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Comparative study on microstructure, crystallite size and lattice strain of as-deposited and thermal treatment silver silicon nitride coating on Ti6Al4V alloy

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Abstract. Silver silicon nitride coating were deposited on Ti6Al4V alloy using physical vapor deposition magnetron sputtering technique. Field Emission Spectroscopy (FESEM), Electron Dispersive Spectroscopy (EDS) and X-ray diffraction (XRD) were used to characterize as-deposited and after heat treatment of AgSiN coatings in order to understand the morphology, compositions and structure. Meanwhile, in determining the crystallite size and lattice strain, the simplified Williamson-Hall plot method was utilized. The heat treated coated sample shown to reveal granular surface structure, bigger crystallite size and lattice strain as compared to the as-deposited coated sample.

1. Introduction

Titanium and its alloys had been used in wide range of applications such as machining [1], medical and aerospace. The choice of this alloy is due to its excellent properties such as high strength to weight ratio, corrosion resistance [2] and good biocompatibility [3]. Nevertheless, taking into consideration releasing of Al and V elements as well as implant associated bacterial infections, investigation and modifying titanium alloy surface are still needed and ongoing [4]. The investigations including during fabrication process like coating the surface as well as the post- treatment process like heating.

In coating, structure morphology, particle size and lattice strain play a significant role while x-ray diffraction peaks has become a very powerful tool to extract the information and to study the coating properties. There are several analysis methods that could be used to analyze the crystallite size and lattice strain of the coating. Some of the analysis technique are Scherer's equation, Warren-Averbach analysis (W-A), Williamson-Hall plot analysis (W-H), Rietveld refinement [5, 6] and Fourier analysis technique. Scherer's equation is a well-known equation use to estimate the crystallite size by using the full width at half maximum (FWHM) of diffraction peaks. However, the Scherer's formula give the lower bound of the crystallite size since the equation neglect the broadening from other important factors such as inhomogeneous strain and instrumental effect. Meanwhile, Warren-Averbach analysis

need at least two reflections along the same crystallographic direction [7]. Warren-Averbach followed by Fourier technique, which need to convolute size and strain broadening make these method quite difficult to carry out [8]. At the same time, Williamson-Hall plot analysis which consider to be an average method but still hold an unavoidable position for crystallite size determination [9].

In this study, the titanium alloy (Ti6Al4V) substrates were coated with silver silicon nitride coating using a reactive magnetron sputtering physical vapor deposition (PVD) [10, 11]. In order to investigate and compare the crystallite size and lattice strain for the as-deposited and heat treatment sample, Williamson-hall plot analysis method was employed.

2. Materials and Method

The material selected for this study was Ti6Al4V and they were cut into sizes of 15 x 15 x 2 mm using wire cut electrical discharge machining (EDM) machine. The samples then were grounded with silica papers starting from 800, 1000, 1500, 2000 and 2500 grit by rotation 90^0 at every change of silica paper grit. Next step, samples were polished using polishing cloth with the help of diamond liquid of 6 μm. In order to remove grease, contaminants and dirt, samples were ultrasonically cleaned in ethanol for 15 mins and rinse with distilled water. Samples were dried using blow dryer before loaded into the deposition chamber.

Deposition process was done using SG Control Engineering Pte. Ltd machine which utilized the physical vapor deposition magnetron sputtering technique (PVDMS). The chamber was vacuum to base pressure of $2x10^{-5}$ Torr and working pressure was maintained around $6.5x10^{-3}$ Torr after flow in of argon gas. Silver and silicon target both with 99.99% purity were connected to DC and RF power supply respectively. Oxide layer and dust on target were removed by pre-sputtering in pure argon gas for 15 minutes with the shutter shut the targets. Silver interlayer was deposit for 15 mins meanwhile the second layer was co-sputtering both silver and silicon target for 20 mins. Other deposition parameters can be referred to Table 1.

Table 1. PVD deposition parameter variable.

Parameter variables	Values
DC power (Watt)	20
RF power (Watt)	100
Bias voltage (V)	150
Argon flow rate (sccm)	20
Nitrogen flow rate (sccm)	8
Temperature (^{0}C)	100
Deposition time (mins)	20

The specimens were taken out of the chamber after thin film deposition completed. In order to investigate the effect of heat treatment on coatings, the as-deposited coatings were put inside an Argon purged furnace. With continuous monitoring, the samples were heated up to 400°C in pure argon gas environment with heating rate of 1°C/min. The samples were kept in the 400°C conditions for 60 minutes. Samples then were let cooled down naturally before they were taken out for characterization. The schematic diagram of temperature as function of time of thermal treatment was shown as figure 1.

