



Microstructure, hardness and corrosion properties of laser processed Ti6Al4V-based composites

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Abstract: Nb and Ti–13Nb powders were used for improving the surface of Ti6Al4V alloy. The deposition of the powders was carried out at various laser powers. The scanning electron microscopy (SEM)–EDS and optical microscopy were used for characterization. X-ray diffractometer (XRD) was used for analyzing the elemental composition and phase constituents. The hardness, wear and corrosion properties were achieved. The corrosion and the wear behaviours of the deposited layers were studied in a Hanks solution (simulated body fluid, SBF). The microstructures of Nb coatings reveal the presence of orthorhombic, dendritic α'' and metastable β -Nb phases which produce uneven hardness with an average of HV 364. For Ti–13Nb coatings, martensitic α' and metastable β -Nb phases with an average hardness of HV 423 were observed. The resistance of wear on dry sliding of Ti–13Nb coating is attributed to the increase in hardness. Experimental results indicate that deposition of Nb and Ti–13Nb on Ti6Al4V grossly reduces the mass fractions of Al and V in all coatings. In SBF, Nb reinforcement produces the best coating that reveals the best wear and corrosion resistances as compared with the substrate. Hence, this coating will perform best for orthopaedic implant material enhancement.

Key words: Ti6Al4V-based composite; Nb; simulated body fluid; laser deposition; passivation; microstructure; corrosion property

1 Introduction

Metal alloys are the most common materials used as surgical implants for artificial hard-tissue replacement [1]. The research on light mass metals [2–4] indicates that Ti6Al4V is widely used for diverse applications such as automobile and aerospace; however, commercial pure titanium and Ti6Al4V are the metals widely used even for bio-engineering applications. The concerns regarding the orthopaedic applications of this alloy are on the application of Ti6Al4V for biological structures which have increased investigations. The challenges around Ti6Al4V alloys are poor shear strength when they are subjected to severe wear rubbing between them and other metals [5]. The solution to the challenges of Ti alloys has been provided in a form of coatings using laser metal deposition. This is the state-of-the-art method capable of fabricating material with improved properties. The principle of this technology is based on laser cladding, in which metal powder particles are injected onto the laser

focal zone and melted and then solidified onto the substrate. As the laser beam moves on the surface of the substrate, it is melted to form a pool molten substrate plus the powder that results in a coating [6]. Therefore, the synthesis of disparate materials for the manufacturing of improved materials creates interfaces whose properties and processing make the formation of novel properties with enhanced service performance possible. The original properties of the substrate are retained successfully because the bulk properties are not altered [7].

The corrosion behaviour of amorphous niobium oxide coatings on AISI 316L stainless steel was investigated by ROJAS and RODIL [8]. They focused on the corrosion deterioration of the coatings in two different electrolytes used to simulate body fluid conditions (0.89% NaCl (mass fraction) and Hartman solution). The Nb coatings display better corrosion resistance in both solutions as compared with AISI 316L stainless steel (SS) substrate. Also, supporting the effectiveness of Nb to corrosive environment is the study

done by FATHI and MORTAZAVI [9] on tantalum, niobium and titanium coatings on AISI 316L for biocompatibility improvement of dental implants in 0.9% NaCl and Ringer lactate solution. Experimental results indicated better corrosion resistance on all the coatings in both solutions as compared with the stainless steel (SS) substrate. Nb coating produced better result compared with the substrate only. According to LEE et al [10], phases such as the acicular martensitic, orthorhombic, metastable β and equiaxed β occurred with different mass fractions of Nb being 15%, 17.5%, 27.5% and 35%, respectively. The phases affected the microstructure and the corrosion behaviour of the alloys. The critical anodic current density of the coatings was lower than $100 \mu\text{A}/\text{cm}^2$, which is the critical point of corrosion for dental application. The passivation of Ti–15Nb, Ti–27.5Nb and Ti–35Nb was recorded to be high than that of C_pTi and Ti–17.5Nb which presented similar behavior as C_pTi .

In this work, laser metal deposition (LMD) of Nb and Ti–13Nb onto the surface of Ti6Al4V alloy was carried out. Niobium is termed to be biocompatible and applicable [8,9,11] especially in areas of strength because of its memory alloy effect. In combination with Ti, it is described as a stabilizer of the β phase which gives it the super-elastic behaviour. These categories of materials are useful as they create passivation layer when exposed to corrosive environments such as the body fluid.

Therefore, resultant microstructure, hardness and corrosion behaviour of the composites were investigated. Corrosion behaviour of the coated materials was determined in the simulated body fluid (SBF) environment (Hanks solution) to determine their performance as suppressants of toxic aluminium and vanadium ions.

2 Experimental

Two different types of reinforcement materials were investigated. Nb and Ti–13Nb were respectively deposited onto a Ti6Al4V substrate. Ni powder had particle size of 10 and $210 \mu\text{m}$, while Ti powder had particle size of between 45 and $300 \mu\text{m}$. Ti–13Nb pre-alloyed powder was 10 and $350 \mu\text{m}$ conglomerated using the Restch ball mill as indicated in Table 1. The powder was fed through the hopper and deposited onto plate

specimen with dimensions of $30 \text{ mm} \times 30 \text{ mm} \times 8 \text{ mm}$. The surfaces of the specimen were sandblasted and cleaned to enhance the adherence of deposited materials.

The fed powder was melted and solidified onto a Ti6Al4V substrate using a Roffin Sinar DY044, CW Nd:YAG laser machine equipped with a robotic arm, as indicated in Fig. 1.



Fig. 1 Laser deposition system

The head mounted on the robot arm was set to a standoff distance of 12 mm above the substrate. A $600 \mu\text{m}$ optical fiber was used to guide the laser beam to an optical system focusing the beam at 4 mm on the surface. The laser power directed to the powder-substrate interaction zone was varied from 500 to 1500 W. In order to prevent oxidation in the melt pool, the process was conducted into a rectangular container which was covered and filled with argon gas at 5 L/min. Table 2 shows the process parameters in the experiments.

Table 2 Process parameters for laser deposition

Type of alloy	Power/W	Scan speed/ ($\text{mm}\cdot\text{s}^{-1}$)	Beam diameter/ mm	Powder feed rate/ ($\text{g}\cdot\text{min}^{-1}$)	Carrier gas flux/ ($\text{L}\cdot\text{min}^{-1}$)
Nb	500,	9	4	3	5
	1000,				
	1500				
Ti–Nb	1000,	9	4	3	5
	1200,				
	1500				

To determine the produced phases in the deposited material, the specimens were prepared by cutting the samples transversely across the clad layer and identified by the X-ray diffraction (XRD) at 40 kV and 30 mA with the X-ray crystallography performed using a Ni-filtered $\text{Cu K}\alpha$ radiation source. Their matching phases were identified with the characteristic peaks in the files of the joint committee on powder diffraction standards (JCPDS). Metallographic specimens were also prepared by cutting the samples transversely across the clad layer

Table 1 Parameters of powder

Material	Particle size range/ μm	$D_{50}/\mu\text{m}$	Mass fraction/%
Nb	10–210	100	100
Ti–13Nb	10–350	32	13–87

and mechanically polished them, and then etched with Keller's reagent (5 mL HNO_3 , 1.5 mL HCl , 1.0 mL HF and 95 mL distilled water) and Kroll's reagent (5 mL HNO_3 , 1.0 mL HF and 95 mL distilled water). The microstructures and elemental compositions of the Nb and Ti–13Nb were examined with an optical microscope and the Joel scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

The hardness profiles were obtained using a Matsuzawa hardness tester with a load of 300 g in an interval of 100 μm from the top of the clad to the substrate.

