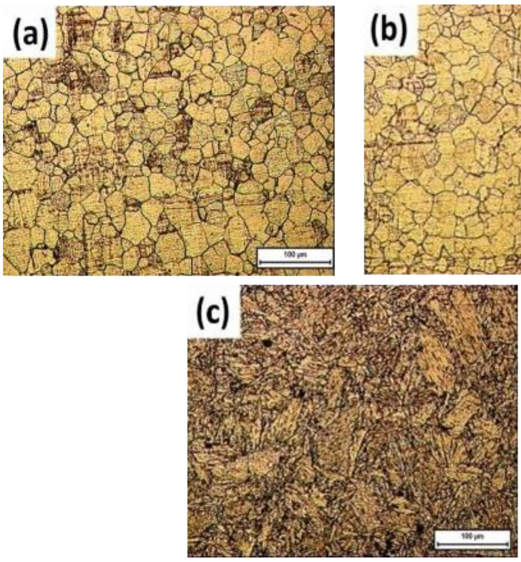

Figure 1 Optical micrographs of (a) Annealed, (b) Normalized, (c) Quenched Substrates samples

3.2. Coating Thickness Measurement of TiN film

Fig.2 shows the optical images of the impressions made during Calotesting. The boundaries of impressions are also highlighted to evaluate their diameters. The thickness of film is shown in the Table 2. It is clear from the table that the thickness of TiN is almost the same for all substrates.

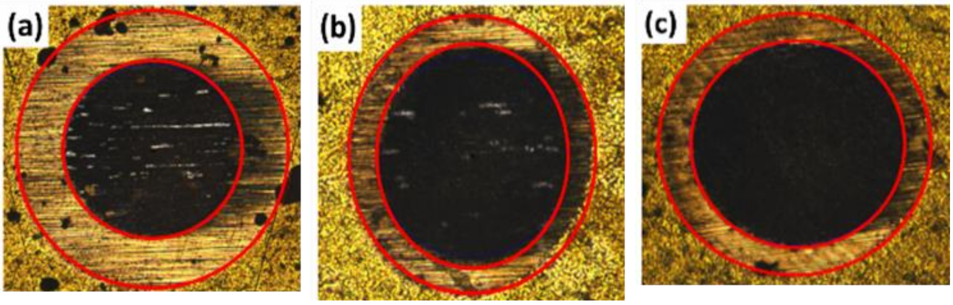

Figure 2 Spherical depression onto the TiN films (under optical microscope at 20×)

Table 2 TiN Film thickness measured by Calotest

Parameter	Annealed (a)	Normalized (b)	Quenched (c)
Thickness (micron)	3.35	3.15	3.01

3.3. Nano indentation

Fig. 3 presents characteristic nano indentation load-displacement curves for TiN film on respective substrates with a Berkovich tip (indenter) at a maximum load of 40 mN. A maximum penetration depth of ~300 nm is observed against the film thickness of about 3350 nm, deposited on annealed substrate, which gives an indication that substrate is not revealed and hence mechanical properties of pure film are obtained. There is no particular event i.e. as pop-in and/or pop-out observed during the loading or unloading procedure. Further, there is clear peak shift for the respective heat-treated sample i.e. annealed sample undergoes highest while quenched one experiences least penetration depth. However, normalized sample shows in between response of penetration depth versus applied load, for clear view inset is shown in the Fig.3.

In order to have more evidence of substrate microstructure effect on film adhesion, it is necessary to study the bounce back effect of film since it has direct relation with elastic modulus (E) i.e. more the film bounce back higher will be the elastic modulus (E). Nano indentation data is employed to take Penetration depth (Pd) maxima and minima at unloading curve for each sample and bounce back distance is reported in Table-3. It is evident that quenched microstructure exhibits extreme bounce back (higher Elastic Modulus) while annealed microstructure (with coarser gain size) shows least bounce back (least Elastic Modulus). These facts support the results reported in Fig. 3.

