



A microabrasion wear study of nitrated α -Ti and β -TiNb PVD metallic thin films, pre-deposited onto titanium alloy substrates

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ABSTRACT

In this paper, we study the structure, mechanical properties and abrasion resistance of two triode-plasma nitrated (TPN) titanium alloys, pre-coated with metallic α -Ti or β -TiNb layers deposited by physical vapour deposition (PVD). The chosen alloys were Ti-6Al-4V and Ti-4Al-10V-22Mo, which are predominantly alpha- and beta-phased, respectively – each presenting different challenges, in terms of their nitriding response. Although duplex nitriding + PVD coating is now quite widely employed on steels (and increasingly on titanium alloys) to improve load-bearing capacity and wear resistance, the use of PVD coatings prior to diffusion treatment to control surface roughness – and, in the case of Ti-alloys particularly, to optimise their ‘challenging’ diffusion kinetics has received little or no attention so far. The TPN process enables diffusion treatments to be carried out at 700 °C – which is lower than the beta-transus temperature of Ti (and of most Ti alloys). Optical microscopy, scanning electron microscopy, atomic force microscopy, X-ray diffraction, nanoindentation, and surface profilometry were used to characterize the nitrated and coated/nitrated samples. It was found that the nitrogen concentration and surface hardness for all samples was significantly increased, and that the surface roughness values significantly increased for uncoated Ti alloy substrates after TPN treatment – due to intense, grain orientation-dependent plasma etching effects. However, our novel approach of PVD pre-deposition of a nanostructured metallic coating prior to nitriding reduces surface roughening effects quite dramatically. The microabrasion resistance of Ti- and TiNb-coated Ti-6Al-4V substrates was significantly enhanced after nitriding treatment; on the other hand, similar improvements were not found for the metastable-beta Ti-4Al-10V-22Mo substrates – due to the different nitriding behaviour of the pre-deposited PVD surface layers. The “sputter removal” rates for the metallic coatings were high, but all coatings survived in part until the end of the nitriding process.

1. Introduction

Due to their superior properties (such as biocompatibility, high corrosion resistance, and high strength to density ratio), titanium and its alloys are used in many different applications today [1]. In contrast, their poor wear performance compared to other candidate metallic tribological systems limits the use of titanium and its alloys in wear-resistance applications [2] and it is virtually impossible to use titanium-alloy substrates in tribology applications without applying some kind of surface engineering treatment – such as nitriding, and/or ceramic hard coating deposition. Although improving the wear performance of titanium alloys by surface modification methods is of

significant scientific and commercial interest/importance, the magnitude of the contact load applied during use is a significant (yet often poorly considered) factor in choosing the right combination of surface modification methods; i.e. a single technique is rarely sufficient – and novel duplex/hybrid methods are often a necessity for satisfactory performance in commercial practice. For example, when a Ti-alloy substrate – of typically low elastic modulus and hardness – is coated with a hard material, the substrate frequently cannot support the coating because of the differential normalised contact stress levels involved (often described as an “egg-shell” effect) [3]. At the moment, the default solution for this undesirable condition is to apply a preliminary thermochemical diffusion treatment (such as plasma nitriding) before hard

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coating deposition [4].

A number of different nitriding techniques can be used for the purpose of substrate strengthening of pure titanium and titanium alloys [5–8]. Although nitriding treatments can be highly-effective in increasing the surface hardness of titanium, they often do not change sufficiently the surface tribochemistry of the substrate, and may therefore provide little tribological benefit – particularly if the treatment layer is thin (in which case, mechanical load support may also be inadequate). Furthermore, although higher nitriding treatment temperatures near to, or above, the beta-transus temperature of the Ti-alloy being treated can boost the nitrided case depth, this generally comes at the expense of significant bulk grain growth, which reduces core strength – and similarly leads to an unacceptable lack of load-bearing capacity. To address such issues, it is preferred that multi-layered coatings, duplex or hybrid techniques be used for the purpose of combined load-support enhancement and tribochemical-friction/wear behaviour optimisation. The combination of thermochemical diffusion treatment followed by hard coating deposition using plasma-assisted physical vapour deposition is an excellent example of such a technique [9,10]; however, most solutions explored so far (both for titanium and for other engineering metals/alloys) have been based on the sequential application of plasma nitriding, followed by PVD ceramic coating. On the other hand, to increase the efficiency of this preliminary thermochemical treatment (and/or control surface finish more precisely), there is recent evidence that Ti-alloy substrates can beneficially be pre-coated with a pure, or alloyed, metallic PVD thin film [11,12], and then nitrided after (rather than before) coating, to provide a modified nitride-based hardened surface, with potentially superior properties. The hardened layer formed after diffusion treatment can be substantially different, depending on both the chosen titanium alloy composition, and the thickness, morphology and composition of the pre-deposited metallic thin film. Besides this, the nitrogen diffusion zone thickness (and/or hardness) inside the substrate can be improved by using the pre-deposited metallic coating to either accelerate or retard the nitrogen diffusion kinetics, depending on the phase constitution of the chosen substrate alloy. The different phases of titanium and its alloys have very different behaviours in terms of nitrogen interstitial diffusion. In the case of Ti-alloys that are predominantly alpha-phased, particularly, if the formation of a thick compound layer occurs rapidly in the early stages of the nitriding process, nitrogen will not diffuse into the substrate material efficiently because the compound (ceramic nitride) surface layers formed inhibit further nitrogen inward diffusion. On the other hand, in the case of predominantly beta-phased Ti-alloys particularly, if the nitrogen inward diffusion is too rapid, it becomes difficult to achieve an interstitial nitrogen concentration at the near-surface that is sufficient to effectively harden the material. An appropriate surface coating deposited before nitriding can increase or decrease the local nitrogen diffusion rate, but the effect will depend strongly on which surface coating composition is chosen for which titanium alloy – and this may also be influenced by the precise prior heat-treatment path of the chosen alloy. The thickness of the surface layer is also important and needs to be selected depending both on the nitriding temperature/time [13], and on whether it is desirable to completely (or only partially) sputter-remove the pre-deposited PVD layer, over the duration of the nitriding treatment.

Nitriding treatment duration is one of the more critical parameters which can influence the composition and structure of the nitrogen-affected zones in the alloy near-surface. It has been mentioned in previous literature studies [11,14–17] that increasing the process duration can change the nitride phase structure from ϵ -Ti₂N to δ -TiN and/or increase the intensity of the phase peaks detected under XRD analysis, depending on the structure and thickness of the compound layers formed. Since, for most α and $\alpha + \beta$ Ti-alloys, the amount of nitrogen incorporated at the near-surface tends to increase significantly with treatment time [14–16], a significant nitrogen concentration depth-profile from the surface to the bulk of the alloy arises and,

consequently, the hardness values from bulk to surface will also be measurable increased within most of the nitrogen-modified zone [17]. The treatment thickness is reported to follow a linear dependency to the square root of the process duration and the (temperature-dependent) diffusion coefficient [18]; the efficiency of the nitriding process should therefore in principle be improved by increasing both time and temperature of treatment. However, as alluded to above, the precise treatment temperature should be selected carefully depending on which titanium alloy is being nitrided. A previous study [19] reported that the use of high nitriding temperature could severely affect the bulk mechanical properties – due to excessive grain growth. It was also reported that the use of temperatures above the alpha-to-beta transus temperature, in particular, could affect the nitriding process negatively [20,21]. It can be deduced that an increase in the process duration can sometimes be a better option for the overall nitriding performance – but this significantly reduces the cost-effectiveness in practical (commercial) applications. On the other hand, changes in nitriding process parameters can also influence the structure of the titanium alloy by causing different local distributions of alloying elements inside the substrate, which can be related to the particular affinity of these elements for nitrogen [22]. A longer nitriding time also allows these elements to diffuse more extensively, which can lead to the formation of different phases (such as martensitic Ti and Ti-Al intermetallic phase) in the bulk structure, which can affect the mechanical properties and the wear performance of the alloy. It is also known [1,23] that the strong alpha-stabilising effects of nitrogen will tend to convert beta-phased constituents to alpha with increasing nitrogen content/treatment time.

