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G. Yumusak, A. Leyland, A. Matthews

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The effect of pre-deposited titanium-based PVD metallic thin films on the nitrogen diffusion efficiency and wear behaviour of nitrided Ti alloys

G. Yumusak ^{a,b}, A. Leyland ^a, A. Matthews ^c

^a Department of Materials Science & Engineering, The University of Sheffield, UK

^b Department of Metallurgical and Materials Engineering, Marmara University, Istanbul, Turkey

^c Department of Materials, The University of Manchester, UK

ABSTRACT

Low-temperature Triode Plasma Nitriding (TPN) has been reported to increase the load-bearing capacity of titanium alloys without compromising either core strength or fatigue resistance. It is known also that the effective adhesion between PVD hard coatings and titanium alloy substrates can be improved significantly following substrate diffusion pre-treatment. In TPN treatment the diffusion of the nitrogen can be achieved more efficiently (than conventional nitriding techniques) at a comparatively low substrate temperature - and after relatively short treatment times. Moreover, there is evidence to suggest that the effectiveness of the triode-plasma diffusion treatment can be further increased by depositing a suitable thin PVD metallic layer on to the titanium alloy substrate before plasma nitriding treatment, to beneficially modify the diffusion kinetics. In this paper, both hcp- α and bcc- β titanium coatings (the latter stabilised by the addition of Nb) are applied to (α + β) Ti-6Al-4V and (β) Ti-4Al-10V-22Mo substrate materials; the effects of α Ti and β Ti-Nb PVD pre-coating on the diffusion treatment efficiency (and nitride phase development) and the wear behaviour of each of the Ti alloy substrates after TPN treatment at 700°C is evaluated.

1 Introduction

Titanium is a very popular engineering metal due to its outstanding properties, such as low density and high specific strength. However, the wear resistance of titanium is very poor in

many practical contact conditions. Wear-resistant hard coatings can be used to increase the service lifetime of manufactured products, but the effectiveness of these coatings on titanium is often low due to the inadequate load-bearing capacity of the substrate. Therefore, titanium alloys can benefit significantly from the application of a substrate-strengthening thermochemical diffusion pre-treatment, prior to plasma-assisted Physical Vapour Deposition (PVD) of a ceramic hard coating [1]. To date, numerous examples relating to coating layers combined with diffusion hardening and/or hard coating treatments can be found in the literature for the light alloys. Examples are; PVD metal layers deposited on titanium alloy substrates prior to Triode Plasma Nitriding (TPN) thermochemical treatments, to decrease surface roughening during the TPN process [2], NiTi (superelastic) interlayers deposited between an aluminium alloy substrate and a CrN hard coating (to increase tribological performance of a stiff and wear-resistant coating on a compliant substrate) [3] and Cr or Ni interlayers deposited before TiN coating of 304 austenitic stainless steel to improve corrosion protection [4], [5].

Numerous types of nitriding techniques (such as plasma, ion-beam, laser or gas nitriding) can be used for the purpose of substrate-strengthening of pure titanium and titanium alloys in the temperature range between 400 °C to 1000 °C [6]. Due to the end products having different mechanical properties (different hardness and compound layer thickness), the nitriding technique should be chosen depending on the application area. Conventional plasma nitriding of titanium (which is applied at higher temperatures and for longer process times than TPN) often brings about a degradation of substrate properties such as an unacceptably higher surface roughness (for tribological applications), or significant grain growth (that reduces the core strength). The treatment temperature and time both need to be decreased if possible, to reduce or eliminate these problems but, in many cases, such measures will affect the diffusion kinetics, and it will not be possible to obtain sufficient diffusion treatment strength and/or depth to provide adequate load support. Therefore, different approaches need to be found to

accelerate the nitrogen diffusion rate. The literature suggests some attempts to achieve higher diffusion rates such as applying explosive shock treatment [7], or severe plastic deformation treatment [8] before plasma nitriding, applying plasma-based ion implantation techniques [9], [10] or using low-pressure, high-intensity plasma nitriding treatments (such as the TPN technique applied in this work) [1], [11]. Moreover, the polymorphic nature of titanium could also provide some advantages in increasing the diffusion efficiency in TPN process. The literature suggests that nitrogen diffusion coefficients in β -Ti tend to be about three orders of magnitude higher than in α -Ti [12], [13] at equivalent temperatures. On the other hand, the rate of nitrogen diffusion in a surface nitride compound layer is claimed to be 20-30 times lower than that of α -Ti [14]. In this context, pure α Ti and β Ti-Nb coatings were deposited on ($\alpha+\beta$) Ti-6Al-4V (Ti-64) and (β) Ti-4Al-10V-22Mo (Ti-AVM) substrate materials (before nitriding) in order to observe their effects on diffusion treatment efficiency for each alloy type (ie. predominantly alpha and metastable beta, respectively).

The high-temperature bcc beta polymorph of titanium can be stabilised to ambient temperatures by using suitable amounts of bcc alloying elements (such as Nb, V, Mo). Achache et al. [15] reported the deposition of β phase titanium alloy coatings (Ti-Nb) on glass substrates by sputtering of pure metallic targets. They found a fully hcp α -phased structure when the Nb concentration was between 3 and 9 at. %, but a mixture of α and β phases was seen above 17 at. % Nb. A fully β -stabilised structure appeared at 34 at. % Nb (and it was reported that there was no sign of the α'' martensitic phase). Gonzales et al. [16], [17] showed that the phase structure of sputtered Ti-Nb coatings (on AISI 316L stainless steel substrates) was fully beta-stabilised from only 15 at. % Nb. Photiou et al. [18] however reported that sputtered Ti-Nb alloy coatings (on Si substrates) containing 15 at. % Nb showed the martensitic α'' phase, that was only fully converted to β above 20 at. % Nb. All of these examples related to Ti-Nb alloy coatings show how the phase structure of such coatings can vary, depending on either Nb concentration or substrate type.

Significant differences in the abrasive wear performance of the Ti-64 and Ti-AVM substrates compared to the untreated condition were seen after TPN treatment. The formation of a nitride compound layer on the surface of the Ti-64 substrate in particular, and the presence of a nitrogen-stabilised diffusion zone beneath it (which means a gradual mechanical property transition from surface to bulk) was observed by the cross-section nanoindentation hardness tests. This type of surface/cross-section structure for the Ti-64 substrate after 4 hours TPN treatment at 700 °C can be beneficial for some tribochemical applications such as adhesive wear and galling. The friction coefficient can be reduced when the TPN treated Ti alloy (with its improved mechanical properties which vary gradually from the surface to the bulk) is in tribological contact with another metallic or ceramic material [19]. It will also prevent the (soft and ductile) Ti alloy surface from being damaged whilst in contact with a harder surface.

2 Experimental details

The production sequence of the duplex plasma diffusion/coating system includes two main stages. The first part is Ti and Ti-Nb surface layer deposition on Ti-64 and Ti-AVM substrates. The second part is the triode plasma nitriding process which was applied to uncoated, Ti coated, and Ti-Nb coated titanium alloys.

2.1 Ti and Ti-Nb coating deposition

An unbalanced magnetron sputtering rig was used for deposition of pure Ti and Ti-Nb alloy coatings. The stainless steel substrate holder (300 mm x 130 mm) was placed in the middle of the chamber and positioned parallel to the sputter target (see Figure 1). It was possible therefore, to adjust the concentration of the coatings on the substrates (which were clamped on the holder) by changing their positions vertically. Three pieces (2 x Ti + 1 Nb) of metallic target segments (each of 127mm x100mm x 7mm) were used for Ti-Nb alloy coating deposition; on the other hand, a rectangular single-piece pure Ti target (380mm x100mm x

7mm) was used for the α -Ti coatings. A constant distance between target and substrate of 21 cm was maintained.

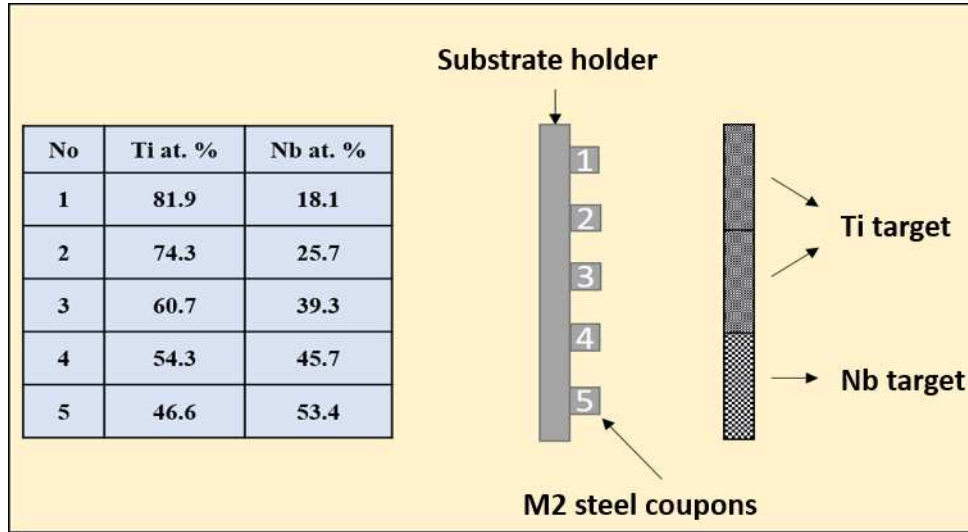


Figure 1 Schematic representation of the substrate holder and target materials (for Ti-Nb pilot coating run) with resultant coating compositions.