Table 3 Bounce back distance of PVD deposited films on samples (a, b & C)

Annealed (nm)	Normalized (nm)	Quenched (nm)
116	117	120

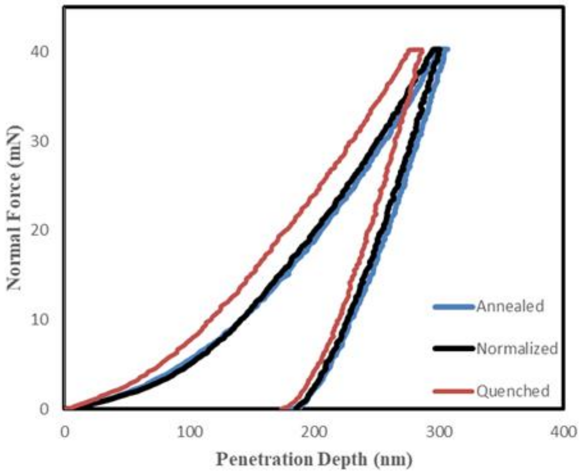

Figure 3 Load (F_n) -Penetration depth (P_d) curve for TiN coated samples (a, b & C)

Nano indentation technique is imperative technique to evaluate instrumented hardness (H_{IT}) and elastic modulus (E_{IT}). These two could be quantified as follows;

Instrumented Hardness= $H_{IT}= \frac{Fm}{Ap}$ Eq. (2)

Instrumented Elastic Modulus=$E_{IT}= \frac{\sqrt{\pi}S}{2\beta\sqrt{Ap}}$ Eq. (3)

Where F_m is maximum load at ordinate (y-axis), A_p is the projected area, "S" is stiffness of film, "β" is indenter geometry correction factor (for Berkovich=1.034).

H_{IT} & E_{IT} of respective samples TiN films are evaluated according to the Oliver and Pharr (O&P) rule [17] and presented in Fig. 4. Highest value of H_{IT} is found for quenched substrate film and lower most is observed for annealed one, however normalized substrate film H_{IT} is found to be transitional. As far as TiN film instrumented elastic modulus (E_{IT}) is concerned, its behavior has been found in connection with H_{IT} i.e. E_{IT} increased with rise in cooling rate (from annealed to normalize and quenched substrate).

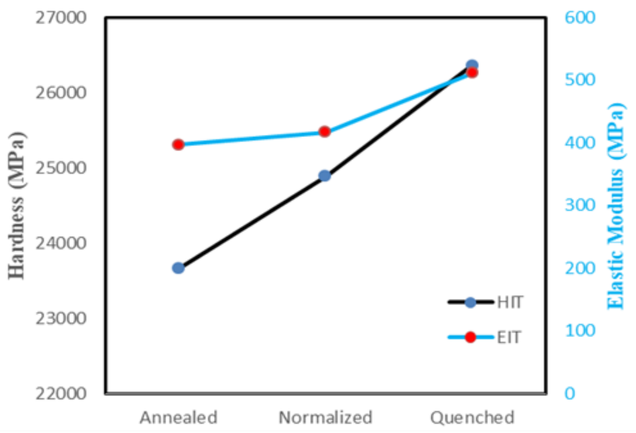

Figure 4 Instrument Hardness (H_{IT}) and Elastic Modulus (E_{IT}) variation for TiN films

In order to evaluate Vicker's hardness (H_V) and Stiffness (S) of thin films Oliver and Pharr rule has been used. H_V and Stiffness (S) of film could also be determined via following relation;

$$\text{Hardness}= H_V= \frac{Fm}{Ad} \qquad \text{Eq. (4)}$$

$$\text{Stiffness}= S= \frac{dP}{dh} \qquad \text{Eq. (5)}$$

Where A_d is developed area ($\therefore A_p=9.81A_d$), dP/dh determines the slope of unloading curve during indentation testing. Vicker's hardness "H_V" and stiffness "S" have been evaluated and reported in Table 5. For reference purpose slope of respective film unloading curve is presented in Fig. 5. All the parameters show average values taken from three (03) indents marked by nano-indentation technique.