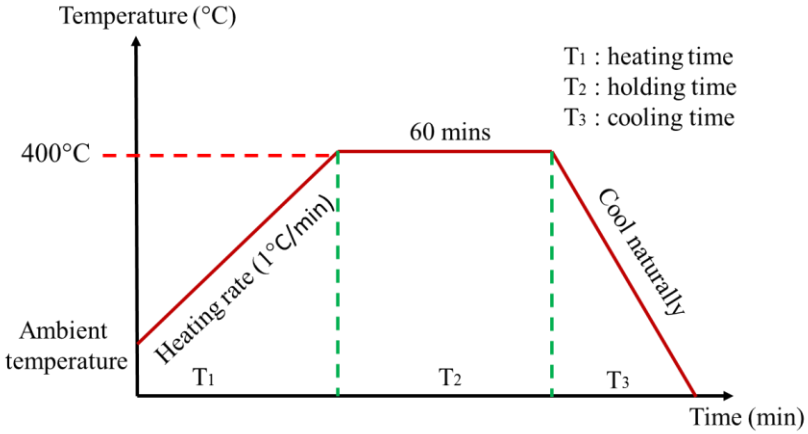

Figure 1. Schematic diagram of temperature as function of time of thermal treatment.

3. Results and discussion

Figure 2 (c)(d) illustrated the digital photograph and FESEM image of as –deposited coating and after thermal treatment at 400^0C, respectively. In digital photograph, we can see that no obvious changes were observed on the coating surface. In order to get detailed image, we further investigated samples' microstructures using field emission electron microscope (FESEM) attached with electron dispersive spectroscopy (EDS). The detailed image presented in Figure 2 (b)(d) showed all coatings had granular surface structure background with some white particles were spotted that labelled as a, b and c on the surface. Using point and spot analysis from EDS, white particles were confirmed to come from silver element. Meanwhile, the backgrounds of coatings were mixture of silver, silicon and nitrogen elements with atomic percentage of 33.1, 1.9 and 1.9 atomic%, respectively. It looks like there were no significant difference between the compositions of as-deposited and after heat treatment coating. At the same time, other elements were also noticed like carbon, insignificant gases and moisture which believed to come from the deposition chamber and environment thus will not further discussed.