The chamber was pumped down to approximately 2×10^{-5} mbar (0.002 Pa) base pressure with rotary and diffusion oil pumps. The deposition stage was started directly after finishing the substrate and target sputter cleaning processes. An argon flow rate of 12.5 sccm (working pressure of 0.5 Pa) was used for the deposition process. The power supplied to both the Ti and the Ti-Nb target was 1000 W. During deposition, the substrates were biased at -50 V with a plasma current density of ~ 0.3 mA/cm². The maximum substrate temperature was ~ 200 °C. The deposition time was adjusted to 70 (and 60) minutes for Ti (and Ti-Nb) coatings (respectively), in order to produce approximately 1.25 μm thick coatings in each case.

2.2 TPN treatment

Uncoated, Ti coated, and Ti-Nb coated Ti-64, and Ti-AVM coupons (20 mm x12 mm) were TPN diffusion treated in a modified Tecvac IP70L PVD coating machine using the previously mentioned low-pressure d.c. triode configuration [1], [11]. The uncoated samples (mean surface roughness, R_a , about 0.02 μm) and Ti and Ti-Nb coated samples (taken from the magnetron sputtering system) were cleaned ultrasonically with acetone and isopropanol and

then dried by compressed air jet. Six samples (uncoated, Ti coated, and Ti-Nb coated Ti-64; uncoated, Ti coated, and Ti-Nb coated Ti-AVM) were mounted to the sample holder and were processed together in the same TPN treatment. The chamber was pumped down to less than 2×10^{-5} mbar (0.002 Pa) base pressure to minimise undesirable residual gas (such as oxygen or hydrogen) inside the chamber. A working temperature of 700°C was chosen for the nitriding runs. When the desired temperature was reached (via combined radiant heating and Ar plasma bombardment), the nitrogen working gas was introduced to the system. The ratio of the Ar and N flow rates (gas partial pressures) was kept constant (70 %N and 30 % Ar). The total pressure was maintained at around 4×10^{-3} mbar. The substrates were biased at -300 V during TPN and a constant substrate current density of ~ 0.8 mA/cm² was applied by adjusting the thermionic electron emission of the hot tungsten filament used to support the triode plasma. A nitriding time of 4 hours was selected, this being carefully chosen, so as to sputter-remove the pre-deposited PVD Ti and Ti-Nb metallic coatings from the Ti-alloy substrates shortly before the end of the TPN treatment (such that the coatings influenced the diffusion kinetics of the TPN treatment, but not the resulting surface phase composition (and/or mechanical properties)).

2.3 Characterisation

Phase analysis was carried out using a PANalytical X'Pert3 X-ray diffractometer (Cu K- α radiation) for as-deposited PVD metallic coatings and for nitrided samples, with a step size of 0.02° and a step time of 3s in the 30° to 80° 2θ range, with 2-degree glancing angle mode. Glancing angle mode was selected to suppress substrate reflection contributions to the diffraction data.

A Philips XL 30 scanning electron microscope (field emission gun) was used to investigate the cross-sectional surface morphology of the substrates after Ti and Ti-Nb coating deposition and the TPN process. It was operated at 10 and 20 kV, and the samples were placed at a

working distance of 5 to 10 mm for taking SEM micrographs. An Energy-Dispersive X-ray (EDX) spectrometer attached to the Philips XL 30 FEG-SEM was used for chemical composition analysis of the Ti alloy substrates after coating deposition and/or plasma nitriding. The microscope was operated at 20 kV and the samples were placed at a working distance of 5 mm for EDX analysis. The chemical composition of treated and untreated samples was calculated using INCA (Oxford Instruments) software.

The hardness measurements were performed using a Hysitron Triboscope® nano-indenter with Berkovich three-sided pyramidal diamond tip. The hardness measurements (which were applied from the surface of the coated samples) were performed using a matrix of 4 x 4 indents. The 2 mN indentation load for pure Ti and Ti-Nb coating surface hardness measurements was chosen in consideration of (particularly) the coating thickness, to minimise substrate contributions to measured coating hardness. A higher load of 5 mN was chosen for the diffusion treated samples' surface hardness measurements because the surface roughness of the samples increased after the nitriding process thus requiring a larger indentation load (and depth) for reduced data scatter.

A Veeco Dektak 150 stylus profilometer (with 12.5 μm radius diamond tip) was used to obtain surface roughness values, with a tip load of 3 mg. Six scans (randomly placed) were performed on each sample, and an average R_a value was calculated for all samples. The scan length was kept at 1mm, and the scan duration was set to 120 seconds.

2.4 Abrasion resistance tests

Micro-abrasion wear testing was performed using a Plint TE-66 micro-abrasion test rig. The abrasive slurry was prepared by using SiC particles (F1200, ~3–4 μm particle size) and distilled water. The concentration of the slurry was 80 g/100 ml for all experiments. A 25 mm diameter SAE52100 bearing steel preconditioned ball (running for at least five dummy abrasion runs with different orientations prior to testing) was used. The rotation of the ball

was adjusted at a tangential velocity of 0.1 ms^{-1} which corresponds to about 80 rpm. The time of the experiments was decided by the number of ball revolutions, and the applied load was selected as 0.1 N. Wear coefficients (K) of the untreated substrates (for comparison purposes), nitrided only substrates and duplex-treated (ie. coated, then nitrided) substrates were calculated.

3 Results and Discussion

3.1 Characterization of Ti and Ti-Nb coatings before nitriding

The XRD diffraction patterns for PVD Ti coatings (average crystallite size: 9.7 nm) deposited on Ti-64 and Ti-AVM alloy substrates are shown in Figure 2. It can be seen that the coatings include only one phase in which all the XRD peaks were HCP structure (pure α -Ti). There is little or no change in the HCP α -Ti PVD coating texture for the Ti-AVM beta alloy substrate, compared to Ti-64.

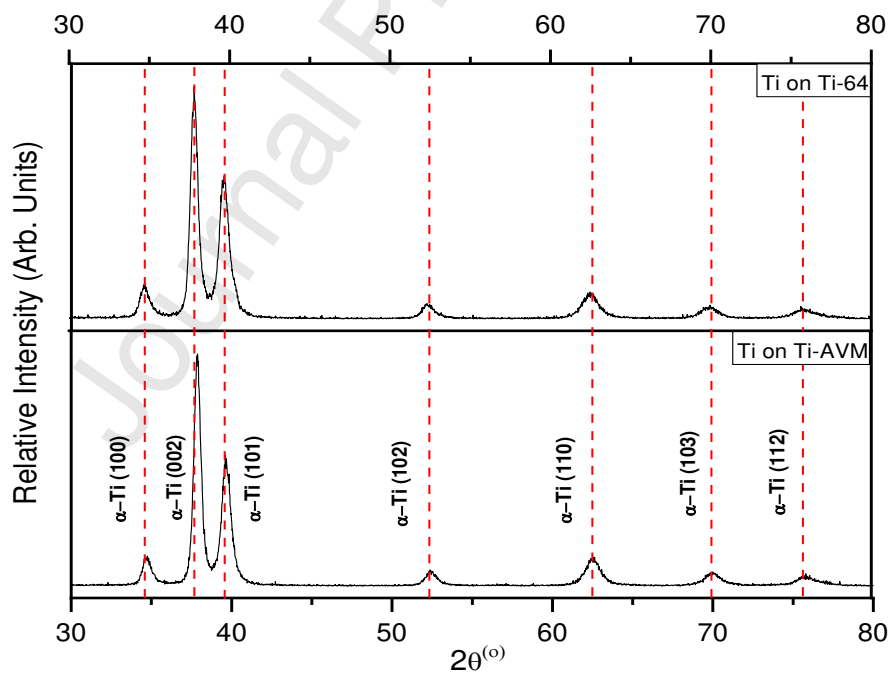


Figure 2 GAXRD (2° angle of incidence) diffraction patterns for PVD Ti coatings

On the other hand, the binary-alloy Ti-Nb BCC PVD metallic coatings required compositional optimisation. The elemental compositions of five different Ti-Nb pilot coatings deposited onto M2 tool steel substrates can be seen in Figure 1. The XRD diffraction patterns

for each of the five coatings are given in Figure 3. All coatings (the lowest Nb concentration is 18.1 at. %) showed a BCC structure, with the principal (110) peak is clearly visible. Other BCC peaks, (200) and (211) started to become apparent with Sample 4 which has a Nb content of 25.7 at. %. A fracture cross-section SEM image of the Ti-33 at. % Nb alloy coating is shown in Figure 4. It can be observed that the coating has a dense columnar structure. Considering the results of the optimisation run, a coating composition between sample 2 and sample 3 could be a good candidate for a Ti-Nb surface layer deposited before triode plasma nitriding. It was also reported in the literature that the phase constitution of sputtered Ti-Nb coatings was seen to be entirely BCC β with at least 34 at. % Nb concentration [15], in good agreement with our findings.