The wear profiles of the substrate and coatings were obtained using CETR–UMT 2 micro-tribometer ball on flat sliding wear test. The diameter of tungsten carbide ball was 8 mm and the load was 25 N. Oscillation frequency of 5 Hz was used to slide for 1000 s travelling for 10 mm. The sample with dimensions of 10 mm $\times$ 10 mm $\times$ 5 mm was positioned onto the sample holder clamped to avoid any movement during sliding. The results were captured after elapse sliding time.

The polarization and qualitative electrochemical impedance spectroscopy were investigated in 500 mL Hanks solution at room temperature using Metrohm Autolab PGStat101 compact potentiostat. The set-up consists of a three-electrode cell (saturated calomel electrode (Ag/AgCl_2) in saturated KCl as the reference electrode and platinum as the counter electrode). The samples were placed in a glass cell and about 1.1 cm^2 of samples were exposed in the Hanks electrolyte under standard condition. The system was interfaced with a computer to determine the open circuit potential (OCP). The anodic and cathodic Tafel plots were recorded using the NOVA software. The dynamic polarized corrosion potential (ϕ_{corr}) and corrosion current density (J_{corr}) were calculated using the cross point method on the anode and cathode Tafel curves.

3 Results and discussion

3.1 Characterization of developed clads

3.1.1 Microstructural analysis

Figure 2 reveals the effect of laser power (input temperature) on the microstructure after the deposition of pure Nb on Ti6Al4V substrate. Because of the high energy input on the material, there is dilution of Nb onto the Ti matrix. The heat input into the substrate changes the characteristics of the microstructure. The cooling behaviour also changes, as clearly indicated by the developed dendritic structures at 500 W and they are less evident at 1000 W and fainter at 1200 W as indicated in Fig. 2. The morphology of Nb-deposited coatings appears to contain a mixture of structures. The structures

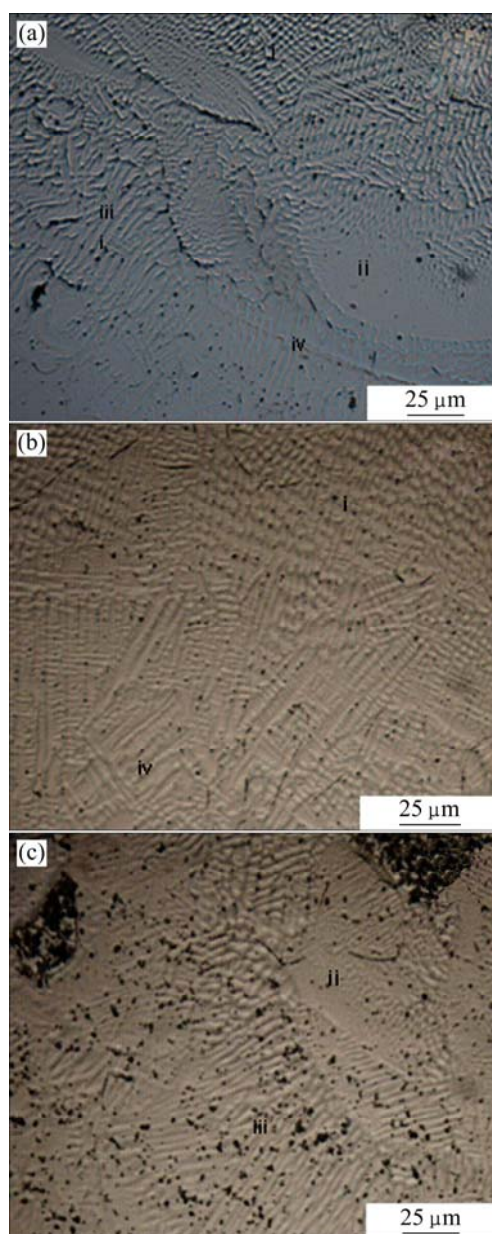


Fig. 2 Optical micrographs of laser-deposited Nb on Ti6Al4V at different laser powers: (a) 500 W; (b) 1000 W; (c) 1200 W

are dominated by the dendrites which occur at high concentration at the bottom of the coatings. The dendrites in the coatings are much concentrated at 500 W and decrease as the laser power input increases. All achieved microstructures revealed by Nb deposition appear to be complex with the presence of smooth honey comb structures.

The optical microstructures in Fig. 3 are the results achieved from laser deposition of Ti–13Nb, which demonstrate the effect of laser power (input temperature) on the microstructure evolved. It shows that with these composites, the type of microstructure is quite different from that of Nb. Grain boundaries occur, which are supported by color coded type of grains. The size of the

grains displayed by the Ti–13Nb deposited coatings increases as the temperature increases. At lower heat input, the grains are small (Fig. 3(a)), as compared with higher heat input in Figs. 3(b) and (c).

This type of response to heat by metals can be correlated to the effect of cooling rate in conventional heat treatment, which indicates that quenching of metals concedes smaller grains compared with normalizing mode of cooling. At high magnification, the images present martensitic structure that varies in appearance as the power increases. Faint martensitic structure is observed at 1000 W, and at 1200 W coarse martensitic structure is presented, while at 1500 W needle-like structure is displayed.