In a previous pilot study by the authors [13], thin α -Ti and β -TiNb PVD coatings were deposited on to Ti-6Al-4V (designated ‘Ti-64’) and Ti-4Al-10V-22Mo (designated ‘Ti-AVM’) substrates. Then uncoated, Ti-coated and TiNb-coated Ti-64 and Ti-AVM samples were TPN diffusion treated for 4 h at 700 °C. It was found that the 1.25 μ m thick surface coatings were sputtered off completely after 4 h of intense triode plasma nitriding. The hardening effects for TiNb-coated Ti-64 and Ti-coated Ti-AVM substrates were found to be greater, but the relatively short nitriding time made precise differentiation challenging, since the diffusion-treated layers were quite thin. Furthermore, benefits in reduced surface roughening due to fine-grained structure of the protective PVD layers were visible, but were difficult to quantify – since the later stages of TPN treatment occurred after the PVD layer was sputter removed (whereby substrate roughening would start to accelerate, for a time period that was impossible to accurately quantify). Micro-abrasion wear resistance was also noticeably improved by the effect of pre-deposited Ti and TiNb surface layers – but, again, the precise benefits were difficult to quantify due to perforation of the (thin) treatment layers. In the present study therefore, a longer 8-hour nitriding time is used, together with substantially thicker PVD metallic layers (to increase TPN treatment thickness, whilst at the same time allowing all coatings to survive until the end of the 8 hour nitriding treatment). The effects of these revised coating/treatment parameters on the final morphology and micro-abrasion wear resistance of the different pre-coated titanium alloy substrates are observed and evaluated.

2. Experimental details

2.1. Duplex plasma diffusion/coating

The duplex plasma diffusion/coating system used to carry out the treatments has been explained in detail in our previous pilot study [13]. Similar to the previous work, firstly, an α -Ti or a β -TiNb surface layer was deposited by sputter PVD onto $\alpha + \beta$ -phased Ti-6Al-4V (‘Ti-64’) and metastable β -phased Ti-4Al-10V-22Mo (‘Ti-AVM’) substrates. The power supplied to both the pure Ti and the composite Ti-Nb target was 1000 W; the rectangular target dimensions being 380x100mm in each case. During deposition, the substrates were biased at –50 V. The deposition time was adjusted to 280 (and 240) minutes for Ti (and TiNb) coatings

respectively, resulting in a coating thickness of approximately 5 μm for each. Then, the triode plasma nitriding (TPN) process was applied to uncoated, Ti-coated, and TiNb-coated samples of the two above mentioned titanium alloy substrates at 700 °C for 8 h in total. The increase in thickness of the Ti and TiNb coatings from 1.25 μm [13] to (approximately) 5 μm was designed to ensure that all coatings survived until the end of the TPN treatment, allowing the behaviour of the surface layers to be analysed with more clarity and confidence than was previously possible. The extended 8 h nitriding process was applied by dividing the process into two runs (4 h + 4 h) to inhibit any problems related to over-heating of the chamber walls and failure of the hot tungsten wire filament used to intensify the plasma. The substrates were biased at -300 V during TPN treatment and the volumetric ratio of the Ar and N₂ partial pressures was 30%Ar and 70% N; the total chamber pressure was maintained at around 4×10^{-3} mbar. This set of nitriding treatments was intended to be sufficiently long as to provide detailed information related to the uncoated substrate nitriding behaviour for 8 h; i.e. the effect of the process duration on nitriding efficiency and surface roughening could also be understood and compared – as a ‘baseline’ to the performance of the PVD pre-coated samples. All other processing parameters were kept constant throughout the treatment cycle.

2.2. Characterization

Phase analysis was carried out using a PANalytical X'Pert3 X-ray diffractometer (Cu-K α radiation), with a step size of 0.02° and a step time of 3 s in the 30° to 80° 2 θ range, with 2-degree glancing angle mode. An extra set of XRD experiments was established (for X-ray phase-*depth* analysis) between 30–50° from 2 to 10° angle of incidence.

A Philips XL 30 scanning electron microscope was used to investigate the cross-sectional surface morphology of the substrates after plasma nitriding. It was operated at 5 to 10 kV, with 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 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.

Hardness measurements were performed at a load of 5mN, using a Hysitron Triboscope® nano-indenter with Berkovich three-sided pyramidal diamond tip. The hardness measurements were performed using a matrix of 4 × 4 indents. In each hardness test the number of indents was therefore 16, and every matrix run was repeated twice to gain a more reliable data set of 32 indents in total. 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 1 mm, and the scan duration was set to 120 s.

2.3. Abrasion resistance

Abrasion resistance was evaluated using a Plint TE-66 micro-abrasion test rig. The abrasive slurry was prepared by using SiC particles (F1200, ~3–4 μm mean particle diameter) 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 was used. The rotation of the ball was adjusted at a tangential velocity of 0.1 ms⁻¹ which equals about 80 rpm. The time of the experiments was determined by the number of ball revolutions, and the applied load was selected as 0.1 N. Three different abrasion craters were produced for each sample and multiple measurements across each of the craters were taken. Wear coefficients (κ) of the untreated substrates (for comparison purposes), nitrided only substrates, and duplex treated (coated, then nitrided)

substrates were calculated by using Archard's standard wear equation approach [24].

3. Results and discussion

3.1. Surface and cross-sectional morphology

Surface optical microscopy and SEM cross-sectional images of the treated samples were helpful to confirm the continued presence of the PVD layers, both pure-Ti and TiNb-alloy. The optical microscopy images of the surface topography of samples TPN treated at 700 °C for 8 h can be seen in Fig. 1. The Ti-coated (g) and TiNb-coated (h) Ti-AVM substrates in particular did not show a similar morphology to the TPN-treated uncoated substrate (f). Their microstructures looked more like that of the uncoated (b) Ti-64 substrate after nitriding; i.e. small-grained. Although, due in part to the initially much finer microstructure of the alloy, the nitrided Ti-64 samples look quite similar (whether coated or not), the Ti-AVM results support the fact that both Ti and TiNb 5 μm thick coatings partially survived after 8 h' nitriding. If all the coatings would be sputtered off, the microstructure of Ti-coated (g) and TiNb-coated (h) Ti-AVM substrates would tend to represent that of the underlying (much coarser-grained) substrate microstructure of the uncoated Ti-AVM substrate (f). Furthermore, although the post-nitrided topographies of the coated substrates look quite similar to each other (and to that of the uncoated Ti-64 substrate), the actual surface roughness values do vary quite significantly – as will be shown later in Section 3.5.