Table 4 Bounce back distance of PVD deposited films on samples (a, b & C)

Specimen ID	**Annealed**	**Normalized**	**Quenched**
Hardness (MPa)	23662	24885	26361
Elastic Modulus (MPa)	397	417	511

Table 5 Mechanical properties of TiN films of samples (a, b & c)

Parameter (O&P)	**Annealed**	**Normalized**	**Quenched**
H_V	2191	2304	2441
S	0.482	0.486	0.543

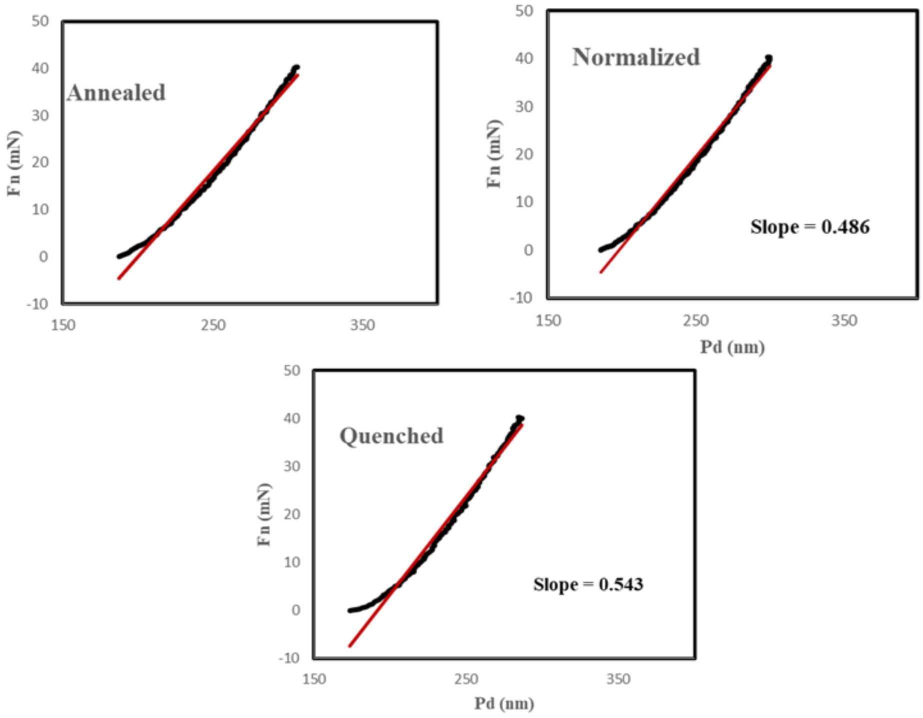

Figure 5 Stiffness (S) evaluation for TiN films of samples (a, b & c)

3.4. Adhesion Strength

Micro scratch testing has been carried out to evaluate the adhesion of film with substrate and to assess the critical loads (Lc1, Lc2 & Lc3) of failure. All coated substrates (annealed, normalized & quenched) are undertaken three (03) scratches by setting parameters presented in Table 6.

Table 6 Scratch parameters and indenter specifications

Scratch Parameters			
Type	Progressive	F_n contact	0.03 N
Begin Load (N)	0.1	F_n Speed	5 N/s
End Load (N)	20	F_n Remove speed	10 N/s
Loading rate (N/min)	10.02	Approach speed	2 %/s
AE Sensitivity	7	Speed (mm/min)	1.51
Scanning load (N)	0.03	Length (mm)	3
Indenter Specifications			
Type	Rockwell	Material	Diamond
Radius (µm)	100	Sr. No.	I-105

Pattern of film deformation during scratch testing for respective substrate is presented in Fig. 6 (a, b & c). Critical loads (LC1, LC2 & LC3) are marked while last image shows the end of scratch. Commonly, LC1 is assigned where “fish bone” cracking initiates, merging of these cracks from both sides of crack trajectory is designated by LC2, while LC3 identifies the film chipping off. The appearance of bright spots inside the crack route indicates the film failure. Most radical failure is observed from LC3 till end of the crack.