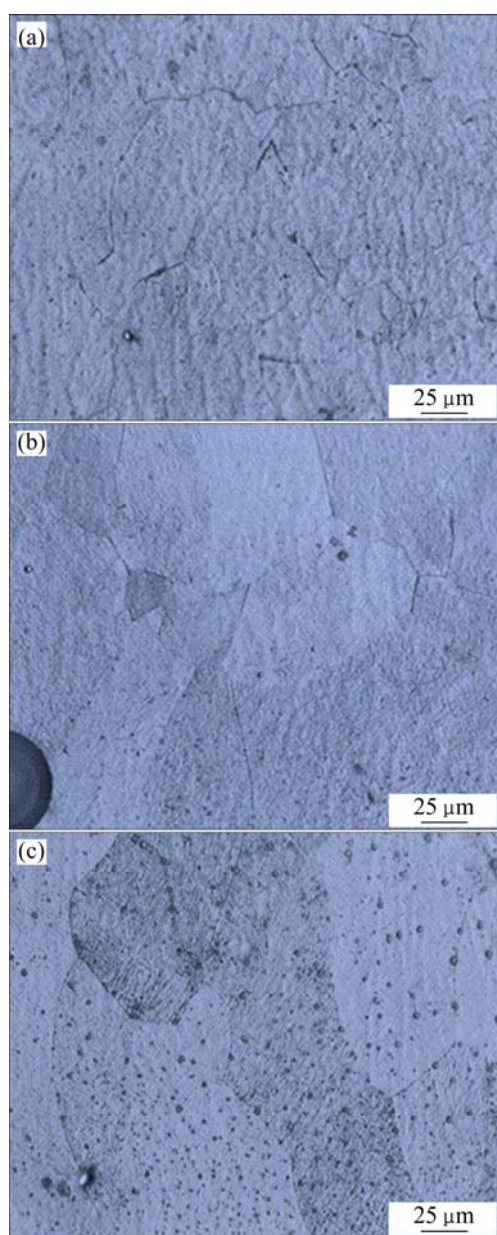


Fig. 3 Optical micrographs of laser-deposited Ti–13Nb on Ti6Al4V at different laser powers: (a) 1000 W; (b) 1200 W; (c) 1500 W

To validate the details in the optical microstructures of the deposited materials, SEM was used to obtain images of the two coatings at higher magnifications. Elemental Nb laser deposited onto Ti6Al4V indicates the development of dendrites, as seen in Fig. 4, proving the optical micrographs to be correct. The SEM images of the Ti–13Nb deposited coating show mixtures of martensite microstructures via the presence of bright and dark phases. These kinds of phases occur when there are additional elements to the Ti lattice structure as the β stabilizer and also the drastic change in temperature. As Nb is listed as a transition element on the periodic table, it is also classified as a stabilizer in such regard, i.e., β phase. The elements present are indicated by the EDS analysis shown in Figs. 4 and 5. In confirmation to different structures in a single track coating, the Ti concentration in Nb melt pool rearranges the orientation of the ideal Nb structure because of chemical reactions. CREMASCO et al [12] studied the effect of Nb on Ti for possible property improvement of Ti surface, but it was found that the bright and dark phases are actually acicular type of martensite which was observed after a water quenching process. Relating to the microstructures in Fig. 5, it is observed that as the deposition temperature increases, the martensite Ti–13Nb phase becomes more. Therefore, it can be explained that at lower input power, the solidification is faster than that at higher input power.

3.1.2 Phase analysis

The XRD patterns in Fig. 6 confirm the presence of Ti–Nb in both coatings which can be attributed to the melting of Ti from the substrate; as indicated in the optical microscope that more than 50% of the deposited layers sunk into the substrate. Figure 6 shows the typical Ti–13Nb type of crystal structure with the presence of β phase.

The XRD pattern in Fig. 6(a) is the result for Nb coating and this identifies the presence of α -Ti, definitely resulting from the substrate. The pattern indicates the presence of orthorhombic (α'') phase and a metastable β phase. The α'' phase originates from the reaction of the molten Nb powder and the Ti6Al4V substrate, while the β phase is due to high content of Nb in the melt pool. Figure 6(b) shows the XRD pattern for Ti–13Nb coating. The spectrum identifies the presence of Nb. The pattern indicates the presence of α acicular Ti lattice crystallography and the presence of the metastable β Ti–Nb peak. Common peak can also be seen at a 2θ of 41° , which is recorded as Ti–Nb in this pattern. Some of the observed Ti–Nb peaks are seen at very low level of intensity. Ti–13Nb system indicates the occurrence of hexagonal (α' -Ti) phase.

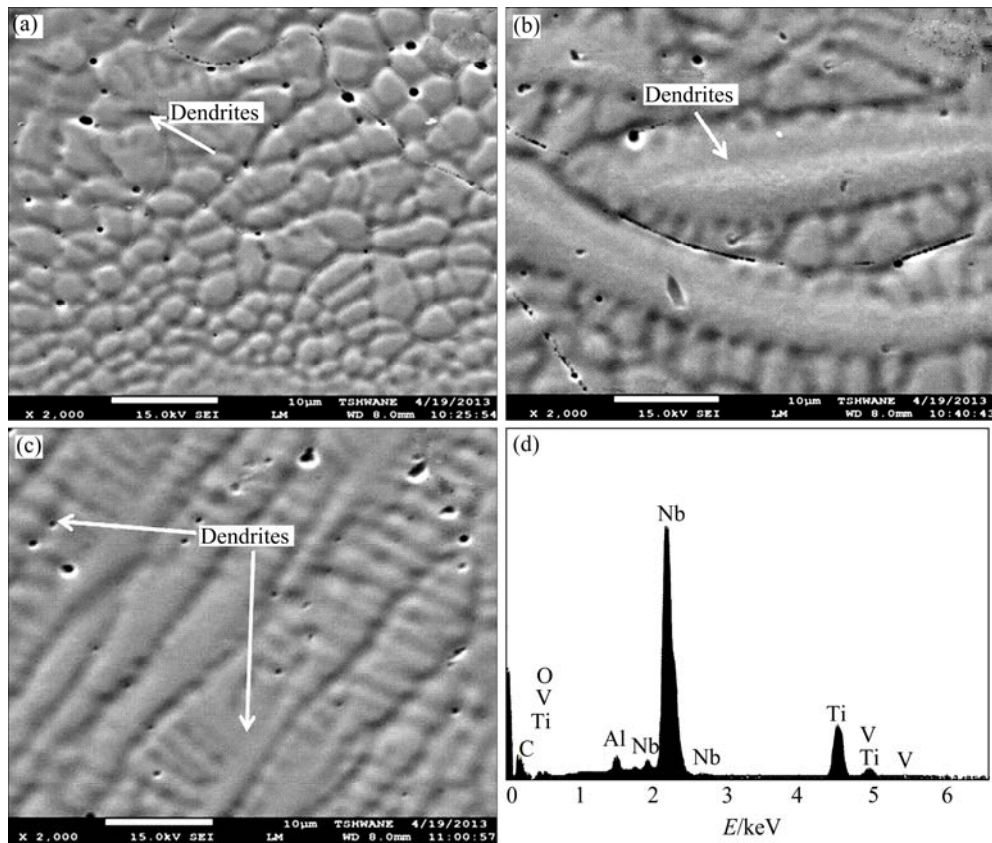


Fig. 4 SEM-EDS micrographs of laser-deposited Nb on Ti6Al4V at different laser powers: (a) 500 W; (b) 1000 W; (c) 1200 W; (d) EDS map