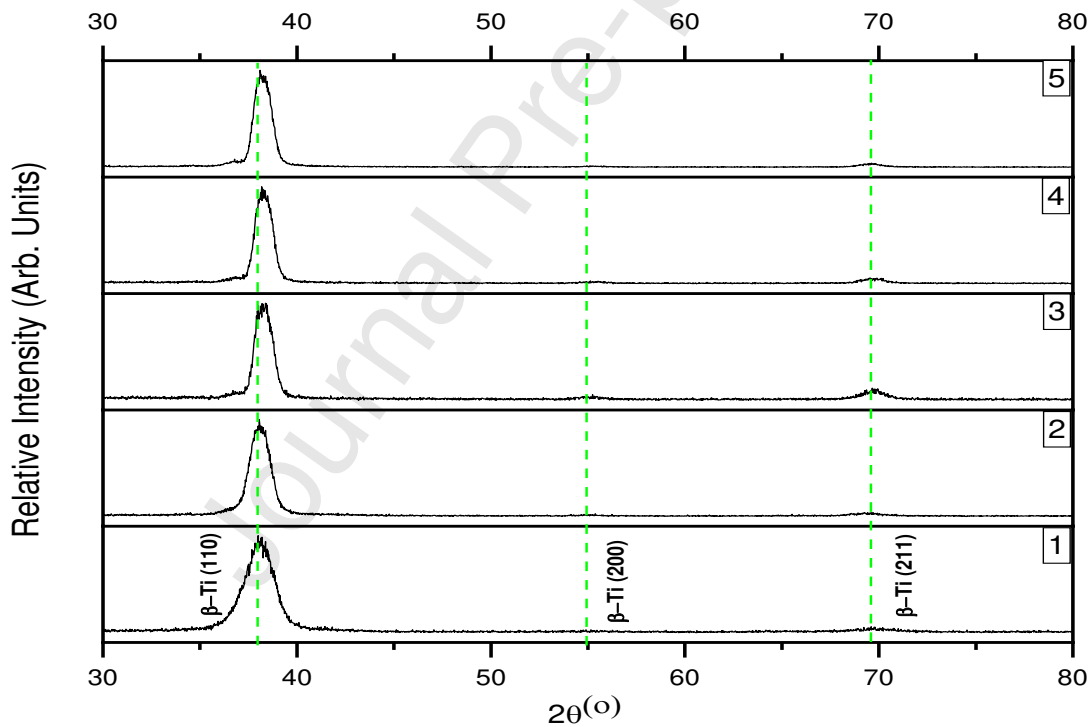


Figure 3 GAXRD (2° angle of incidence) diffraction patterns for Ti-Nb surface coating pilot study (1 to 5 are sample positions in Figure 1)

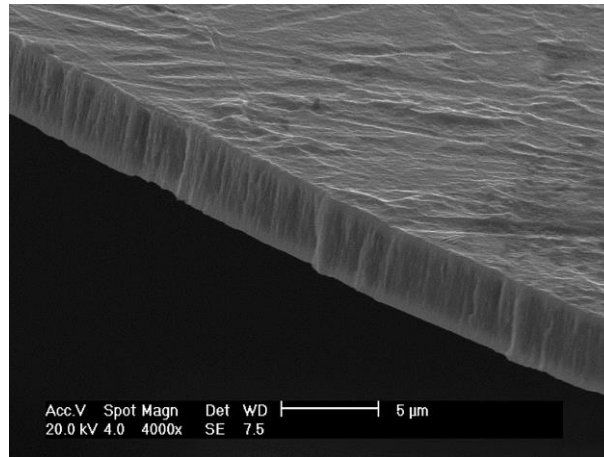


Figure 4 SEM fracture cross-section of Ti-39.3 at. % Nb trial coating (deposited on M2 tool steel substrate). Dense and nanocolumnar microstructure (average crystallite size: 8.4 nm) is typical for all pre-deposited metallic coatings used in this work.

Following the optimisation run, a Ti-Nb alloy coating (with planned 2:1 Ti:Nb atomic ratio) was deposited on Ti alloy substrates before applying the triode plasma nitriding process. The required exact position of the substrate on the holder was predicted and a new Ti-Nb coating was deposited. The XRD diffraction patterns for the Ti-Nb coating (33 at. % Nb) deposited on Ti-64 and Ti-AVM substrates are shown in Figure 5. It can be seen that the coating has a fully cubic structure on both substrate materials, with a slightly higher degree of coating crystallinity (average crystallite size: 10.1 nm) apparent on the (predominantly cubic) Ti-AVM substrate.

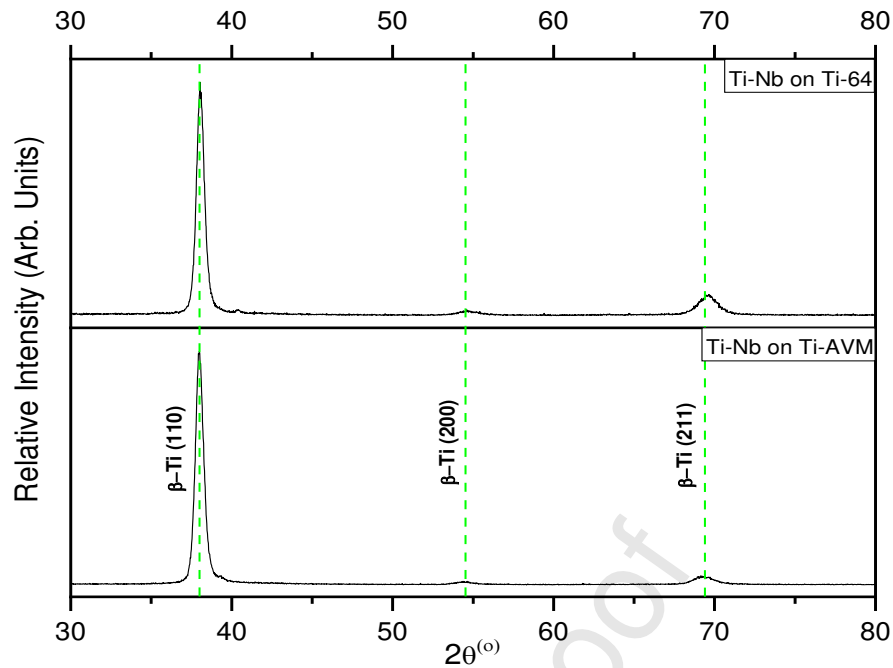


Figure 5 GAXRD (2° angle of incidence) diffraction patterns of the Ti-Nb coating (33 at. % Nb) layers deposited on Ti-64 and Ti-AVM substrates

3.2 Triode Plasma Nitriding at 700°C (TPN700)

3.2.1 EDX and X-ray Diffraction phase analysis

The near-surface EDX results after TPN700 process for uncoated, Ti coated (1.25 μm thick), and Ti-Nb coated (1.25 μm thick), Ti-64 and Ti-AVM substrates (for 4 hr TPN process duration) are presented in Table 1. The most immediate deduction from EDX results is that the atomic percentage of nitrogen on the surfaces is nearly the same for all samples. However, despite having similar overall nitrogen concentrations in their near-surface, the XRD results (see Figure 6 and 7) showed that, after 4 hours nitriding, a Ti_2N nitride phase is created on the uncoated Ti-64 substrate. On the other hand, there is no evidence of a nitride phase on the surface of the uncoated Ti-AVM substrate; due to the different crystal structure of beta titanium alloys, the nitriding behaviour is very different (it is much more difficult to reach a critical nitrogen concentration for Ti_2N formation in Ti-AVM). XRD peak shifts can be seen for uncoated Ti-AVM alloy because nitrogen diffuses inside the substrate and alpha

stabilisation starts to occur (the formation of α -Ti peaks can be seen in Figure 7) because of the interstitial incorporation of nitrogen in the Ti lattice.