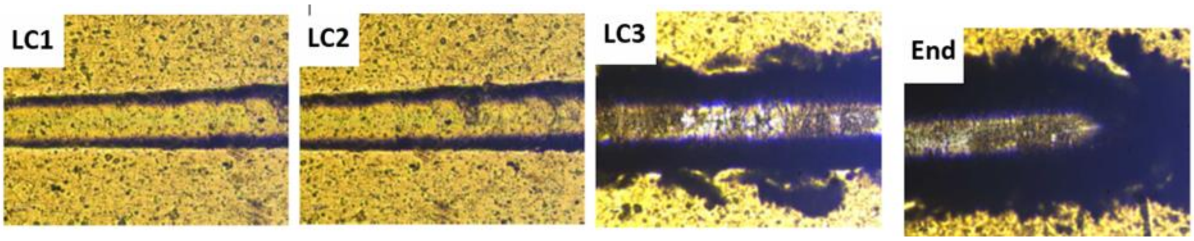

Figure 6 (a) Optical view of critical loads (Lc1, Lc2 & Lc3) and end of scratch for TiN film on Annealed substrate

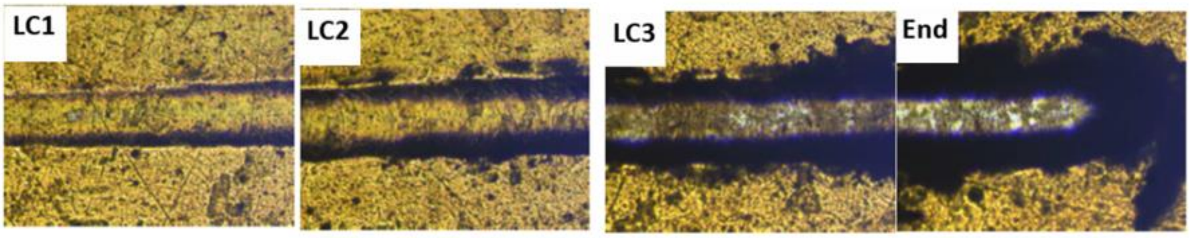

Figure 6 (b) Optical view of critical loads (LC1, LC2 & LC3) and end of scratch for TiN film on Normalized substrate

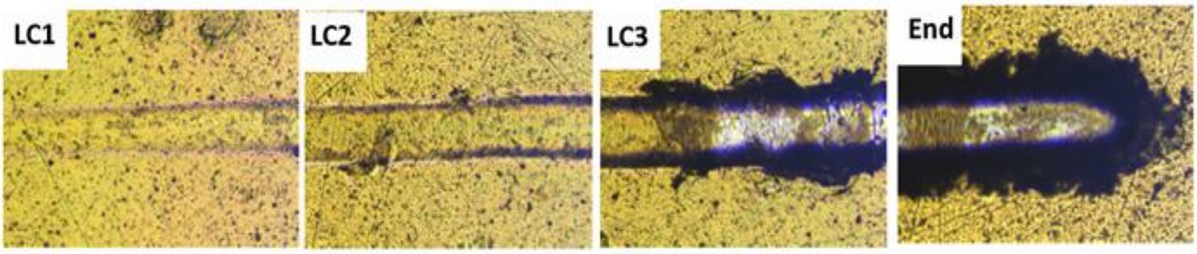

Figure 6 (c) Optical view of critical loads (LC1, LC2 & LC3) and end of scratch for TiN film on Quenched substrate

Comparison of critical loads is presented in bar graph given in Fig. 7. It can be seen in results that there is vivid difference in critical loads of respective samples, which shows variation in film adherence and strengthen the argument of heat treatment process variance on film adherence. The first critical load is highest for quenched coated sample, while the final load of complete failure is also highest in case of quenched one.