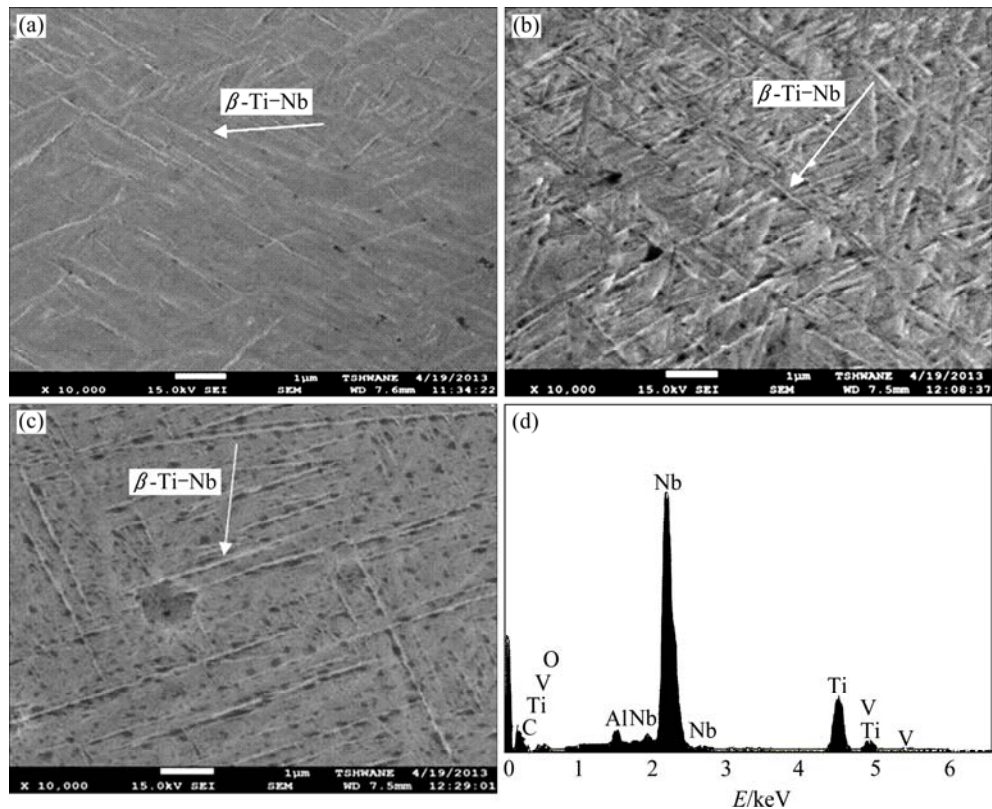


Fig. 5 SEM-EDS micrographs of laser-deposited Ti-13Nb on Ti6Al4V at different laser powers: (a) 1000 W; (b) 1200 W; (c) 1500 W; (d) EDS map

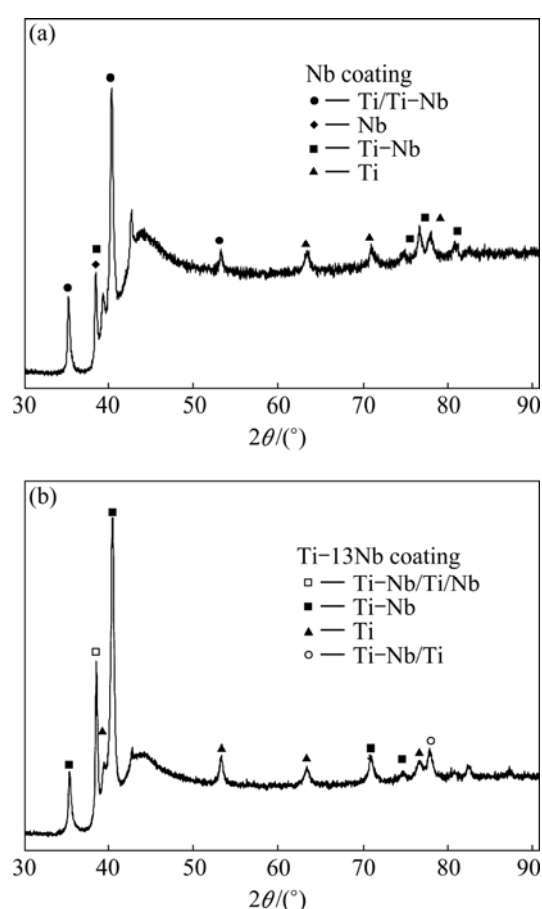


Fig. 6 XRD patterns of laser-deposited Nb (a) and Ti-13Nb (b) coatings

3.2 Microhardness

Microhardness profiles for Nb and Ti-13Nb coatings as plotted in Fig. 7 present the variation of the transverse hardness profile of the clads starting from the top of the clads to the base which is the substrate. The column graph represents the respective microhardness of the materials. Nb powder deposited clad presents uneven behaviour of hardness: at the top of the clad, low hardness of HV 275 is obtained, then the hardness increases until 1.0 mm distance from the surface (HV 490), and measurement of the hardness along the coating results in an average hardness of HV 364. Ti-13Nb coating displays the hardness profile similar to that of Nb; but the values achieved with this system are a little higher than those of the Nb coating. On the surface of the coating (150 μ m), the measured hardness is similar to that of the substrate (1.65–2.40 mm). The achieved hardness at the top of Ti-13Nb coating is HV 390, similar to that of Ti6Al4V alloy of HV 394. With the through thickness indentation, however, the average hardness value of HV 423 is recorded. This indicates that the presence of Ti has a positive effect on the clad presenting harder phases. The increase of the hardness is presumed to be affected by the change in Ti content

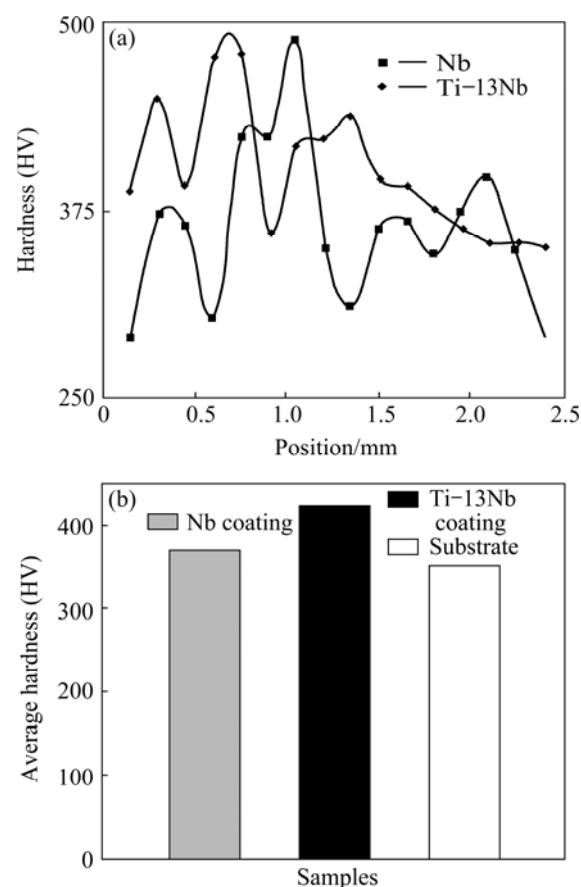


Fig. 7 Microhardness property for Nb and Ti-13Nb coatings (a) and average hardness (b)

when measuring hardness in direction from top of coating to the substrate. Percentage decrease in hardness value for Nb coatings (0.05%) is attributed to the microstructure with high content of Nb consisting β -metastable phases which are soft materials. The hardness of Ti-13Nb coating increased by 8.4% can be influenced by the increase of Ti content in the coatings and the presence of α -Ti martensite observed in the coatings which result in martensitic microstructure.