The SEM cross-sectional images of samples nitrided at 700 °C for 8 h can be seen in Fig. 2. The BSE mode of the SEM technique shows different areas of Z-contrast, which are very significant for TiNb coatings on Ti-64 substrates due to the significantly higher atomic number of the Nb atoms. On the other hand, a difference in contrast can be seen for Ti coatings on Ti-AVM substrates mainly because of the high substrate Mo content, which again provides a much higher average Z-number (compared to either the Ti-64 substrate or a pure Ti-coating), whereby the Ti-AVM substrate appears brighter in BSE mode [25]. The surface nitride layer which forms after 8 h' nitriding for the uncoated Ti-64 substrate appears to be approximately 1.50 μm thick, followed by a brighter layer containing vanadium-rich grains. A similar layer that was about 0.85 μm thick was also seen after nitriding for 4 h [13]. Moreover, this compound layer is not fully dense but exhibits a columnar structure, as can be seen in Fig. 2 (a). The nitriding behaviour of the uncoated Ti-AVM substrate after 8 h was very similar to the 4 h' treatment. A modified zone containing nitrogen stabilized α phase with acicular (needle-like) features was seen near the surface of the Ti-AVM substrate.

The Ti-coated Ti-AVM substrate showed a different final nitride morphology to the Ti coated Ti-64 substrate. It is visible from the cross-section SEM image in Fig. 2 (e) that some of the 5 μm PVD-Ti coating remains in place and that its maximum residual thickness is about 0.85 μm . XRD results (Figs. 3 and 4) also showed 2 different peaks of Ti₂N phase for the Ti-64 substrate; on the other hand, only one small Ti₂N peak was seen for the Ti-AVM substrate. The reason for these two different nitride morphologies (for Ti-coated Ti-64 and Ti-AVM) must be related to the substrate chemistry and phase constitution, because all other processing parameters were identical (i.e. performed in the same chamber/run).

The structures of the remaining TiNb coatings on the Ti-64 and Ti-AVM substrates look similar. The black spots (acicular structure) in the coatings seen in Fig. 2 (c) and (f) reveal what appears to be stabilized alpha phase; this conclusion also being supported to some extent by the phase constituents identified under XRD examination. The same spots were seen in both coating and substrate for TiNb-coated Ti-AVM substrate, revealing alpha stabilisation near the coating/substrate boundary. For the Ti-coated Ti-AVM substrate, the spots formation (in the substrate) is found to be less than that for TiNb-coated Ti-AVM after the 8-hour nitriding treatment, when comparing Fig. 2 (e) and (f). It can

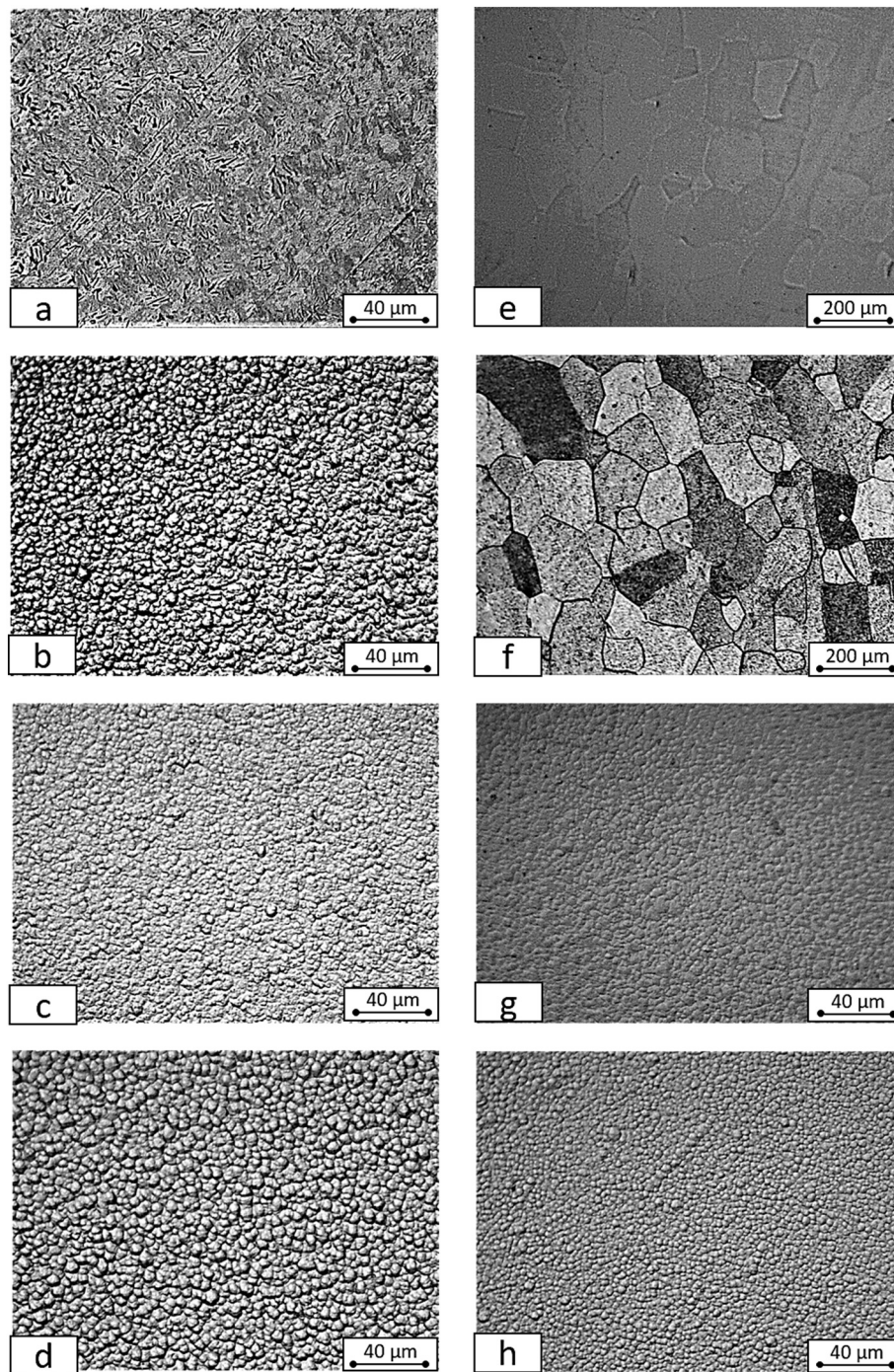


Fig. 1. Optical microscopy images of the surface topography of untreated samples and samples TPN treated at 700 °C for 8 h. (a) untreated Ti-64 substrate (b) uncoated Ti-64 (c) Ti-coated Ti-64 (d) TiNb-coated Ti-64 (e) untreated Ti-AVM substrate (f) uncoated Ti-AVM (g) Ti-coated and (h) TiNb-coated Ti-AVM.

therefore be deduced that the faster nitrogen inward diffusion through the TiNb coating leads to more alpha stabilisation for TiNb-coated Ti-AVM than for the Ti-coated equivalent.