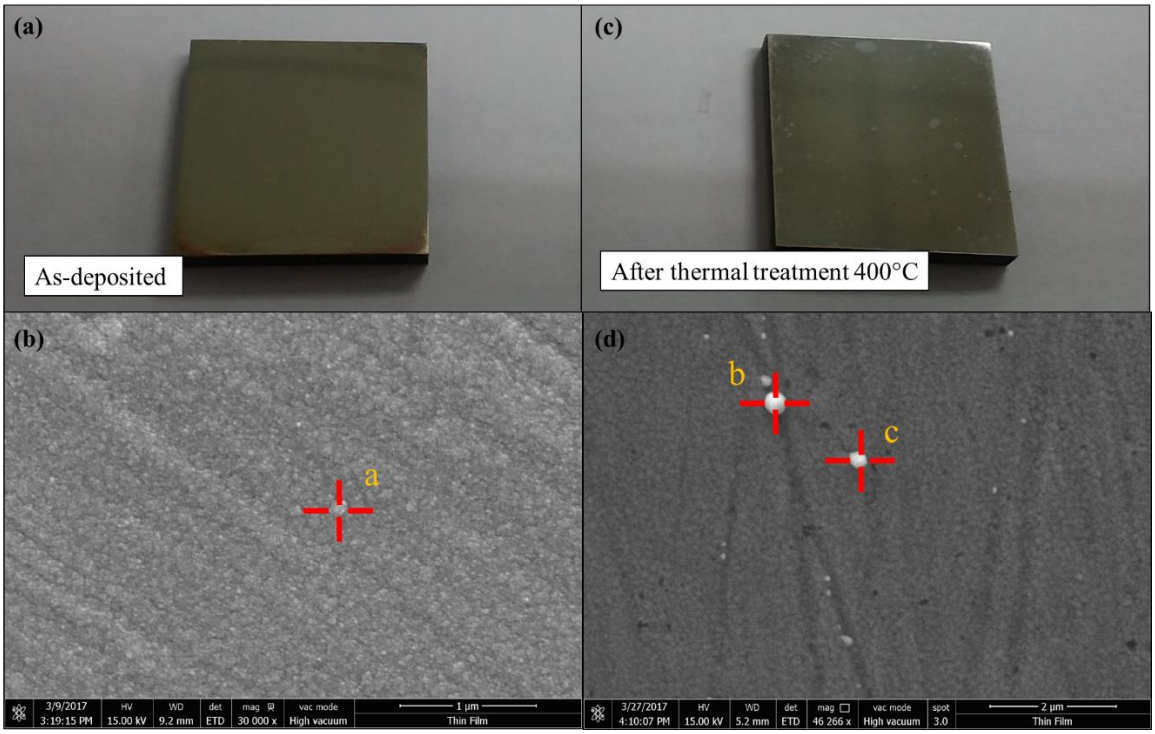

Figure 2. Digital photograph and surface FESEM image of (a-b) as-deposited coating and (c-d) after 400^0C of heat treatment.

Cross-sectional FESEM image and EDS analysis for both as-deposited and after thermal treatment were presented in Figure 3 and Figure 4 accordingly. It was observed that the coating structures were changed from columnar and loose structure bilayer coating for as-deposited sample to dense, compact and homogeneous monolayer of coating after heat treatment sample. It was believed that heat treatment causing the interlayer to diffuse into the subsequent layer or into the substrate therefore forming the monolayer. This can be proved from the mapping EDS analysis in Figure 4 which showed the dispersion of each element in the coating layer. By comparing both coatings, it is assured that after thermal treatment the coating became more compact, dense and displaying small granular size.

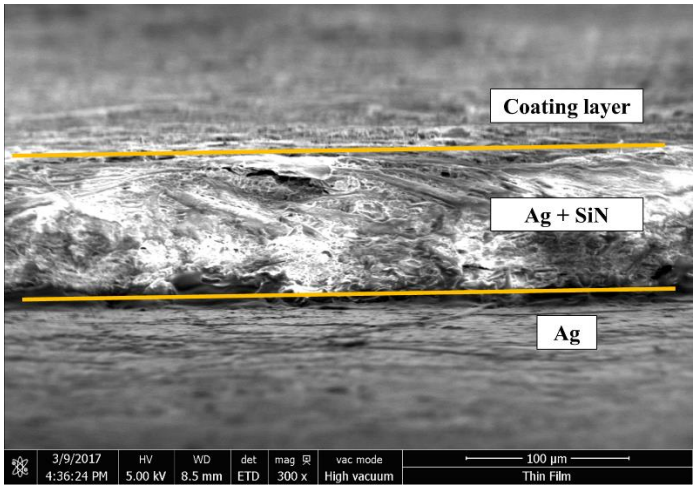

Figure 3. FESEM image cross section of as-deposited silver silicon nitride coating at -150V.