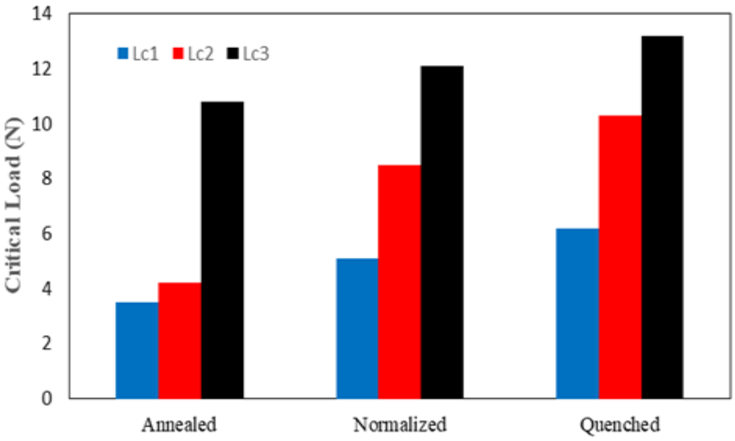

Figure 7 Bar graph showing Critical loads for respective (Annealed, Normalized, Quenched) samples

During scratch testing, high acoustic emission sensitivity was set (as mentioned in Table 5). Acoustic emission (AE) comes out in the form of peaks when coating chips off or delaminates from substrate. In current study comprehensive

AE has been recorded by the MST sensor which is re-plotted against Load in Fig. 8. Most intense peaks of AE sensitivity are obtained for the quenched specimen, showing signs of better film adhesion.

It can be clearly seen in Fig. 8 that AE is recorded for TiN thin film deposited on quenched substrate possess the highest intensity which depicts excellent adhesion on this particular type of substrate.

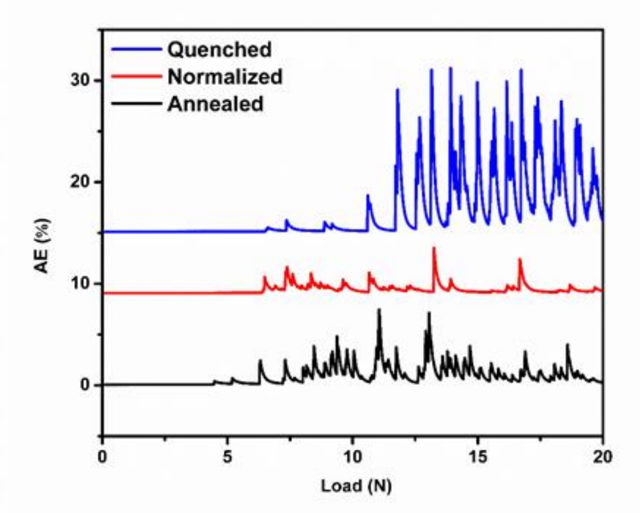

Figure 8 Acoustic emission curves vs MST applied load for studied TiN thin films

During Micro-scratch testing (MST) there is pretty much possibility that impurity/dust particles (available on thin film surface) may come in contact with indenter. These factors create complications in concluding whether the thin film chipped off properly under the MST or not. In order to verify the exfoliation of substrate SEM/ EDX analysis of scratch (marked on thin films) is carried out. Fig. 9 shows the scratch geometry surface while Fig. 10 (a & c) shows localized SEM images of Micro-scratch on TiN thin film (with "spectrum-1" for film analysis) with respective EDX in (b) while spectrum-5 for surface exfoliated after scratch with respective EDX in (d). It is quite clear that spectrum-1 (thin film) shows the presence of Titanium (Ti) and Nitrogen (N) peaks while spectrum-5 (exfoliated surface) shows the composition of steel which confirms the substrate composition. These outcomes strengthen the MST and critical load analysis. EDX analysis have been done for all studied samples, for convenience purpose only fine grain substrate thin film results are reported in Fig. 10.