3.2. EDX composition and X-ray diffraction phase analysis

The near-surface EDX results after TPN700 treatment for uncoated, Ti-coated, and TiNb-coated Ti-64 and Ti-AVM substrates (after 8 h of TPN treatment duration) are presented in [Table 1](#). The observed behaviour was somewhat different from the 4 hour nitriding treatment we previously reported in [\[13\]](#) – and is easier to interpret unambiguously, because all PVD coatings survived until the end of the 8-hour TPN

treatment, due to their selected thickness.

The most efficient way to understand if any TiNb coating remains – or whether it is sputtered off entirely by the intense plasma bombardment during nitriding – is to check the surface Nb concentrations for TiNb-coated substrates, because there is no Nb present in either Ti-64 or Ti-AVM alloy substrates. It can be seen from [Table 1](#) that both TiNb-coated Ti-64 and Ti-AVM substrates have Nb on their surfaces at about 24–26 at.%. Examining the EDX-Mo signals for the coated Ti-AVM substrates after TPN treatment – and comparing them to those of the untreated and TPN-treated (but uncoated) substrate – it can be seen that both Mo signals for TPN-treated coatings are visible, yet somewhat reduced, indicating that some of the coating (whether Ti, or TiNb)

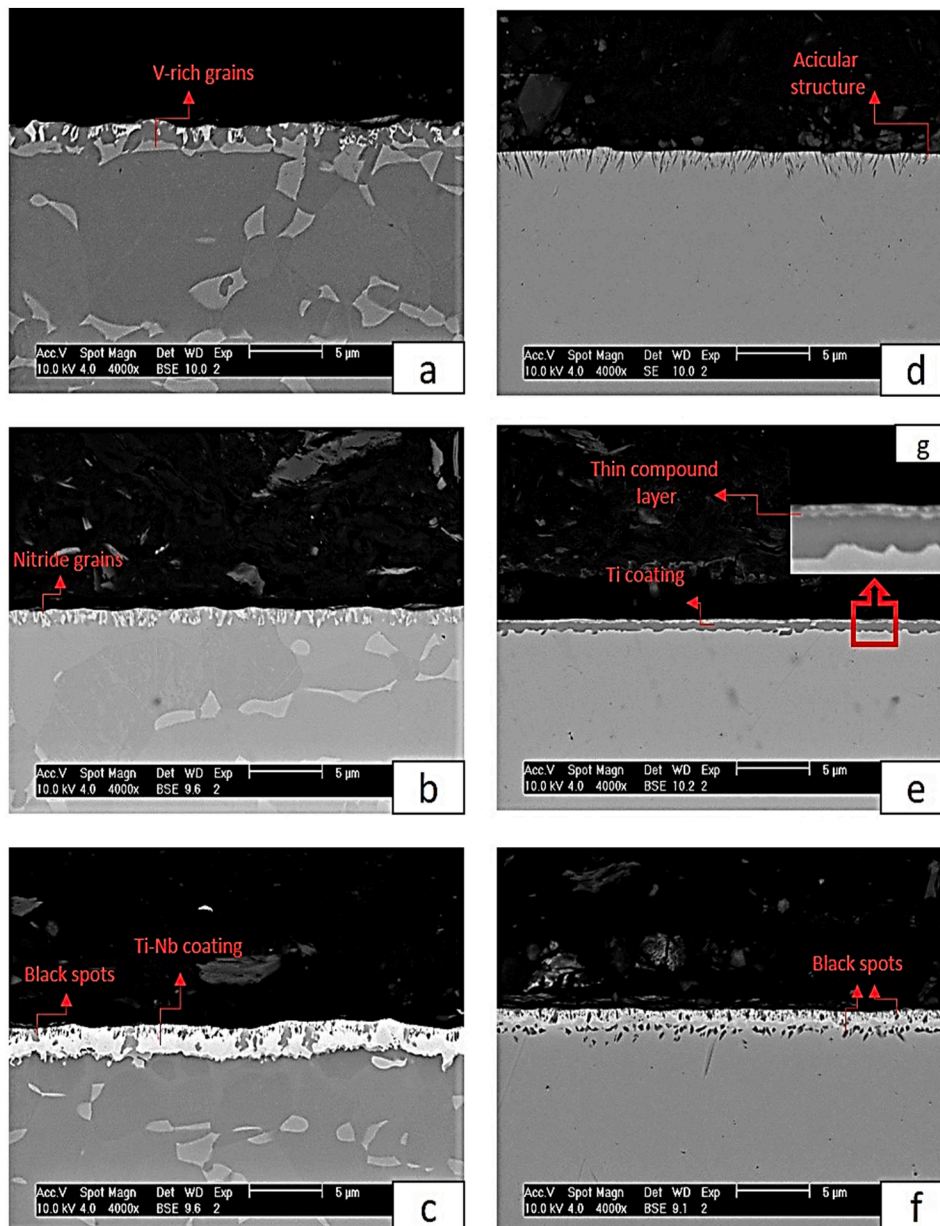


Fig. 2. SEM cross-sectional images of the samples treated at 700 °C for 8 h; (a) uncoated Ti-64, (b) Ti-coated Ti-64, (c) TiNb-coated Ti-64, (d) uncoated Ti-AVM, (e) Ti-coated and (f) TiNb-coated Ti-AVM; (g) shows an enlargement of the near-surface region of Ti-coated Ti-AVM.

remains after TPN treatment. Additionally, it can be seen that the Mo signal for the Ti-coated Ti-AVM substrate is substantially higher than that of the TiNb equivalent; i.e. measured values of 6.4 vs. 1.6 at.% in [Table 1](#). This discrepancy indicates that the sputter removal rate of the Ti coating is substantially higher than that of Ti-Nb – but also that neither coating was completely removed during the TPN treatment. On this latter point, it should be mentioned that, without additional detailed SEM studies, it remains difficult to estimate precisely what the optimal treatment time for complete PVD coating sputter removal might be, since there is a small (but significant) decrease also in local Mo-content in the Ti-AVM substrate, caused by the TPN treatment – comparing Mo signals of 12.4 vs. 10.1 at.% for uncoated/un-nitrided vs. uncoated/TPN-treated Ti-AVM substrates, shown in [Table 1](#). Although not of critical importance to the key findings of this paper, these observations nevertheless emphasise the potential complexities involved in choosing the right PVD metallic pre-coating (and as-deposited coating thickness) for optimal TPN-treatment of any particular Ti-alloy substrate chosen.

The X-ray diffraction patterns for Ti-64 and Ti-AVM substrates – both uncoated and pre-coated – nitrided for 8 h at 700 °C are shown in [Figs. 3 and 4](#). It can be seen from the XRD patterns that there are some signs of the Ti_2N nitride phase for both Ti- and TiNb-coated Ti-64 and Ti-AVM substrates. However, it can be said that these are minor phases in which the substrate peaks were seen with more powerful intensities – despite this XRD characterization being made with 2° glancing angle mode. The XRD patterns show the availability of nitride phases on the surface but the weakness of the nitride phase peaks in the XRD patterns can be explained by the nitride compound layer being very thin (nanometre levels) or these phases being discontinuous at/near the sample surface; they might therefore be fine-grained (possibly nano-) precipitates formed within the nitrogen diffusion layer itself.