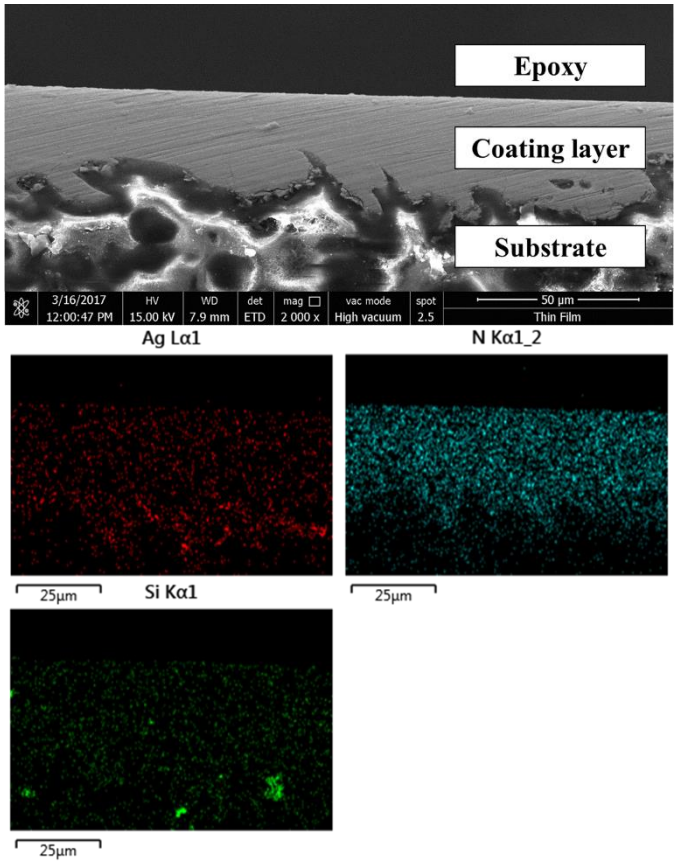

Figure 4. FESEM image and EDS analysis cross section of silver silicon nitride coating after heat treatment.

The X-ray diffraction profile analysis were conducted for all samples and all peaks with their respective phases and h, k, l (hkl) values were presented in Figure 5. For both samples of as-deposited coating (Figure 5.a) and heat treatment (Figure 5.b), phases detected in the diffractogram were identical. Silver phase with ICSD No. 98-004-4387 was found at peak positioned $2\theta = 38.1°$, 44.19°, 64.48° and 77.46° with crystal orientation of (111), (002) and (113) respectively. The interaction between substrate which is titanium alloy (Ti6Al4V) with the coating was noted with the present of intermetallic phase of $AgTi_3$ (ICSD No. 98-005-8370) at positioned $2\theta = 38.1°$. In addition, silver nitride, AgN peak was identified at $2\theta = 53.17°$ (ICSD No. 98-018-5555). Silicon nitride, Si_3N_4 was noted at $2\theta = 40.35°$ with ICSD No. 98-003-5660. The silicon nitride amorphous phase contributed to the relatively low intensity peak in the diffraction pattern in Figure 5 (a) and (b). Whereas, there was one peak that belong to the combination of all three elements namely silver Bis (silicate) nitrate with chemical formula Ag_9 (SiO_4) NO_3 or $Ag_9NO_{11}Si_2$ (ICSD No. 98-006-2402). Clearly, after heat treatment was applied to the samples, all peaks in diffractogram become well defined while the intensity was doubled (sharper). Applying heat treatment usually may cause the materials to reorganize and re-oriented themselves, which then contributed to the well-defined structure of peaks.

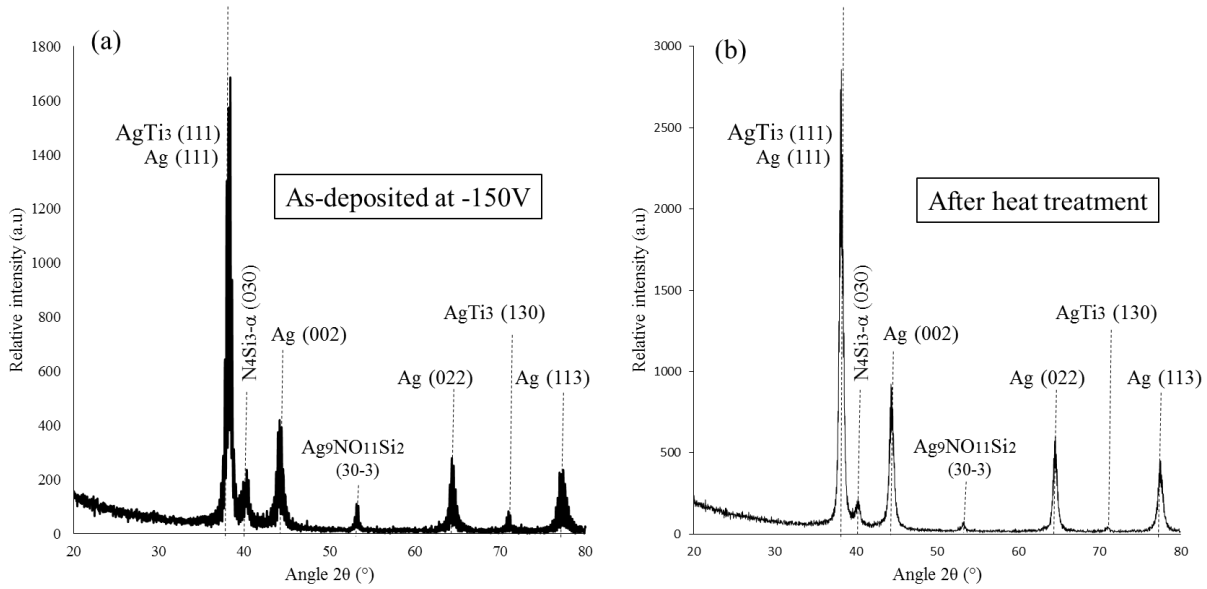

Figure 5. XRD diffractogram of silver silicon nitride coating on Ti6Al4V alloy (a) as-deposited and (b) after heat treatment.