Table 1 Near surface EDX results of the samples nitrided at 700°C for 4 hours

Samples	Ti (at. %)	Al (at. %)	V (at. %)	Nb (at. %)	Mo (at. %)	N (at. %)
Ti-64 Substrate (untreated)	85.2	11.3	3.5	-	-	-
TPN700, 4h, Uncoated Ti-64	72.9	12.9	2.1	-	-	12.1
TPN700, 4h, Ti-coated Ti-64	73.5	11.7	1.9	-	-	12.9
TPN700, 4h, Ti-Nb coated Ti-64	74.8	11.1	1.3	0.0	-	12.8
Ti-AVM Substrate (untreated)	69.9	7.6	10.1	-	12.4	-
TPN700, 4h, uncoated Ti-AVM	61.3	6.4	8.6	-	11.2	12.6
TPN700,4h, Ti-coated Ti-AVM	61.4	6.4	8.9	-	11.1	12.2
TPN700, 4h, Ti-Nb coated Ti- AVM	61.7	6.5	8.7	0.0	11.4	11.7

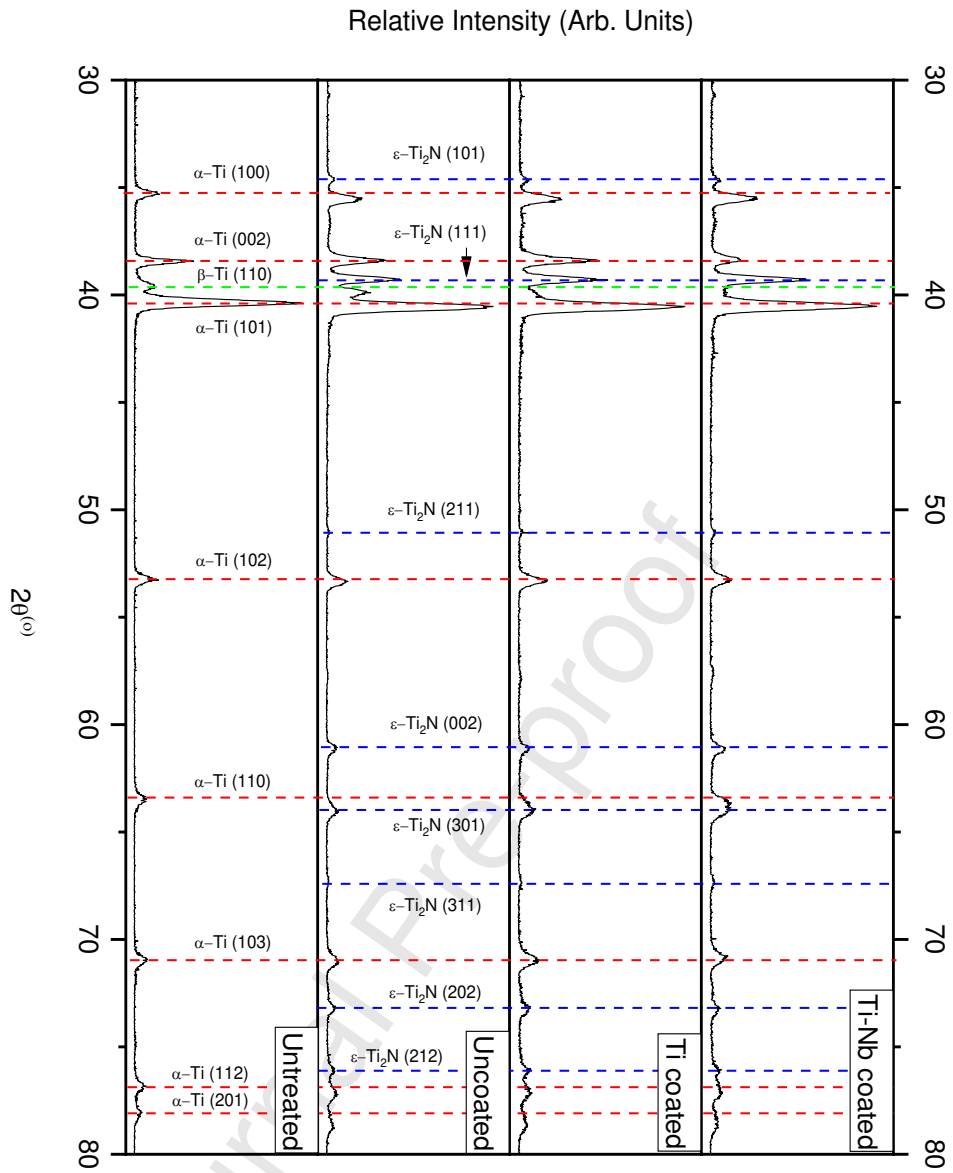


Figure 6 GAXRD (2° angle of incidence) diffraction patterns of untreated (substrate only) and nitrided Ti-64 substrates at 700°C for 4 hours

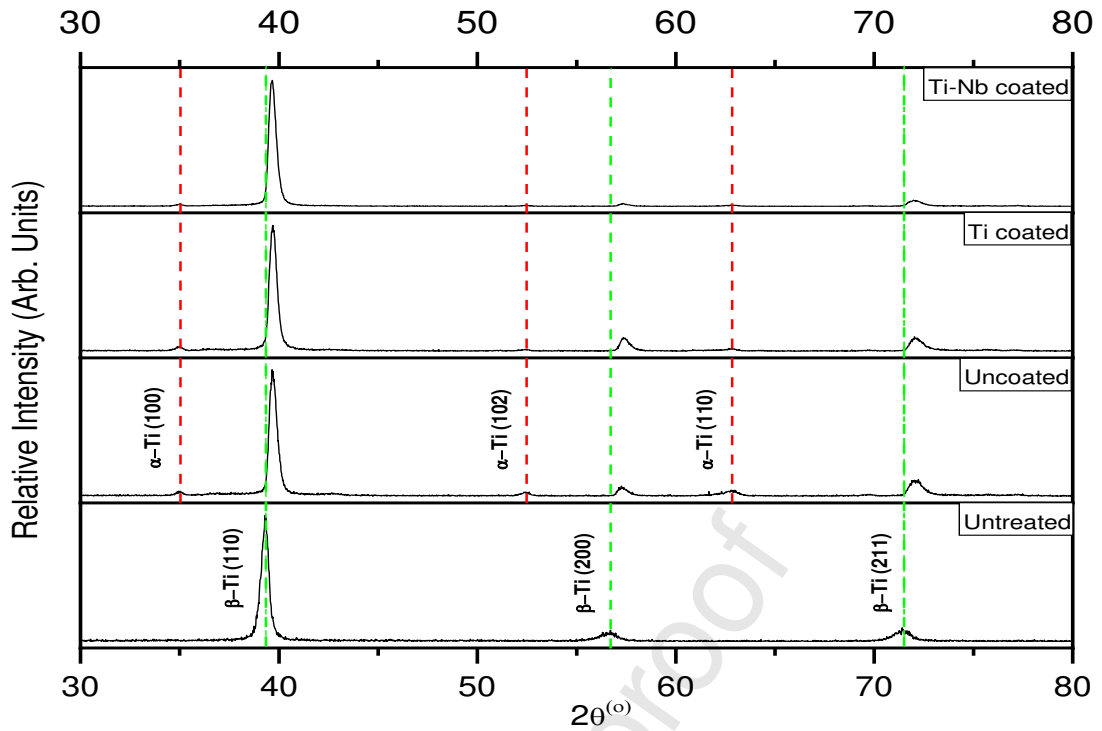


Figure 7 GAXRD (2° angle of incidence) diffraction patterns of untreated (substrate only) and nitrided Ti-AVM substrates at 700°C for 4 hours