3.3 Electrochemical property

The potentiodynamic polarization curves of the Nb coatings in simulated body fluid (Hanks solution) electrolyte under standard working environment are plotted in Fig. 8(a). The results are selected because of the nearest mean values of the current densities, and indicate constant behaviour especially during the first 5 min of immersion. The Tafel calculations are deduced from the available data and listed in Table 3.

Figure 8(a) shows the polarization curves for the Nb coatings fabricated at different laser powers. The Nb coating fabricated at a laser power of 1500 W shows the most improved corrosion resistance for this set of coatings, which can be attributed to the increased ϕ_{corr} value. In addition, it is more useful to clad Nb on

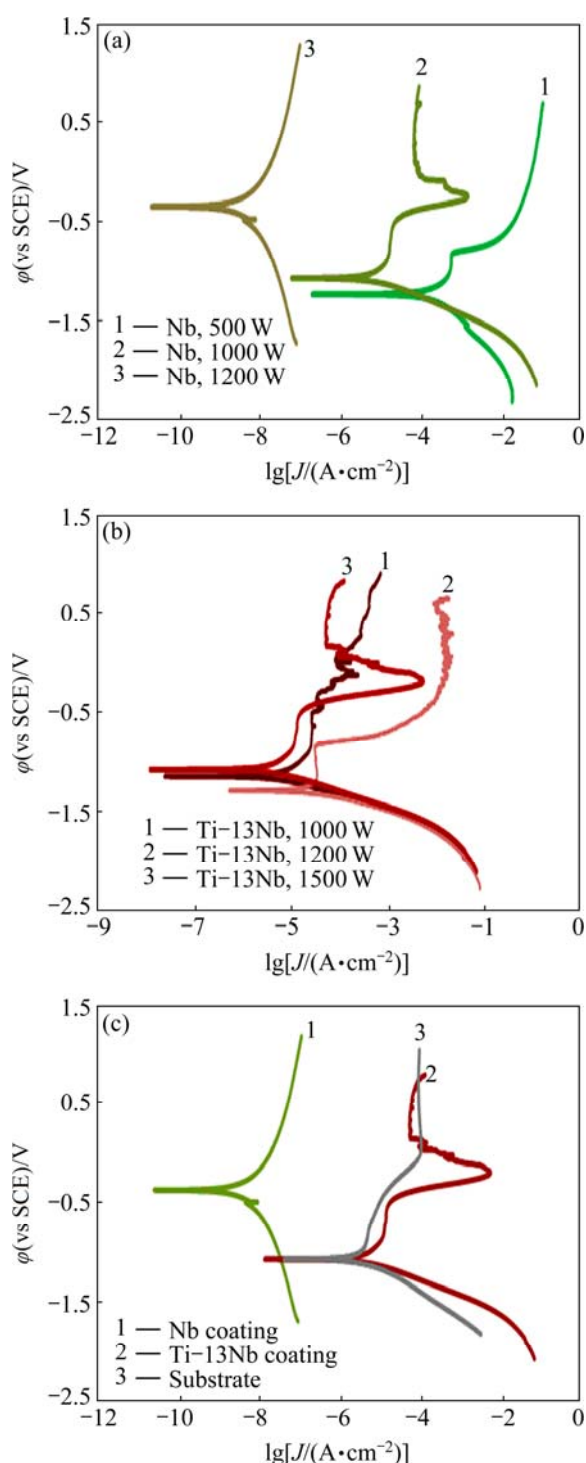


Fig. 8 Potentio-dynamic polarization curves: (a) Nb coatings; (b) Ti-13Nb coatings; (c) Joint graphs of both Nb and Ti-13Nb coatings immersed in Hanks solution under standard conditions

Ti6Al4V at higher laser power if corrosion properties are considered. Higher laser power provides better dilution, less segregation, good dispersion of the Nb in the matrix of Ti6Al4V, inevitably resulting in less dendritic structure. The difference in ϕ_{corr} between the most improved Nb coating and the substrate is about 1.275 V. While the ϕ_{corr} difference between the coatings with the highest and

lowest corrosion resistance is 0.876 V, establishing that the effect of laser power and hence phase formation and microstructure refinement can affect the corrosion behaviour of materials significantly.

Figure 8(b) shows polarization curves for Ti-13Nb coatings. It can be seen that the coating made at the highest laser power of 1500 W displays the highest corrosion resistance informed by the highest ϕ_{corr} value, the lowest corrosion current density and the highest polarization resistance in Table 3. Based on the results of the two sets of coatings (Nb and Ti-13Nb), one can conclude that it is useful to clad Ti6Al4V alloy at high power for improving corrosion behaviour. It is also observed that all the Ti-13Nb coatings have approximately the same ϕ_{corr} ; the increase in their ϕ_{corr} values is marginal, which can be attributed to the same composition of substrate and powder (Ti) with very low content of Nb. The effect of Ti is very much more dominant in the corrosion property evolved, while that of Nb is almost insignificant. The difference in ϕ_{corr} between the most improved Ti-13Nb coating and the substrate is about 0.566 V, while the ϕ_{corr} difference between the coatings with the highest and lowest corrosion resistance is 0.085 V, which is not as good as the ϕ_{corr} values recorded for the Nb coatings. The effect of surplus titanium in this coating controls the corrosion performance.

Figure 8(c) presents the joint polarization curves of the substrate material and the best coatings that display the best corrosion properties from Nb and Ti-13Nb coatings. It is also observed that the corrosion potential (ϕ_{corr}) of the materials varies distinctly. ϕ_{corr} of Nb clad is more positive than that of Ti-13Nb coating. Actually, ϕ_{corr} value of the Nb coating is 0.709 V higher than that of Ti-13Nb, which is quite significant. The mixture of Ti-13Nb as surface coating does not perform well as expected. Based on ϕ_{corr} values alone, the Nb coating is more corrosion resistant than other materials tested, while the Ti-13Nb coating has similar corrosion resistance as the substrate material. Similarly, from the data for corrosion current density (J_{corr}), the Nb coating exhibits the lowest corrosion current density while the Ti-13Nb coating and the substrate display similar J_{corr} values. This also indicates that the Nb coating is more corrosion resistant than other materials tested. In fact, its J_{corr} is reduced by three orders of magnitude (see Fig. 8 and Table 3). A six order magnitude decrease in corrosion rate is observed for the Nb-coated sample indicated by 2.16×10^{-8} mm/year and 1.80×10^{-2} mm/year for the Nb-coated and substrate materials, respectively. Chemical reactions occurring in the melt pool between the substrate and the Nb powder lead to newly formed microstructure/phases that are responsible for the increase in corrosion resistance.