The other significant finding from the EDX results – that is not apparent from the (very similar) surface topographies seen in [Fig. 1](#) – is a different response of the uncoated Ti-64 to the 8-hour nitriding treatment, when compared to Ti- and TiNb-coated Ti-64. The nitrogen

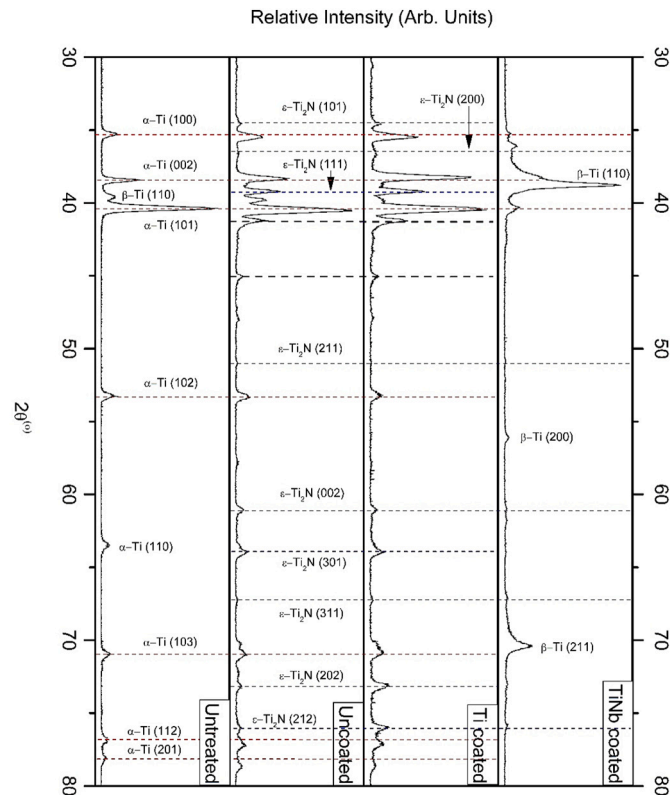


Fig. 3. GAXRD (2° angle of incidence) diffraction patterns of untreated Ti-64 (i.e. substrate only) and Ti-64 nitrided at 700°C for 8 h.

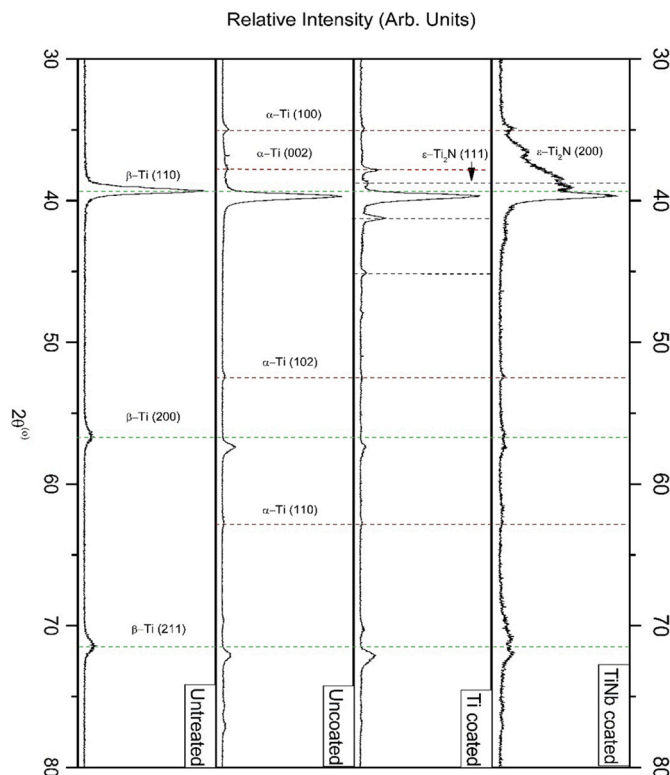


Fig. 4. GAXRD (2° angle of incidence) diffraction patterns of untreated (substrate only) and nitrided Ti-AVM substrates at 700°C for 8 h.

Table 1

Near surface EDX results of the samples nitrided at 700°C for 8 h.

Samples	Ti (at. %)	Al (at. %)	V (at. %)	Nb (at. %)	Mo (at. %)	N (at. %)
Ti-64 substrate (untreated)	85.1	11.4	3.5	–	–	–
TPN700, 8 h, Uncoated Ti-64	62.8	8.4	2.9	–	–	25.9
TPN700, 8 h, Ti-coated Ti-64	61.5	7.0	1.6	–	–	29.9
TPN700, 8 h, TiNb-coated Ti-64	39.3	1.6	1.8	26.4	–	30.9
Ti-AVM substrate (untreated)	69.9	7.6	10.1	–	12.4	–
TiNb-coated Ti-AVM substrate (untreated)	65.2	–	–	34.8	–	–
TPN700, 8 h, uncoated Ti-AVM	62.7	6.0	5.5	–	10.1	15.7
TPN700, 8 h, Ti-coated Ti-AVM	42.8	3.0	5.5	–	6.4	33.3
TPN700, 8 h, TiNb-coated Ti-AVM	38.5	1.9	3.0	23.4	1.6	31.6

concentration for the uncoated Ti-64 substrate was found to be about 26 at.%, which is almost double that obtained previously after 4 h of nitriding treatment (where the N concentration was only 12.1% [13]). The XRD pattern for the uncoated Ti-64 substrate (after 8 h of nitriding treatment) is almost identical to that obtained after 4 h of nitriding treatment. The only difference between the two XRD patterns is that there are some extra peaks (at about 41.5° , 45° and 48°) after 8 h of nitriding. The XRD match analyses (seen in the light of previous studies by Morgiel et al. [21]) suggest that these peaks belong to martensitic Ti and Ti-Al intermetallic phases. It is interesting to note that the formation of both α' -Ti and Ti-Al intermetallic phases were seen only for Ti-coated substrates and uncoated Ti-64 substrates. This suggests that the presence of Ti atoms (as the HCP α -Ti polymorph) on the surface of the samples – together with the nitrogen diffusion inside the substrates – is leading to the mobilization of the Al atoms towards the surface in the alloy, resulting also in the substrate grains below the treated layer being proportionally enriched in V. On the other hand, these segregation phenomena were not seen for either of the Ti-Nb coated substrates, or for the uncoated Ti-AVM alloy – all of which are predominantly BCC β -Ti phased.

The diffusion phenomena of the alloying elements (movement of the Al and V atoms) inside the uncoated Ti-64 substrate after 8 hour nitriding process was observed by EDX mapping (Fig. 5). The figure illustrates how a bright (vanadium-rich) layer follows the surface nitrogen-rich area. In some grains, the V concentration was seen to rise to about 15–16 at.%. The deficiency of Al in this vanadium-rich area may be the cause of the formation of a different phase – such as the observed α' -Ti martensite. The enrichment of Al towards the sample surface may also be the reason for the local formation of a Ti-Al intermetallic phase.