Furthermore, EDX analysis of the Ti-Nb coated substrates shows that the niobium concentration is zero after the TPN700 process. This can be explained by the nature of the plasma nitriding process, that “sputtered off” the $1.25\mu\text{m}$ thick coating after 4 hours of nitriding at 700°C . It is also expected that the α -Ti coatings on both substrate types were sputtered off after plasma nitriding. It is easy to say (from the EDX data) that the Ti-Nb coating was sputtered off because both substrate alloys do not contain Nb which avoids any ambiguity or misunderstanding. It is seen in Figure 6 that the Ti-Nb coated Ti-64 substrate shows a similar XRD pattern to the uncoated Ti-64 substrate after TPN700 processing for 4hrs. This indicates that the Ti-Nb PVD surface coating ($1.25\mu\text{m}$ thick) did not survive until the end of the process. It was sputter-removed completely (after approximately 190 to 200 minutes, according to our calculations [20]), by energetic argon and nitrogen species, resulting in the same crystallographic structure of an uncoated substrate being observed after nitriding. If there was any significant Ti-Nb coating remaining, it would give strong XRD peaks belonging to the cubic (beta) structure. A similar argument can be made for the Ti coating

which was deposited on the Ti-AVM substrate. It is seen in Figure 7 that the Ti coated Ti-AVM substrate shows a similar XRD pattern to the uncoated Ti-AVM substrate after TPN700 processing for 4hrs. If any Ti coating remained, it would give strong XRD peaks belonging to the HCP α -Ti structure (and/or titanium nitride phase peaks, due to conversion of the residual α -Ti coating layer); no such effects are visible in Figure 7. The Al and V concentrations were also found to be different for uncoated and coated Ti-64 substrates after the nitriding treatment. The concentrations of these alloying elements are decreasing from uncoated, through Ti coated to Ti-Nb coated. On the other hand, same elements do not show any difference after nitriding of Ti-AVM substrates (neither uncoated, nor Ti or Ti-Nb coated). Moreover, the concentrations of alloying elements (Al and V) in Ti-64 substrates after TPN700 process for 4h showed that aluminium diffused from the matrix to the nitrogen-rich area (near-surface) with the vanadium content decreases in the nitrogen-rich areas close to the surface. Although a thin Ti_2N nitride compound layer formed on the uncoated Ti-64 substrate, the near-surface Al concentration was found to be higher (see Table 1) than for the untreated sample (substrate only). The different distribution of these alloying elements (compared to the untreated condition) can be related to the particular affinity of the elements with nitrogen [21] (ie. Al is a stronger nitride former than V).

3.2.2 Surface morphology and topography

Figure 8 shows the surface roughness data after nitriding of untreated, Ti coated, and Ti-Nb coated Ti-64 and Ti-AVM substrates. It can be observed from the results that the uncoated substrates were significantly rougher than the Ti and Ti-Nb coated substrates after TPN treatment. This demonstrates that PVD pre-coating helps to keep the roughness of the Ti-alloy substrate low [1]. The PVD layers (with dense nanocolumnar structure) act to protect the surface of the substrates (by suppressing preferential surface sputtering of the substrate grains) until they are sputtered off completely by the TPN plasma bombardment in the later stages of TPN treatment. After the surface layer disappears, it is expected that the surfaces of

the pre-coated substrates would then behave as uncoated ones – but for no more than 40-50 minutes, we estimate. Therefore, it can be said that the increase in the surface roughness of the coated substrates was significantly postponed by depositing a PVD metallic layer before nitriding – even though the thickness of the surface layer was not enough to survive the entire nitriding process duration.

It was also found that uncoated Ti-AVM substrates were significantly rougher than uncoated Ti-64 after an identical 4 hour TPN treatment at 700°C. This can be explained in part by the diffusion anisotropy in the cubic structure (β phase) of the alloy, however, Ti-AVM also exhibits a much larger grain size than Ti-64 (that accentuates ‘‘faceting’’ of the grain topography) dependent on the different crystallographic orientations of individual grains to the surface [2]. Optical microscopy images from the surfaces of the treated Ti-64 and Ti-AVM substrates, shown in Figure 9, verify this effect. The as-received grain sizes for the two Ti alloy substrates were $<5 \mu\text{m}$ (Ti-64) and $60\text{-}70 \mu\text{m}$ (Ti-AVM); as Figure 9 also reveals, these grain sizes did not increase significantly after TPN treatment. It is also interesting that there is some difference between the roughness data for coated Ti-64 and Ti-AVM substrates after 4 hours nitriding at 700°C, depending on whether the coating applied is β -TiNb or α -Ti. The surface roughness of the Ti-Nb coated Ti-64 substrate is lower than that of Ti coated Ti-64 after TPN treatment. On the other hand, the roughness of the Ti-Nb coated Ti-AVM substrate is higher than that of Ti coated Ti-AVM.

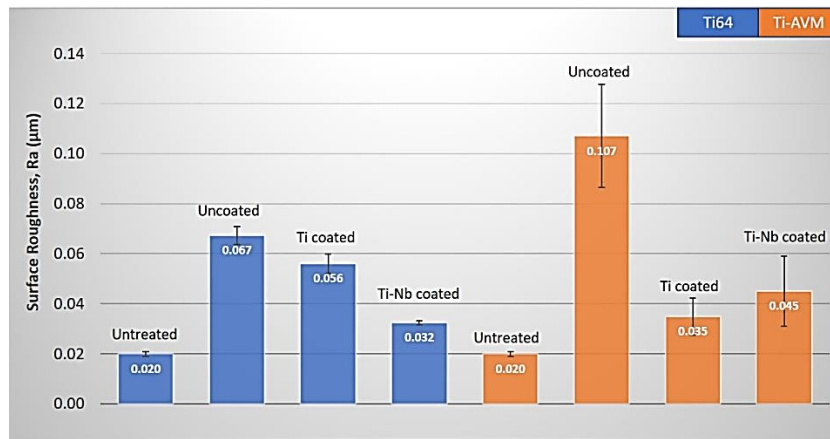


Figure 8 Surface roughness data (R_a , μm) for uncoated, Ti-coated and Ti-Nb coated Ti-64 and Ti-AVM substrates TPN-treated at 700°C for 4 hours

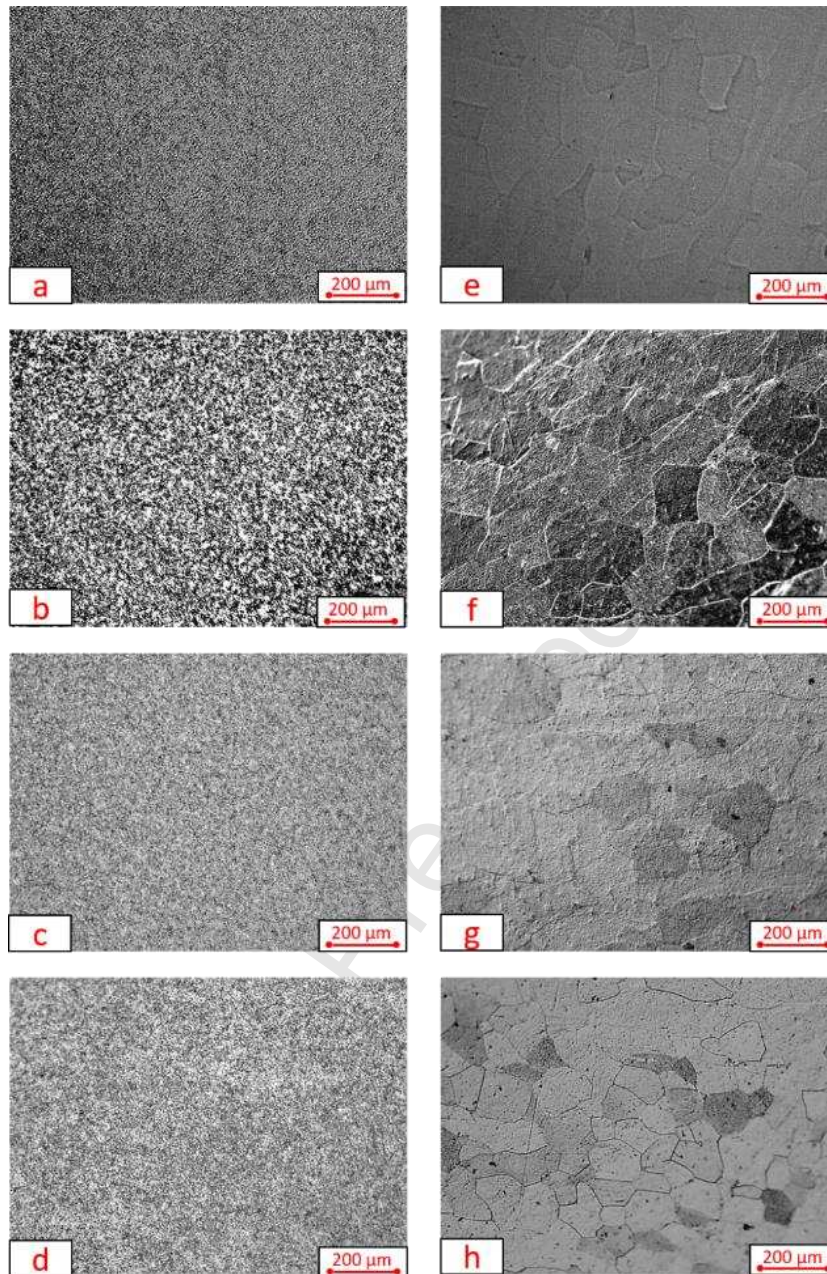


Figure 9 Optical microscopy images of the surface topography of samples treated at 700°C for 4 hours. (a) untreated Ti-64 (b) uncoated Ti-64 (c) Ti coated Ti-64 (d) Ti-Nb coated Ti-64 (e) untreated Ti-AVM (f) uncoated Ti-AVM (g) Ti coated and (h) Ti-Nb coated Ti-AVM