Table 3 Corrosion parameters of laser-deposited materials

Material	Laser power/W	ϕ_{corr}/V	$J_{\text{corr}}/(A \cdot \text{cm}^{-2})$	Corrosion rate/ (mm·year ⁻¹)	Polarization resistance/ Ω
Substrate		-1.619	4.42×10^{-7}	1.80×10^{-2}	1.80×10^4
Nb coating	500	-1.220	1.00×10^{-5}	5.20×10^{-2}	7.69×10^2
	1000	-1.052	8.00×10^{-7}	2.95×10^{-4}	1.86×10^4
	1200	-0.344	1.00×10^{-10}	2.16×10^{-8}	1.22×10^8
Ti-13Nb coating	1000	-1.138	5.00×10^{-7}	2.77×10^{-2}	2.60×10^4
	1200	-1.274	3.00×10^{-6}	1.60×10^{-3}	9.60×10^3
	1500	-1.053	6.00×10^{-7}	1.30×10^{-4}	3.18×10^4

Corrosion property is highly dependent on homogeneous dispersion of reinforcement materials in the surface coating; good homogeneity also plays a very essential function in the reduction of segregation at grain boundaries and attainment of high corrosion performance of the materials. The corrosion rates of the substrate and the Ti-13Nb coating are very similar, so, there is no distinct increase in corrosion performance of the substrate because of laser coating with Ti-13Nb material. XRD results for the Nb coating show an occurrence of orthorhombic (α'') phase, and a metastable β phase resulting from Ti-13Nb system indicates the occurrence of hexagonal (α' -Ti) phase and the presence of the metastable β Ti-Nb phase. These phases are responsible for the improved corrosion resistance of the coating. For the Ti-13Nb coating, the effect of Ti as both substrate and reinforcement seems to be dominant, hence, the corrosion performance of the developed Ti-13Nb coating is almost the same as that of the substrate; however, no deterioration of the corrosion property is observed. Nevertheless, the Nb reinforcement brings change to the corrosion resistance of the substrate significantly.

The enhancement degree of the corrosion property can be attributed mainly to the phases/microstructural changes in the developed Nb coating. According to CREMASCO et al [12], the type of microstructure plays an impotent role in the corrosion behaviour of the material. They mentioned that the equiaxed morphology appears to be more corrosion resistant than the columnar morphology.

The polarization curve passivation, though not perfectly stable, seems to occur especially with the Ti-13Nb coatings. This, however, drastically reduces the corrosion reactions of these materials; the same behaviour was confirmed during the open circuit potential study. TiO_2 passive films were reported by other researchers to be quite a strong mitigation against the degradation of the coatings/substrate surfaces. Such results are correlated to the results for passive films of Ti alloys [9,13]. The Nb_2O_5 passive film is also formed

alongside the TiO_2 as passive films. In the Nb coating, the Nb_2O_5 is more dominant than TiO_2 film. Whereas for the Ti-13Nb coating, TiO_2 film is more dominant, confirming the reason why this coating does not show much improvement in corrosion resistant, but is rather similar to that of the substrate.

Galvanic reactions between Ti and Nb are insignificant since no adverse reactions occur. Ti will not corrode at an accelerated rate as a result of galvanic coupling to Nb.

3.4 Relationship among microstructure, micro-hardness and corrosion properties

The results obtained show the relationship among laser power, microstructure, hardness and corrosion properties. Due to high heat input applied during LMD to melt the feed powder and substrate, some of the heat input affects the properties of the substrate by broadening the heat affected zone (HAZ). The produced coating contains non-uniform grain size, trapped gasses and inclusion particles when compared with that produced by the traditional manufacturing processes. Nevertheless, the laser deposition still holds a number of advantages over these traditional methods which cannot be ignored.

The effects of laser power on the morphologies at fixed scanning speed and powder feed rate are illustrated in Figs. 2 and 3. The results suggest that increasing laser power increases the temperature and therefore lowers the cooling rate. It is observed that at fast cooling rates, Nb samples experience mixed features in the microstructure and the dendrites are less, while at slow cooling rates, the microstructures show more apparent dendrite structures. Ti-13Nb system experiences faint mixture of bright and dark martensitic features at fast cooling rates, and at slow cooling rates, the features are visible and easily defined.

The heat input was provided from the laser power and converted to temperature as calculated from Eq. (1). The calculated values are presented in Table 4. Equation (2) was used for calculating the cooling rate. Converting power to temperature involves the properties of the material such as the absorptivity, thermal

diffusivity and laser processing parameters (laser beam diameter, scanning speed and laser power).

$$T = \frac{8PA\sqrt{\alpha d/\mu}}{\pi k d^2} \quad (1)$$

where T is the temperature (K); d is the beam spot size (mm); P is the power (W); α is the thermal diffusivity; A is the absorptivity; μ is the velocity (mm/s); k is the thermal conductivity (W/(m·K)).

$$\frac{dT}{dt} = -2\pi k \left(\frac{\nu}{PA} \right) (T_m T_0)^2 \quad (2)$$

where dT is the change in temperature; dt is the change in time; T_m is the melting temperature; ν is the scanning speed; T_0 is the initial temperature.

The laser deposition of Nb and Ti–13Nb achieved at 500, 1000 and 1200 W and 500, 1200 and 1500 W respectively embeds the increase in hardness of Ti6Al4V. It also produces layers that react differently to the electrolyte (Hanks solution) at various power inputs for all the tested materials. With Nb deposition, the melting of the materials is not much because the latent heat of the material is high when compared with Ti–13Nb deposition. In this regard, the dilution depth of the Ti–13Nb is larger and is encouraged by the properties of the titanium material (lower melting point compared with Nb). The increase in heat input does not favor the bonding of the coating to the substrate so much, but it results in the formation of intermetallics instead. To correlate the heat input and the microstructures formed, it is observed that the higher the temperature is, the higher the degree of melting is and the wider and the deeper the melt pool is. Therefore, this leads to more Ti in the melt pool and hence in the coating coupled with formation of more phases resulting from the chemical reactions which are indicated by the EDS/XRD.