Figure 9 SEM image of scratch (3mm length) marked by Micro-scratch tester

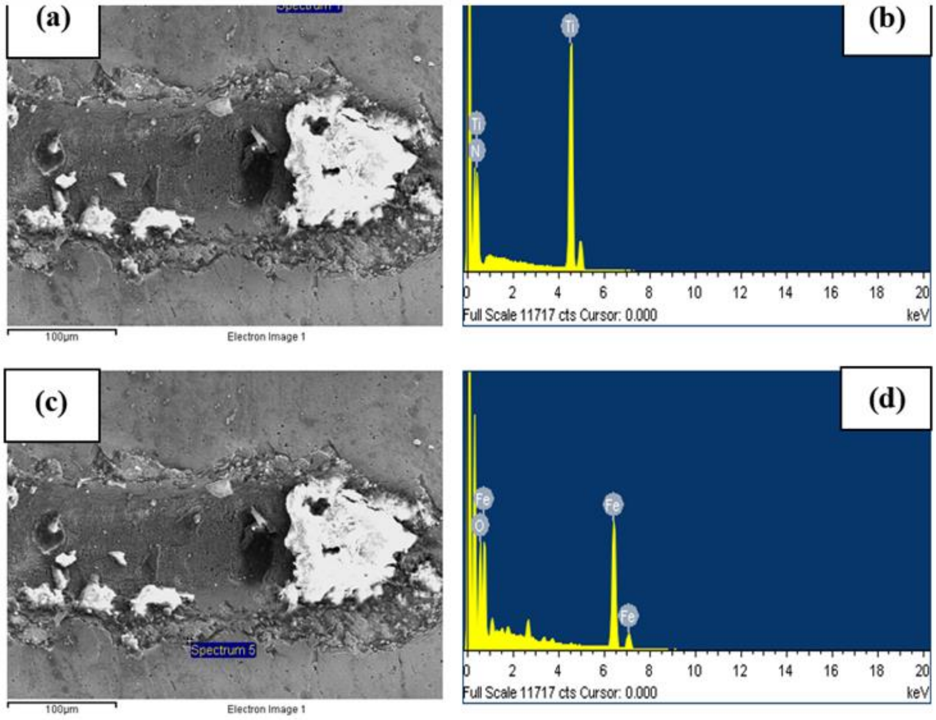

Figure 10 SEM image and EDX analysis of scratch on TiN thin films

4. Conclusion

Microstructure of substrate plays an important role on TiN thin films adhesion strength and mechanical properties. Thin films of TiN have been deposited onto plain carbon steel substrates of different grain size/microstructure. Data obtained from nano-indentation technique revealed Maximum Elastic modulus (E_{IT}) for finest grain substrate (quenched). Micro-scratch testing exposed the film pile up for coarser microstructure substrates and film cracking for fine microstructure based on critical loads L_C) and Acoustic emission peaks. Exfoliation of TiN thin films under critical loads (assigned by MST) and substrate exposition has been verified by SEM/EDX. It can be concluded that TiN films deposited on fine microstructure substrate possess excellent mechanical properties, good adhesion strength as compared to coarser microstructure substrate.

Compliance with ethical standards

Acknowledgments

I would like to acknowledge the support of my research team for producing high quality PVD coatings and their characterization. I also thankful to management of PCSIR Labs., Lahore for their moral support. I expect the benefits of this research work may be quite breedful for the surgical industry of Pakistan.

Disclosure of conflict of interest

The authors declare no conflict of interest.

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