3.2.3 Cross-sectional morphology

SEM cross-sectional images were taken for all six substrate/treatment combinations investigated, as can be seen in Figure 10. The compound layer which formed after the nitriding process for uncoated Ti-64 is approximately 850 ± 42 nm thick, for Ti coated Ti-64 it is about 650 ± 60 nm thick and for Ti-Nb coated Ti-64 it is about 1100 ± 75 nm thick. It was already verified from XRD patterns that all these layers are composed of Ti_2N . The Ti-AVM substrate (with a fully β phase structure) has very different final features than the Ti-64

substrate. It was already verified from XRD patterns that Ti-AVM substrates do not show any evidence of compound layer formation after nitriding. The cross-sectional images for diffusion treated Ti-AVM alloy (Figure 10 d, e, f) show nitrogen stabilised layers (α phase formation) with acicular (needle-like) features [1]. Although the near-surface EDX results (after TPN700 process for 4h) indicated around 12 at. % N content for both types of substrate, the final structures/morphologies are clearly very different from each other. It appears that this level of nitrogen content is not enough to create a nitride compound layer on the surface of the (beta) Ti-AVM alloy (but it is expected to produce Ti_2N precipitates in the sub-surface).

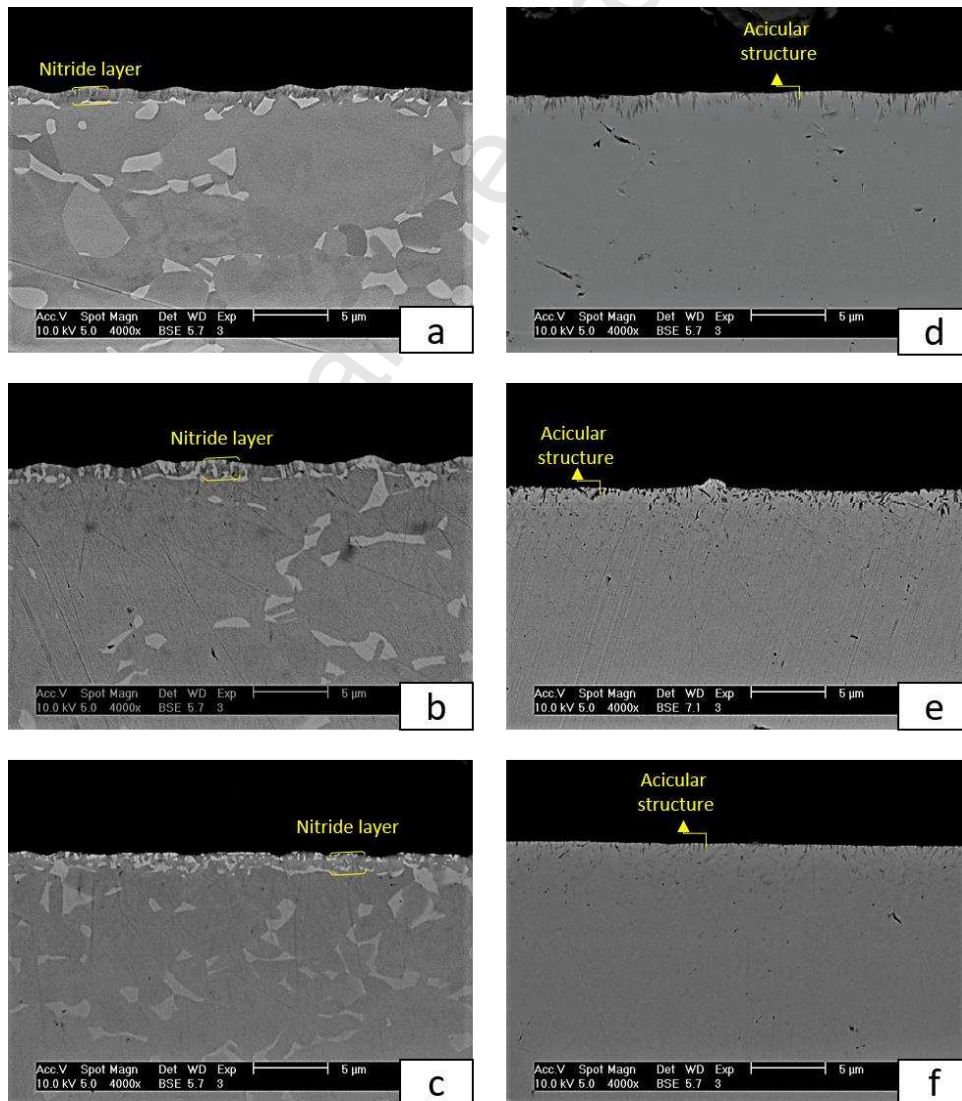


Figure 10 SEM cross-sectional images of the samples treated at 700°C for 4 hours. (a) uncoated Ti-64 (b) Ti coated Ti-64 (c) Ti-Nb coated Ti-64 (d) uncoated Ti-AVM (e) Ti coated and (f) Ti-Nb coated Ti-AVM

3.2.4 Surface and cross-sectional hardness measurement

The cross-sectional indentations were applied about 2 μ m away from the surfaces (see the indentation traces in Figure 11) to avoid damage to the nano-indenter. The indents lie in parallel rows from 2 μ m to approximately 42 μ m depth (relative to the surface), with the hardness values on each row indicative of the local diffusion zone hardenability.

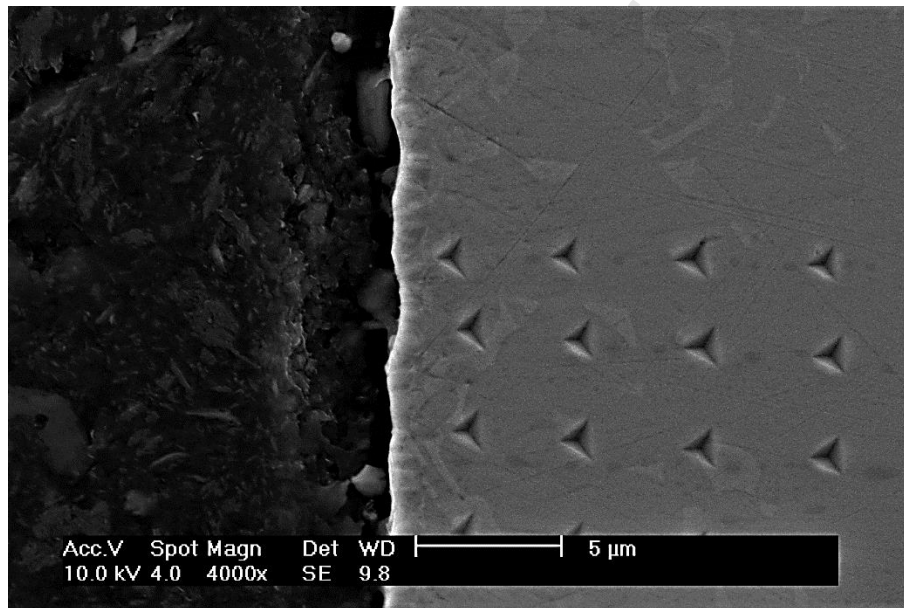


Figure 11 SEM cross-sectional image of the uncoated Ti-64 TPN-treated at 700°C for 4 hours, showing the nanoindentation traces

The cross-section hardness results (see Figure 12) for Ti-64 substrates show that the TPN hardening effect below the surface is higher for the Ti-Nb pre-coated sample than for the Ti pre-coated sample. The hardness values for all samples show a similar trend, with hardnesses approaching that of the untreated substrate core at around 18 μ m depth. Ten repeats used for each data point plotted in Figure 12 gave about ± 0.3 -0.4 GPa standard deviation (error bars are not shown, for clarity of presentation and curve fits generated by using regression method were inserted). The superior hardening effect for the Ti-Nb coated Ti-64 substrate can be explained by the higher diffusion rate of nitrogen (in the beta phase coating) than in the substrate. Nitrogen can diffuse to the substrate faster and the Ti-Nb layer suppresses

compound layer formation (that would hinder N-diffusion) until its final sputter-removal in the late stages of TPN treatment.