Table 4 Power, temperature and cooling rate for Nb and Ti–13Nb laser-deposited materials

Coating	Power/W	Temperature calculated/K	Cooling rate calculated/(K·s ⁻¹)
Nb	500	0.919×10 ⁴	7.241×10 ³
Ti–13Nb	1000	2.324×10 ⁴	2.9437×10 ⁴
Nb	1000	1.838×10 ⁴	2.1271×10 ⁴
Ti–13Nb	1200	2.789×10 ⁴	3.6915×10 ⁴
Nb	1200	2.207×10 ⁴	3.2648×10 ⁴
Ti–13Nb	1500	3.487×10 ⁴	4.8191×10 ⁴

It is closely observed that for Nb coating, high Ti content is not expected, but it contains more than 20% Ti, and also Ti–13Nb coating has reduced Nb content by approximately 10%. That is why the hardness cannot

follow the traditional decrease until it reaches the substrate hardness in the through thickness indentation measurement adopted. The scattered acicular α -phase in the Ti–13Nb coatings raised the average hardness measured to HV 423 at a depth of around 1 mm of the coating. The difference in cooling rates (2.9437×10⁴ K/s, 3.6915×10⁴ K/s and 4.8191×10⁴ K/s) calculated using Eq. (2) from the temperature values recorded in Table 4, affects the resultant microstructure from the honey comb to a lath of arm-dendritic intermetallics structures of Ti–13Nb. FALLAH et al [14] found that β phase stabilizing Ti alloy increased as the cooling rate increased. The correlated microhardness of the layers shows that the higher the cooling rate is, the softer the layer is, and vice versa.

The uneven hardness profiles show that at the top of the coating, the materials experience fast cooling, which leads to solidification of dendritic structures. With rapid homogenization and cooling from laser surface interaction process, intense thermo-capillary convection will happen due to high temperature gradients within the melt pool [13]. In laser metal deposition, the powder comes in contact with the laser power and melt instantly, and drastic temperature drop is experienced from the substrate and the surrounding environment.

According to ROJAS and RODIL [8], the types of microstructures are corrosion resistant as they form oxide layers that passivate mitigating against further corrosion reactions. Better results can be obtained at high cooling rate compared with slow cooling rate, because high cooling rate does not favor the deposition of reinforcement into the melt pool, but more substrates will be present. Therefore, the substrate will react with oxygen and produce TiO₂ passive layer. This seems to operate relative to Ti6Al4V as explained by BIDHENDI and POURANVARI [15], ABDULMAGEED and IBRAHIM [16] and CHOUBEY et al [17] that at body temperature Ti6Al4V is passivated at 8×10⁻⁵ A/cm².

3.5 Aluminium and vanadium contents in coatings

Energy dispersive spectroscopy was used to quantify the elemental composition of both the substrate and the coatings. The results recorded from these analyses can be seen in Tables 5 and 6. Nb coatings indicated the decrease in Al and V contents in the materials at different power inputs. Nb-deposited coating at 500 W shows the reduction from 5.87% Al and 3.89% V in substrate to 1.86% Al and 1.13% V, which correspond to a 68.31% decrease of Al and 70.56% decrease of V. 60.81% decrease of Al and 45.69% decrease of V are recorded at 1000 W deposition; and at 1200 W deposition, 72.74% decrease of Al and 62.29%

Table 5 EDS analysis for compositions of substrate and Nb coatings

Element	Mass fraction/%			
	Substrate	500 W	1000 W	1200 W
C	2.09	4.77	5.86	4.36
O	0	2.31	1.89	0
Al	5.87	1.86	2.3	1.6
Ti	88.15	27.87	28.78	37.83
V	3.89	1.13	1.22	1.35
Nb	0	62.05	60.65	54.86
Total	100	100	100	100

Table 6 EDS analysis for composition of substrate and Ti–13Nb coatings

Element	Mass fraction/%			
	Substrate	1000 W	1200 W	1500 W
C	2.09	6.34	2.44	2.38
O	0	0	0	1.46
Al	5.87	3.57	3.91	4.15
Ti	88.15	77.35	83.31	82.64
V	3.89	1.91	2.15	1.93
Nb	0	10.83	8.19	7.44
Total	100	100	100	100

decrease of V are achieved.

For Ti–13Nb deposition, 39.18% decrease of Al and 50.89% decrease of V reduction at 1000 W, 33.39% decrease of Al and 44.73% decrease of V deposited at 1200 W and 29.30% decrease of Al and 50.38% decrease of V reduction were accomplished. The decrease of Al and V contents in the coatings is attributed to the high dilution experienced by the coatings as power increases. High power input gives the powder and the substrate enough time to melt and long solidification time, which favors the formation of Ti–Nb solid solutions.

The coatings showed the following patterns: deposition at low power for the sample containing 62.05% Nb indicated to be the least corrosion resistance for the Nb coatings. The increase in laser power led to the formation of metastable β phases for Nb coatings, slightly reducing the content of Nb due to higher cooling rate, leading to the reduced dendrites; the presence of Nb therefore reduced the existence of the thin film TiO₂ [18], consequently, leading to the best corrosion resistance. Similarly, for Ti–13Nb deposition at low power, the coating contained approximately 11% Nb. This alloy was characterized by α -Ti martensite structure, when laser power was increased to 1500 W, Nb content was reduced to approximately 7%. With the increase in retention time

for cooling, the molten powders are well reacted to form Ti–Nb solid solution, with the presence of β -Ti–Nb phases presenting fairly corrosion resistance. The increase in laser power and consequently the reduction of Nb in the coatings resulted in corrosion resistance similar to that of the substrate.

There is a general decrease in the Al and V contents of all the coatings fabricated.

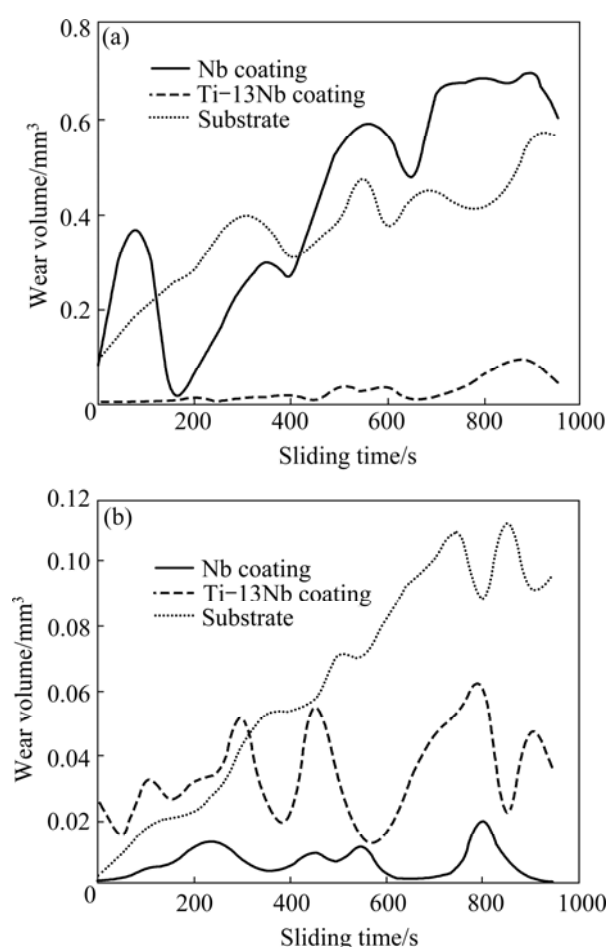
3.6 Wear property

Wear test was conducted using sliding mechanism on the surface of the substrate and the coatings. 25 N load spring adjusted to the surface of the material was used for 1000 s. The experiments were conducted in both the dry environment and Hanks solution. Wear volume was calculated using Archard's wear equation [19]:

$$V = \frac{k_1 L x}{H} \quad (3)$$

where V is the wear volume; k_1 is the wear coefficient; L is the applied load; x is the sliding distance; H is the hardness of the material.