The uncoated Ti-AVM substrate showed only minor differences in nitrogen concentration on the surface after 8 h of TPN treatment. The nitrogen concentration was previously found to be about 12 at.% (after 4 h of TPN treatment [13]), rising only slightly to about 16 at.% after the 8-hour treatment performed in the present study. The XRD patterns for the uncoated Ti-AVM substrate (see Fig. 4) show quite strong alpha peaks – but with the other visible peaks being similar to those found in XRD patterns obtained previously [13]. Common to both present and previous work however, is the apparent absence of any nitride phases, such as Ti_2N , after treatment of uncoated Ti-AVM sample – with the near-surface nitrogen concentration being significantly lower compared to any of the Ti-64 treatments performed. This can be explained by the significantly higher nitrogen diffusion coefficient of the β -Ti – which has been reported to be as much as 3 orders of magnitude higher than for

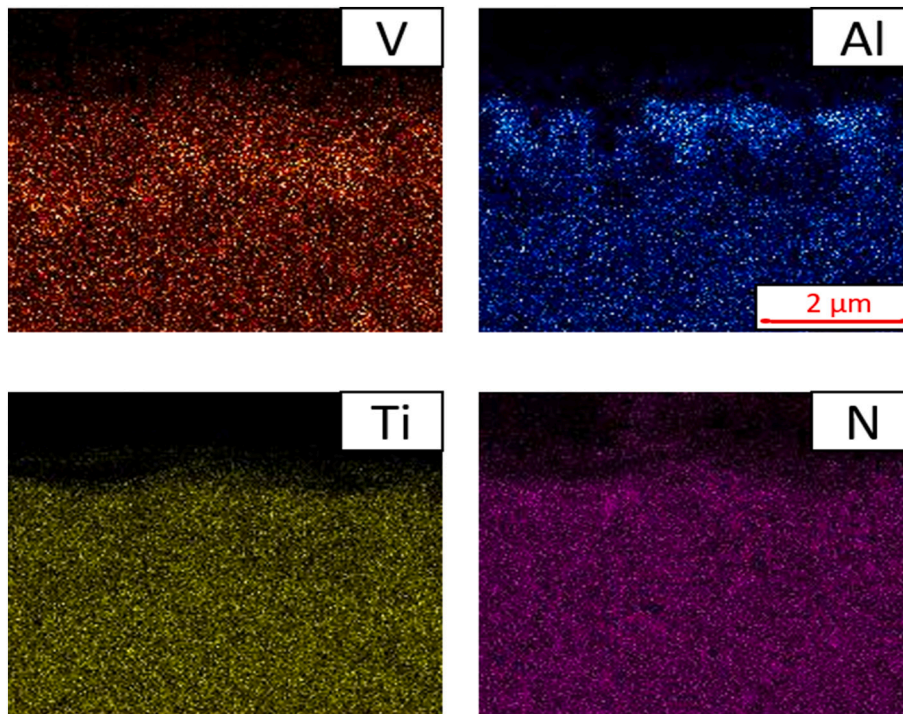


Fig. 5. EDX maps taken from the cross-section of the uncoated Ti-64 treated at 700 °C for 8 h (the upper dark region shows the carbon-rich mounting material).

α -Ti at an equivalent temperature [26,27]. The higher diffusion coefficient allows interstitial nitrogen introduced at the β -Ti alloy surface to disperse more quickly into the substrate and, accordingly, it is difficult to accumulate nitrogen near the surface at a level sufficient to provide significant hardening effects – either by solution strengthening or by nitride precipitation – in such alloys. Another notable point arising is that the EDX results and XRD patterns for the uncoated Ti-AVM substrate after 8 h of nitriding treatment show very good agreement with Ti-Mo-N ternary phase diagram predictions [28]. The estimation made for Ti-Mo alloys at 700 °C suggests that N can be dissolved to a maximum of 16 at.% without creating nitride phases – a value that appears not to be exceeded in any of our TPN treatments of the uncoated Ti-AVM substrate. The precise EDX-measured value for the nitrogen content is 15.7 at.% after 8 h of TPN treatment, (Table 1) and there is no sign of any nitride phase formation in the XRD pattern (although this does not preclude the possible presence of Ti_2N nano-precipitates). In summary, it can be understood that the effective nitriding of β -titanium alloys is difficult (in the context of generating a useful hardening effect). An increase in process duration alone may not be enough to create significant interstitial solution strengthening or precipitation hardening – and/or surface nitride layers – hence our strategy in this work to explore possible nitrogen diffusion retardation by use of a suitable PVD ‘barrier’ coating (i.e. pure α -Ti, in this case).

3.3. XRD analysis at different X-ray penetration depths

A new set of (glancing-angle) XRD experiments was performed to analyse the desired interval of the XRD patterns (i.e. between 30–50°) from 2 to 10° angle of grazing incidence, and thus explore the phase dependence on nitrogen concentration-depth profile (by gradually decreasing the X-ray attenuation). The approximate X-ray penetration depth was calculated (using the AbsorbDX software) to give an estimated value related to the angle of incidence. The X-ray penetration depth was found to vary from approximately 0.8 to 3.3 μ m for pure Ti metal over the chosen range of 2 to 10° X-ray incident angle (for the Cu $K\alpha_1$ line and assuming intermediate 2θ values of around 40° for the diffracted beam). The penetration depth calculation for pure Nb metal

showed a depth range from 0.6 to 2.4 μ m. The penetration depth range was calculated for an uncoated Ti-64 substrate to be between 0.9 and 3.6 μ m, from 2 to 10° angle of incidence. All these values showed that a set of comparable measurements could be performed (from the near-surface inwards) by using the 2–10° angle of incidence range, whilst the X-ray penetration depth calculation for θ –2 θ XRD measurements could be shown to reach to approximately 5 μ m below the surface.

Fig. 6 shows the GAXRD diffraction patterns of the uncoated Ti-64 substrate with TPN700 treatment applied for 8 h. The XRD patterns can be followed by the given colours for each incident angle chosen. The black line which belongs to the 2° angle of incidence showed the lowest intensities for the α -Ti phase, and it did not show any β -Ti peaks. This is because the surface of the Ti-64 substrate is modified (with high nitrogen concentration) after 8-hour TPN700 treatment. On the other hand,

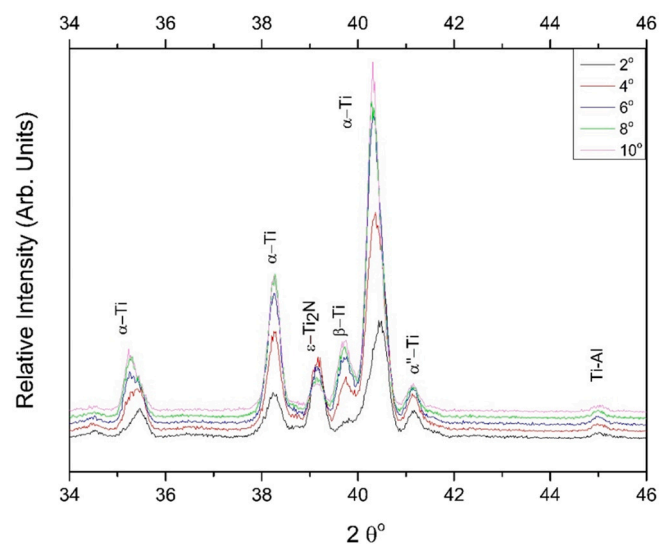


Fig. 6. GAXRD diffraction patterns for an uncoated Ti-64 substrate nitrided at 700 °C for 8 h (2° to 10° angle of incidence).

the Ti_2N peak is the highest for the 2° angle of incidence and 4° angle of incidence (shown in red). Moreover, the intensity of the Ti_2N peak is gradually decreasing from 2° to 10° angle of incidence. The martensitic α'' -Ti phase peak intensity is lowest for the 2° angle of incidence; the pattern for 10° angle of incidence (shown in pink) reveals a low peak intensity for α'' -Ti. The Ti-Al intermetallic phase peak also shows the lowest intensity for 2° angle of incidence. These findings (i.e. the depth-dependent positions and intensities of the phase peaks) showed that the dominant phase at the surface of the uncoated Ti-64 substrate after 8 h of TPN700 treatment is the Ti_2N phase. Below this level, the α -Ti and β -Ti phases are emerging (at 4° angle of incidence), and the phase structure has also started to decompose to α'' -Ti and Ti-Al phases. However, it can also be seen that, besides the Ti_2N phase, the α'' -Ti and Ti-Al lose their intensities in the 10° angle of incidence pattern, indicating that these phases are located between the surface Ti_2N -rich layer and the substrate core. To summarise these rather complex findings, the expected phase structure of the uncoated Ti-64 after 8-hour TPN700 treatment is shown schematically in Fig. 7. It should however be mentioned that the maximum attenuation depth of the X-rays does not increase linearly with increasing angle of incidence from 2° to 10° , making the precise depths at which phases appear (or are extinguished) difficult to assess.