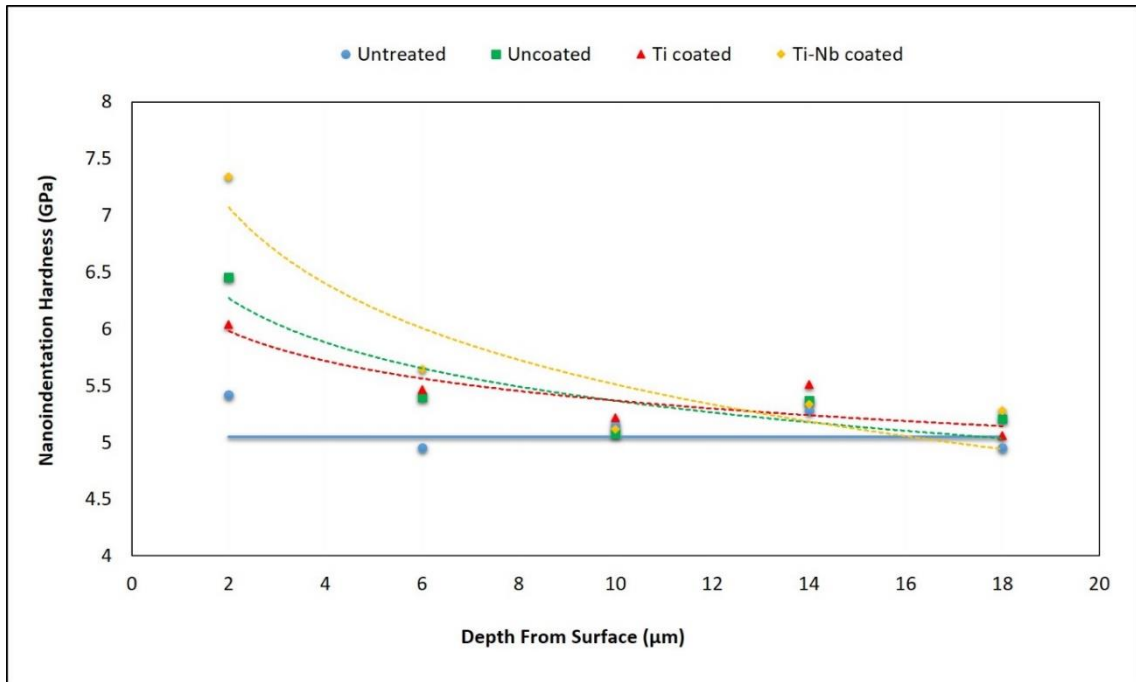


Figure 12 Cross-Sectional Nanoindentation data for bare and pre-coated Ti-64 substrates treated at 700°C for 4h. (each data point is an average from 10 indentation measurement at the selected treatment depth)

Results for the TPN-treated Ti-AVM substrates indicate that the hardening effect under the surface is higher for the α -Ti coated sample. It is shown (in Figure 13) that the uncoated Ti-AVM substrates exhibit a similar hardness trend to the untreated samples (ie. negligible surface hardening occurs; despite the clear evidence of significant nitrogen content from EDX results). It has been discussed before that 4 hours of nitriding at 700°C is not enough to harden the surface of the Ti-AVM alloy. The Ti-Nb coated sample is also not showing a significant hardening effect (if anything, the performance in terms of diffusion-hardening kinetics is marginally worse than uncoated) because the coating and substrate have predominantly the same crystallographic structure (ie. bcc β -Ti phase). The superior hardening effect for the α -Ti coated Ti-AVM substrate can be explained by a lower diffusion rate of nitrogen (in the alpha phase coating) than in the β -phase of the substrate (and/or indeed a Ti-Nb coating). It allows the rapid inward diffusion of interstitial nitrogen in the substrate β -phase to be slowed down,

thereby generating a significant hardening effect by allowing the nitrogen concentration (nb. a much higher solubility limit of N in β compared to α) in the near-surface of the beta alloy to increase to a significant level, to obtain a stronger solution hardening effect (and also some partial α -phase stabilisation).

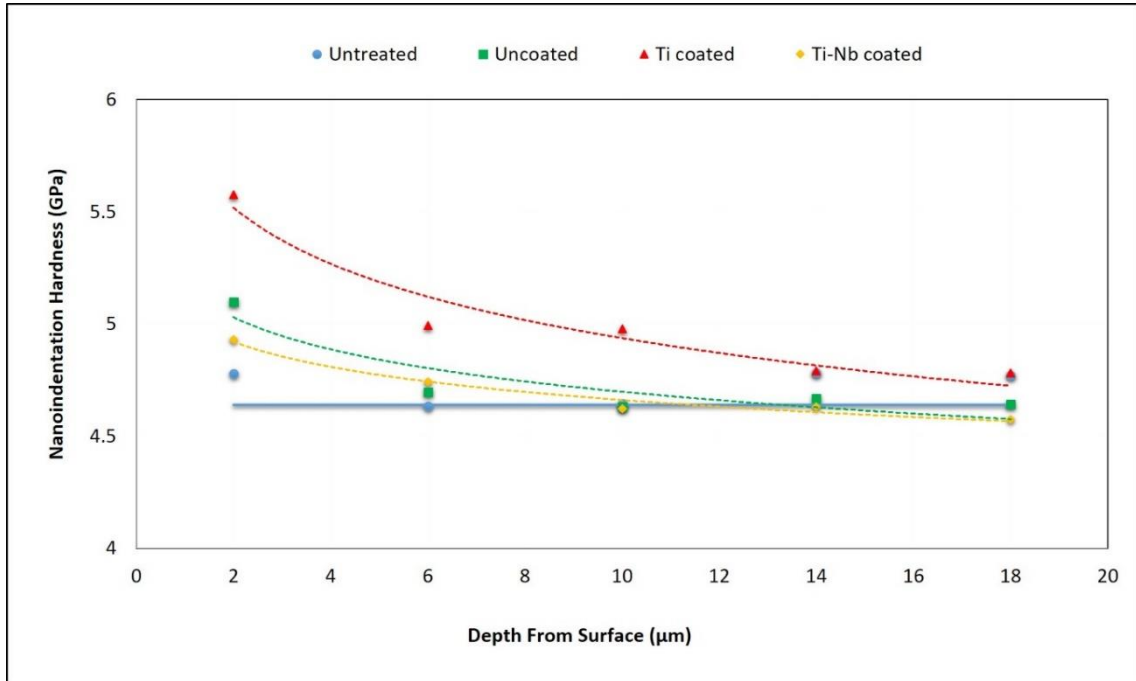


Figure 13 Cross-Sectional Nanoindentation data for bare and pre-coated Ti-AVM substrates treated at 700°C for 4h. (each data point is an average from 10 indentation measurements at the selected treatment depth)

Figure 14 shows surface hardness measurement results for the uncoated and coated Ti alloy substrates. The values are higher than the cross-section hardness data (due to nitride compound layer formation - particularly in the case of Ti-64 substrates) and both Ti alloys showed a significant hardness increase (after TPN treatment) compared to their untreated condition (this is indicated by the horizontal black lines in Figure 14). The somewhat lower hardness values for TPN-treated Ti-AVM substrates can be attributed to a lack of nitride compound layer formation on the surface; however, although difficult to detect, a little nitride precipitation in the substrate near-surface diffusion zone is nevertheless expected – according to the substantially higher surface hardness values of >9 GPa after treatment (which cannot be

explained by nitrogen interstitial solution strengthening and partial α -phase stabilisation alone).

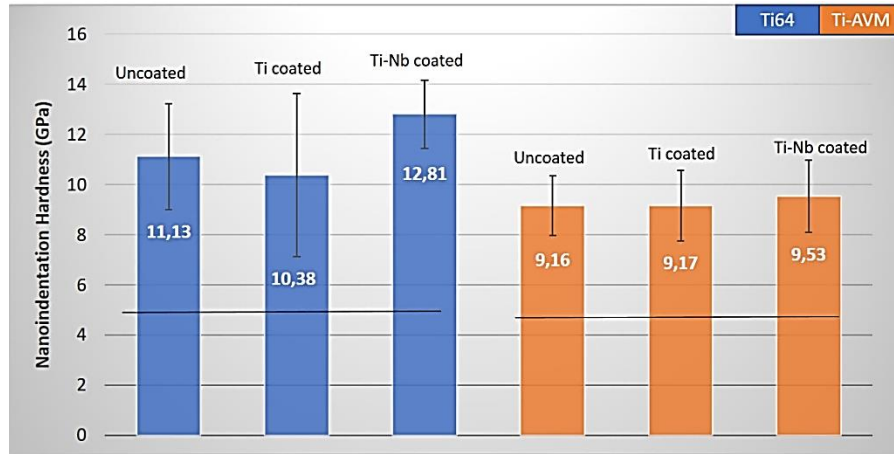


Figure 14 Surface nanoindentation hardness (GPa) for Ti-64 and Ti-AVM substrates prepared under different coating conditions and TPN treated at 700°C for 4h

3.2.5 Micro-abrasion wear tests

The wear coefficient values for the uncoated, Ti coated, and Ti-Nb coated Ti-64 substrates treated at 700°C for 4 hours can be found in Table 2.