Figure 9 shows the variation of the wear volume with the sliding time. Experimental results indicated that

**Fig. 9** Variation of wear volume with sliding time: (a) Dry wear; (b) Wet wear in simulated body fluids

wear occurred in the area between the coating and sliding ball.

Dry wear test for the substrate produced an average wear volume of 0.368 mm^3 at every 200 s of sliding for 1000 s maximum time. Total wear volume of 7.36 mm^3 was recorded for the substrate. Increasing slope of wear volume was experienced throughout the sliding test. Dry wear graphs for Nb coating revealed loss of volume as the sliding time increased. An average wear volume of 0.422 mm^3 and a total wear volume of 8.42 mm^3 were attained. Uneven wear slope which resulted in severe wear volume loss was experienced. At the first 200 s, fluctuation in wear volume was experienced, and a steady increase until 0.70 mm^3 reached. Dry wear for Ti–13Nb coating produced an average wear volume of 0.03 mm^3 and a total wear volume of 0.60 mm^3 . The corresponding wear volume decrease was calculated to be 91.81%. Constant wear volume was experienced at 500 s and the wear volume increased until it reached 0.09 mm^3 . The highest wear volume loss was recorded to be 0.7 mm^3 with Nb coating which was the softest coating with the average hardness of HV 370, showing that the Nb coatings displayed the lowest wear resistance. The substrate was proved to be the most wear resistant during dry wear. This is attributed to the variance in hardness (HV 390) of the substrate and that of the coating (HV 370).

Wet wear graphs are plotted in Fig. 9(b). The substrate wear volume graph revealed a steady increase in wear volume. An average wear volume loss of 0.061 mm^3 and a total wear volume loss up to 1.23 mm^3 were achieved. Nb coating in Hanks solution resulted in an average wear volume loss of 0.007 mm^3 and a total wear volume of 0.148 mm^3 accumulated as sliding time increased. The increase in wear resistance was calculated to be 88.3% in comparison to the substrate. Ti–13Nb coating produced an average wear volume of 0.034 mm^3 and a total wear volume of 0.69 mm^3 , corresponding to 43.87% increase in wear resistance.

Sliding wear conducted in Hanks medium indicated that Nb coating resisted wear when compared with Ti–13Nb coating and the substrate, showing an opposite to the dry wear. As a fact, the two types of coatings produced better results than the substrate (see Fig. 9(b)). Due to solid solution strengthening in the mixed powders and the formation of β -Ti–Nb structures, the hardness of the coating was improved. Resistance to wear as indicated by the two types of coatings is attributed to the formation of $\text{TiO}_2/\text{NbO}_5$ film occurring on the surface due to the reaction of the surface and the medium. According to MAJUMDAR et al [20], metals with microstructures characterized by acicular or globular α , β and martensite structures improved their response to wear failure, and also LEE et al [10] indicated that the

formation of dendrites in Nb coating improved to resist wear when exposed to medium with chloride ions (Hanks solution) because of the presence Nb_2O_5 .

4 Conclusions

1) Nb coating displays orthorhombic, dendritic α'' and metastable β -Nb phases with hardness value of HV 370 compared with Ti6Al4V substrate. A 0.05% hardness decrease is obtained.

2) The best Nb coating (1200 W) contains 1.6% Al and 1.35% V (mass fraction). The ϕ_{corr} and J_{corr} values of -0.344 V and $1.00 \times 10^{-10} \text{ A/cm}^2$ respectively and the total wear volume of 0.148 mm^3 which is 88.3% increase in wear resistance are obtained. The most significance increase in corrosion resistance is exhibited by this coating.

3) Ti–13Nb coating shows acicular, martensitic α' and metastable β -Nb phases with improved hardness value of HV 423, corresponding to 8.4% increase in hardness.

4) The best Ti–13Nb coating (1500 W) contains 4.15% Al and 1.93% V. The ϕ_{corr} and J_{corr} values of -1.053 V and $6.00 \times 10^{-7} \text{ A/cm}^2$ and the total wear volume of 0.69 mm^3 which corresponds to 43.87% increase in wear resistance are obtained. Significance increase in corrosion resistance is attained.

5) Based on the results of the two sets of coatings (Nb and Ti–13Nb), one can conclude that it will be useful to clad Ti6Al4V alloy at high power for improving corrosion behaviour.

6) Nb reinforcement produces the best coating that displays the best corrosion resistance and increase in wear resistance in simulated body fluid (SBF) as compared with the substrate. Therefore, this coating will perform the best as orthopaedic implant material.

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激光加工 Ti6Al4V 基复合材料的 显微组织、硬度和耐腐蚀性能

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摘要: 在不同功率下将 Nb 和 Ti–13Nb 粉末进行激光沉积,以改善 Ti6Al4V 合金的表面性能。采用扫描电镜(附带 EDS 能谱仪)和光学显微镜对样品进行表征,采用 X 射线衍射仪分析样品的元素组成及相组成,获得样品的硬度、磨损和耐腐蚀性能。在 Hanks 溶液(模拟体液)中研究沉积层的腐蚀和磨损行为。显微组织观察结果表明,沉积的 Nb 层为斜方晶系的树枝状 α'' 和亚稳态 β -Nb 相,其硬度分布不均匀,平均硬度为 HV 364;沉积的 Ti–13Nb 层为马氏体 α' 和亚稳态 β -Nb 相,其平均硬度为 HV 423。干滑动摩擦条件下 Ti–13Nb 层的耐磨损性能归因于其硬度的增加。实验结果表明,在 Ti6Al4V 基体上沉积 Nb 和 Ti–13Nb 极大地降低了各层中 Al 和 V 的含量。在模拟体液中,与基体相比,Nb 增强复合材料具有最好的耐磨损和耐腐蚀性能。因此,此复合材料将对改善整形外科植入材料性能发挥最佳作用。

关键词: Ti6Al4V 基复合材料; Nb; 模拟体液; 激光沉积; 钝化; 显微组织; 腐蚀性能

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