3.4. Analysis of residual coating layer thickness after nitriding

The scenarios for the Ti and TiNb-coated substrates are a little different, due to the existence (and persistence) of the pre-deposited surface layers which, as mentioned earlier, were substantially thicker than we previously reported [13]. The initial PVD-Ti coating thickness before the 8-hour nitriding process was $4.85 \mu m$, with a maximum residual thickness of $1.40 \mu m$ remaining after TPN treatment. The residual coating thickness values for all sample options can be seen in Table 2. The thicknesses are expressed as "maximum" values for each condition because the remaining coating thickness across the (small) substrate coupons was not uniform – due to 'edge effects' from the plasma sheath; i.e. more intense sputter bombardment around sharp features. The highest thickness (also representative for 'real' component application, we believe) was seen in the middle of the substrates, and the thickness was observed to decrease from the middle of the samples towards the sample edges. An example of this plasma edge effect can be seen in Fig. 8. This example is chosen due to the significantly larger grain size of the underlying Ti-AVM substrate, that reveals the coating/substrate structural contrast most clearly. The 'topological' contrast between plasma-etched Ti-AVM substrate grains, and unetched grains (i.e. where the coating still exists) gives a good indication of where the coating has been completely removed. The blue arrow in Fig. 8 shows the direction from the edge to the centre of the substrate. Three different areas can be seen, which are affected by plasma-bombardment at different rates. The first

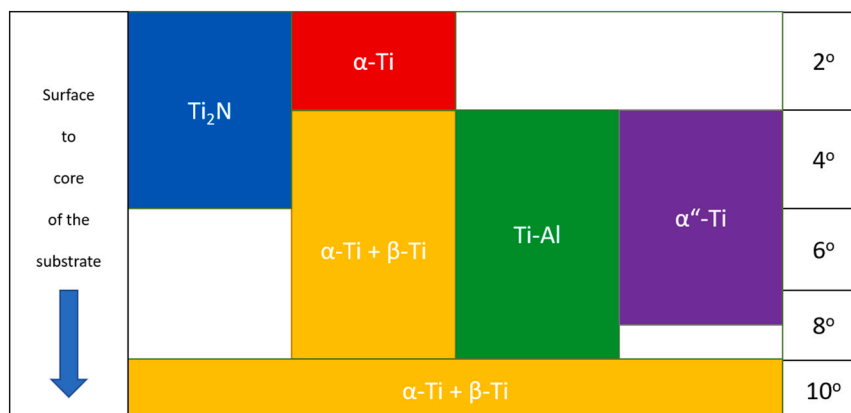


Fig. 7. The estimated phase positions (based on the different glancing angle X-ray penetration depth) in Ti-64 substrate nitrided at $700^\circ C$ for 8 h.

Table 2
Residual thicknesses of the remaining PVD coating layers after TPN treatment.

Sample	Temperature ($^\circ C$)	Duration (h)	Coating thickness (μm)		Thickness reduction (%)
			Before nitriding	After nitriding	
Ti-coated Ti-64	700	8	4.85	1.40	71
TiNb-coated Ti-64	700	8	5.05	1.95	61
Ti-coated Ti-AVM	700	8	4.85	0.85	82
TiNb-coated Ti-AVM	700	8	5.05	1.50	71

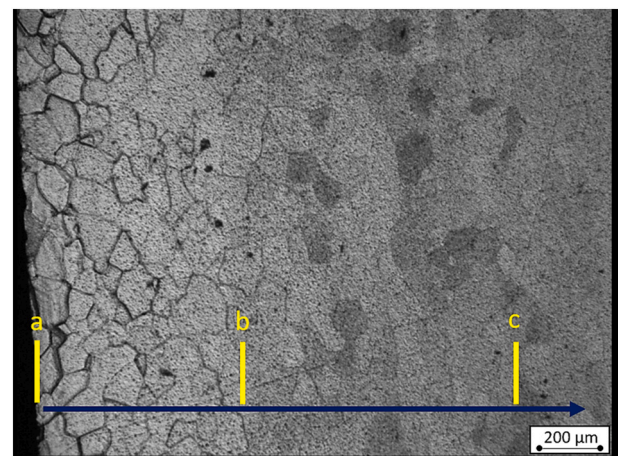


Fig. 8. Optical microscopy images of the surface topography of Ti coated Ti-AVM substrate after 8 hour nitriding process at $700^\circ C$. The points a, b and c (from edge to centre of the sample) were marked to show where the morphology of the sample changed. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

area (between 'a' and 'b') is the most affected part of the sample, in which the coating is sputtered off entirely. The faint appearance of grain boundaries can be seen in the area between 'b' and 'c', which reveals that there is still some coating remaining, but the thickness is lower than the area between point 'c' and the centre of the sample, because the

grain-boundary features cannot be seen from 'point c' onwards. This partial (and localised) coating removal – even for a short time, towards the end of the TPN treatment – reveals very clearly the benefits to substrate surface topology control of the presence of a (nanostructured) PVD coating during plasma diffusion treatment – notwithstanding any beneficial modifications also to the diffusion kinetics.

There is a difference in the rate of change in thickness of the Ti surface coating between the two substrates after 8 hour nitriding (see Table 2). Although the initial thicknesses of the PVD coatings were notionally the same (i.e. $4.95 \pm 0.1 \mu\text{m}$), the final thicknesses were found to be substantially different for Ti-64 and Ti-AVM substrates; i.e. it is not just the coating composition that determines the rate of its sputter removal, but also the chemical composition of the underlying substrate. If the nitriding performance of these two different substrates is believed equal, the differences in the final thicknesses may be attributed to the different resputtering rates of the coating metal ions – or to the nitrogen-containing phase constituents formed during treatment. This must depend to some extent on whether the coating still exists as a metallic phase – or has been converted to a nitride phase (with consequent changes in coating sputter yield), as the TPN treatment progresses. For example, if the Ti coating layer on the Ti-64 substrate is converted more rapidly to nitrides than the Ti layer on the Ti-AVM substrate (not unexpected – bearing in mind the diffusion characteristics of each) then, as we can observe in Table 2, the resputtering rate of the Ti coating on the Ti-64 substrate will be expected to diminish more rapidly with TPN treatment time, resulting in a thicker residual Ti-layer, compared to the same layer remaining on Ti-AVM.