Table 2 Micro-abrasion wear coefficients of uncoated, Ti coated, and Ti-Nb coated Ti-64 surfaces subjected to 4 hours TPN700 treatments

Ti-alloy	Sample	Wear coefficient (K) ($\times 10^{-4} \text{ mm}^3/\text{Nm}$)	ΔK , % (compared to the untreated substrate)
Ti-64	Untreated	10.87	---
	Uncoated TPN700-4h	9.97	-8.3
	Ti coated TPN700-4h	9.60	-11.7
	Ti-Nb coated TPN700-4h	9.18	-15.5

The abrasive wear resistance of the Ti-64 substrate showed some enhancement after 4hrs TPN treatment at 700°C; the wear coefficient was approximately 8% less compared to untreated. Although the surface hardness values were found to be significantly higher after the TPN

treatment, the wear performance of the uncoated Ti-64 substrate was not so remarkable after nitriding. It appears that surface hardness alone is not responsible for improved abrasive wear performance but a gradual change in mechanical properties from surface to core is particularly beneficial.

The highest surface roughness after TPN treatment was found for the uncoated Ti-64 substrate, compared to Ti or Ti-Nb coated Ti-64 substrates. As mentioned previously, the PVD metallic coatings deposited before the nitriding process led to a significant decrease in the final surface roughness values. The higher surface roughness could result in higher local contact pressures at the surface asperities while applying the micro-abrasion test, and this may accelerate the detachment of these (nitride) asperities. Having a lower initial surface roughness appears to give some advantage for the Ti, and Ti-Nb coated Ti-64 substrate, based on the observed wear performance. Moreover, the Ti-Nb coated Ti-64 substrate (which showed deeper cross-sectional hardening from the effect of the higher diffusion rate of nitrogen in the beta phase coating) yielded the best wear performance between the different Ti-64 substrate treatment strategies. This shows the importance of a functionally graded change in the mechanical properties with depth, imparted the nitriding process. In the light of all these findings, the higher surface hardness, lower surface roughness and more gradual hardness change from surface to bulk (compared to the uncoated and Ti coated candidates) appears to make the Ti-Nb coated Ti-64 substrate more effective in application areas requiring abrasion resistance.

The response of the Ti-AVM substrates after TPN700 processing was completely different from the Ti-64 substrates. The wear coefficient values for the uncoated, Ti coated, and Ti-Nb coated Ti-AVM substrates treated at 700°C for 4 hours can be found in Table 3.

Table 3 Wear coefficients of uncoated, Ti coated, and Ti-Nb coated Ti-AVM surfaces subjected to 4 hours TPN700 treatments

Ti-alloy	Sample	Wear coefficient ($\times 10^{-4}$ mm ³ /Nm)	$\Delta \kappa$, % (compared to the untreated substrate)
Ti-AVM	Untreated	8.13	---
	Uncoated TPN700-4h	6.11	-24.8
	Ti coated TPN700-4h	5.63	-30.7
	Ti-Nb coated TPN700-4h	5.72	-29.6

The uncoated Ti-AVM substrate showed about 25% reduction in wear after a 4-hour TPN treatment. It should be mentioned that the changes in surface chemistry of the Ti-AVM substrate were insubstantial (see Figure 7); however, it was seen that some α -Ti peaks appeared on the surface of the Ti-AVM substrate after TPN treatment. The inability to form a nitride compound layer on the surface of the Ti-AVM substrate resulted in lower surface hardness values (see Figure 14) after the nitriding treatment; however, better wear performance was measured for the Ti-AVM substrates (compared to Ti-64 substrates).

In our study, improved (reduced) surface roughness results were obtained depending on the chosen (coating, nitriding) process parameters. The method of pre-depositing a metallic PVD coating (prior to TPN treatment) provided more significant changes in the final properties of the Ti-AVM substrates, not least because the surface roughening of the uncoated Ti-AVM (due primarily to a large substrate grain size) was found to be almost double that of uncoated Ti-64 substrates after an identical TPN treatment. The wear coefficients of the Ti and Ti-Nb coated Ti-AVM substrates were found to be about 5% less compared to the uncoated Ti-AVM

substrate after a 4-hour TPN treatment. The enhancement of the wear performance of the Ti and Ti-Nb coated Ti-AVM substrates can be closely related to the reduced surface roughness because the surface morphologies were found to be similar for all three Ti-AVM substrate conditions after a 4-hour TPN treatment.

4 Conclusions

- Metallic Ti and Ti-Nb coatings (the latter with Nb concentrations in a range from 18 to 88 at. %.) were produced successfully on M2 tool steel substrates by magnetron sputter PVD. In order to obtain fully β stabilised Ti-Nb coatings on Ti-alloy substrates, it was decided to select at around 33 at. % Nb, to balance the phase stability of the Ti-Nb alloy coating and the (in principle) higher nitrogen diffusion efficiency of 'pure' unalloyed β -Ti during plasma nitriding. It is known that alloying elements (whether beta-stabilising, alpha-stabilising, or neutral) will tend also to reduce the interstitial diffusion coefficient in the parent phase.
- The hardening effect for Ti-Nb coated Ti-64 substrate was found to be higher than that of other Ti-64 substrates (after 4-hour TPN700 process) which is related to the higher local diffusion rate of nitrogen (in the β phase coating). Nitrogen can reach the underlying substrate faster and this promotes a higher nitrogen concentration (thicker diffusion-hardened zone) under the surface. It also suppresses Ti_2N/TiN compound layer formation at the near-surface, to maximize nitrogen uptake in the early stages of TPN treatment. The hardening effect for an α -Ti coated Ti-AVM substrate was found to be higher than for the other (uncoated and β -Ti-Nb coated) Ti-AVM substrates after a 4-hour TPN treatment at 700°C. This is explained by a lower diffusion rate of nitrogen (in the alpha phase coating) slowing down inwardly-diffusing nitrogen interstitials, to permit the build-up of a stronger solution hardening effect (and some alpha phase stabilization) in the Ti-AVM (beta phase) substrate by increasing the local nitrogen content in the near-surface, rather than dissipating inside the substrate at a

lower level of concentration (due to the much higher diffusion coefficient of nitrogen in the BCC beta phase compared to HCP alpha phase).

- The 1.25 μm thick Ti and Ti-Nb surface coatings (deposited before plasma nitriding) were sputtered off completely (after about 190-200 minutes, we estimate) during the 4-hour (240 minute) TPN 700 treatment. The sacrificial effect of the fine-columnar PVD surface coatings, however, led to a significant reduction in the final surface roughness of both Ti alloy substrates, compared to their uncoated equivalents. The post-nitrided surface roughness value for the Ti-Nb coated Ti-64 substrate was found to be 52% less than that of the uncoated Ti-64 substrate and a somewhat greater improvement was seen for the Ti-coated Ti-AVM substrate, with a 67% decrease (compared to the uncoated substrate). Therefore, it is suggested that the thickness of the PVD metallic surface coating should be selected by considering both nitriding duration (to select coatings of sufficient thickness that they remain present for the entire TPN treatment duration) and sputter removal effects, that will be coating composition dependent, to obtain smoother surfaces after plasma nitriding – whilst also controlling the diffusion kinetics during treatment.
- Micro-abrasion wear performance was found to be lower for the TPN treated Ti-64 substrate/coating combinations (compared to the Ti-AVM equivalents), which can be attributed in part to the formation of brittle nitride phases at and/or near the surface. The Ti and Ti-Nb surface coatings provided a noticeable benefit in abrasion resistance, with approximately 12 % and 16 % enhancement (compared to the untreated substrate) seen respectively after a 4-hour TPN treatment. On the other hand, the wear performance of the Ti and Ti-Nb coated Ti-AVM substrates yielded an approximate 30 % reduction in wear (compared to the untreated beta-alloy substrate); however, this seemed to be more as a consequence of a significant reduction in surface roughness than improved nitrogen solution strengthening – since the wear reductions afforded by

α Ti and β Ti-Nb pre-coating of the substrate were very similar, despite the enhanced nitrogen diffusion-hardening of the substrate obtained from our HCP α -Ti pre-coating strategy for the (predominantly beta-phased) Ti-AVM substrate.

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G. Yumusak Validation, Software, Investigation, Writing - Original Draft

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Highlights

- To obtain fully β -phase of Ti-Nb coatings, it is selected at around 33 at. % Nb
- The hardening effect for Ti-Nb coated Ti-64 substrate was found to be higher
- The hardening effect for Ti coated Ti-AVM substrate was found to be higher
- The 1.25 μm thick surface coatings were sputtered off completely after 4hr nitriding
- The Ti and Ti-Nb surface coatings provided a noticeable benefit in abrasion

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