From the XRD peaks, the value of crystallite size and lattice strain can be obtained. There were many methods can be used to calculate these values such as Williamson and Hall method (W-H), Warren Averbach analysis (W-A), Rietveld refinement and pseudoVoigt function. In this study, we employed the W-H method which is a simplified method and most commonly used. The Scherer's equation, a well-known equation in determining crystallite size can be expressed as,

$$\tau = \frac{k\,\lambda}{\beta\ cos\,\theta} \tag{1}$$

Where τ is the mean of grain size, *k* is a dimensionless shape factor (typical value of 0.9), λ is the x-ray wavelength (Cu Kα cathode wavelength λ=15.405 nm), **β** is the broadening of full width at half maximum (FWHM) of the peak and θ is the Bragg's angle in degree unit. The broadening peaks can be attributed to crystallite size as in equation (2),

$$\beta crystallite = \frac{k\,\lambda}{L\,cos\,\theta} \tag{2}$$

And broadening due to strain as in equation (3),

$$\beta\varepsilon = C\,tan\,\theta \tag{3}$$

Therefore, the sum of broadening due to crystallite and lattice strain in equation (4) is gained by subtracting the broadening of the instrumental effect and broadening of diffraction peak.

$$\beta total = \beta crystallites + \beta\varepsilon \tag{4}$$

Substituting the equation of $\boldsymbol{\beta}_{crystallites}$ and $\boldsymbol{\beta}_{strain}$ into $\boldsymbol{\beta}_{total}$, we will obtain equation as follows.

$$\beta total = \frac{k\,\lambda}{L\,cos\,\theta} + C\,sin\,\theta \tag{5}$$

Rearrange the equation by dividing both sides with cos θ, the finalize equation in (6) which known as Williamson-hall plot equation in the form of Y= m X + C is shown as follows,

$$\beta\ total\,cos\,\theta = \frac{k\,\lambda}{L} + C\,sin\,\theta \tag{6}$$

Using this equation, we plot cos θ against sin θ for as-deposited coating samples presented in Figure 6 accompanied by tabulated FWHM data in Table 2 meanwhile for heat treatment coating samples presented in Figure 7 with FWHM data were tabulated in Table 3.

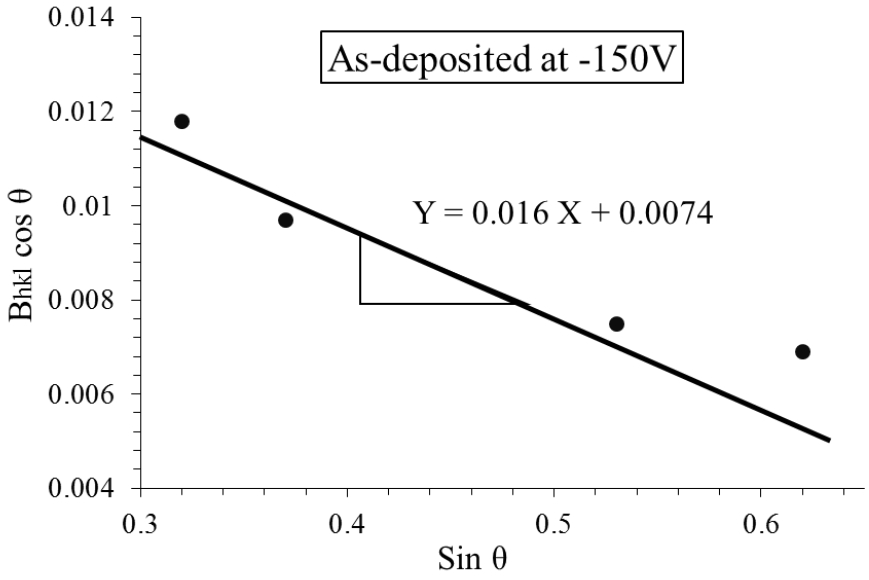

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Figure 6. Plot of B_{hkl} cos θ versus sin θ for as-deposited silver silicon nitride coating on Ti6Al4V alloy.

Table 2. Full width at half maximum (FWHM) of as-deposited silver silicon nitride coating, Cu Kα-1, λ = 1.54060Å.

Peak No.	2θ (°)	*h k l*	FWHM (°)	FWHM (rad)
1	38.21	1 1 1	0.7164	0.01250
2	44.18	0 0 2	0.6140	0.01071
3	64.41	0 2 2	0.5117	0.00893
4	77.28	1 1 3	0.5117	0.00893

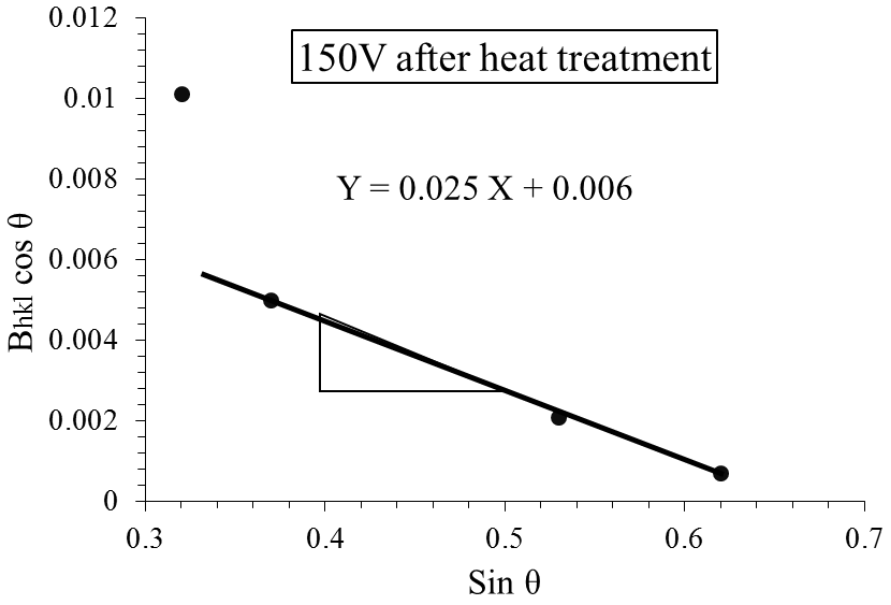

Figure 7. Plot of B_{hkl} cos θ versus sin θ after heat treatment sample of silver silicon nitride (AgSiN) coating on Ti6Al4V alloy.

Table 3. Full width at half maximum (FWHM) after heat treatment of silver silicon nitride coating, Annealed at 400°C, Cu Kα-1, λ = 1.54060Å.

Peak No.	2θ (°)	*h k l*	FWHM (°)	FWHM (rad)
1	38.18	1 1 1	0.6140	0.01071
2	44.37	0 0 2	0.5117	0.00548
3	64.55	0 2 2	0.4605	0.00252
4	77.48	1 1 3	0.3582	0.00090

From the linear fit graph obtained in Figure 6 and Figure 7, the estimation value of crystallite size and microstrain can be obtained by compared with the Williamson-Hall plot equation as in equation 6. Y-intercept will give the estimation of crystallite size value while the slope of the graph represents the lattice strain of the coating. Positive slope is an indication of tensile stress meanwhile negative slope indicate the presence of compressive stress within the material. After comparing with W-H equation, estimated crystallite size and microstrain obtained for as-deposited coating were 187nm and 0.016. The crystallite size estimation and lattice strain of coating after heat treatment were 165nm and 0.031. By comparison, the crystallite size of coating after heat treatment was smaller and the lattice strain was higher than as-deposited coating. The W-H plot crystallite size values showed good agreement with values obtain using Scherer's equation.

4. Conclusions

We prepared silver silicon nitride coating on Ti6Al4V alloy using physical vapor deposition magnetron sputtering technique. Comparison in terms of structure between as-deposited coating and thermal treatment coating showed the crystallite size of coating after heat treatment was bigger and the lattice strain was higher than as-deposited coating.

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