3.5. Surface hardness and topography measurements

An 8-hour nitriding process applied to $5 \mu\text{m}$ thick surface layers shows different surface hardness results to those previously reported for 4 h and $1.25 \mu\text{m}$ [13]. Because of the different nitriding behaviour of the coating, the behaviour of the underlying substrate (once the coating is completely removed by sputtering) will inevitably affect the measured hardness data. Thus, the nitriding performances of the coating/substrate pairs were analysed together to clarify the results. The surface hardness data for the uncoated and coated Ti-alloy substrates treated at 700°C for 8 h can be seen in Fig. 9, and compared with selected 4-hour treatments from Ref. [13], that are also shown.

The overall positive effect of a longer treatment duration on the surface hardness values can be seen for the uncoated Ti-64 and Ti-AVM substrates, with the increases in surface nitrogen concentration at the surface and in the thickness of the nitrided zone providing the expected benefits. What is also apparent, is that – apart from the unexpectedly

inferior results for Ti-coated Ti-AVM – the surface hardness values for the PVD-coated substrates are substantially higher than for the uncoated ones after an equivalent TPN treatment. The results do seem to be strongly related to the residual coating amount on the surface; i.e. the measured trends in hardness do correlate quite closely with coating thickness (after the 8-hour TPN treatments, where the coatings persist), with the level of hardening suggesting that all coatings are being converted (in whole or in part) to nitride phases – although the XRD data does not provide unequivocal evidence of this. As suggested by Fig. 7, the 8 h treated Ti-64 samples are likely to possess a thin Ti_2N surface compound layer – supported by a mixed precipitate-hardened alpha case, rich in Ti_2N precipitates near the surface, and in TiAl precipitates (together with some α'' martensite) near the substrate core – the Ti-AVM samples may also contain a fine dispersion of Ti_2N precipitates within the remaining PVD coating layer. The latter is in addition to the very thin compound layer apparently visible in Fig. 2e – and neither of which can be reliably detected by XRD analysis. Detailed TEM analysis would be required to confirm these suppositions – but this was unfortunately beyond the scope of the present work. Furthermore, the Ti coatings deposited on two different Ti-alloy substrates have different structures (see Fig. 2), and this also affected the surface hardness results. The formation of the nitride/intermetallic precipitates inside the coating for the Ti-coated Ti-64 substrate (see Fig. 2b) resulted in a significantly higher measured hardness than for the Ti-coated Ti-AVM substrate. Although the surface EDX analysis indicated about 33 at.% N, the lower hardness values measured for the Ti-coated Ti-AVM substrate could be related to inferior load support from the underlying substrate diffusion zone. In summary, it is apparent that the composition and thickness of a pre-deposited PVD metallic coating needs to be selected by carefully considering the type of substrate to be treated, the desired TPN treatment duration, and other process-specific parameters, such as gas mixture in the plasma, and applied substrate negative bias.

Fig. 10 shows the surface roughness data after 8-hour nitriding of untreated, Ti-coated, and TiNb-coated Ti-64 and Ti-AVM substrates (4-hour treatments from Ref. [13] are also shown, for comparison). It can be concluded from these data that uncoated substrates were invariably found to be significantly rougher than Ti- and TiNb-coated substrates after plasma nitriding – following a similar trend to that seen previously for pre-coated Ti-alloy substrates [11,13]. The positive effect of the pre-deposited metallic PVD coating on the final surface roughness after plasma nitriding was again observed, with the greatest reduction in surface roughening seen for the larger-grained Ti-AVM substrates, as expected – with both types of metallic surface coating performed extremely well, in keeping the final surface roughness values low. The TiNb-coated Ti-AVM substrate showed a slightly higher surface

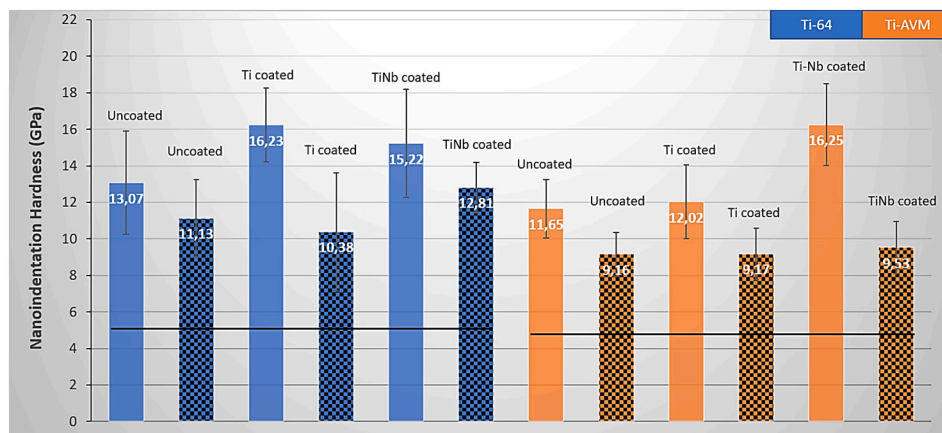


Fig. 9. Near-surface nanoindentation hardness data for Ti-64 and Ti-AVM substrates treated at 700°C for 4 h (pattern-filled [13]) and 8 h (plain coloured). (The black horizontal lines signify the mean hardness value of the untreated substrate.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

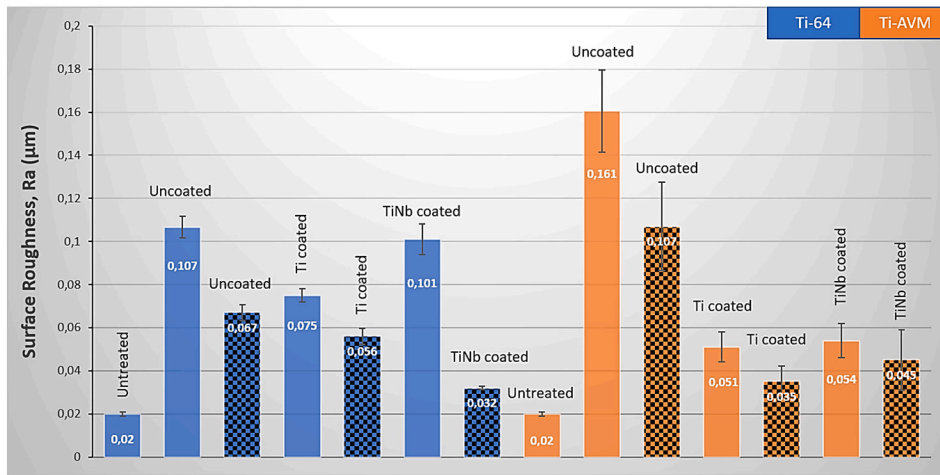


Fig. 10. Surface roughness data for uncoated, Ti-coated and Ti-Nb coated Ti-64 and Ti-AVM substrates treated at 700 °C for 4 h (pattern-filled [13]) and 8 h (plain coloured). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

roughness value than the Ti-coated Ti-AVM substrate after the 8-hour TPN treatment, but the small difference can be neglected since the error bars overlap (i.e. the difference is not statistically significant). Overall, the coated Ti-AVM substrates showed lower surface roughness values than their Ti-64 equivalent – which is a remarkable result, considering the prior substrate grain size of the former. The fine, nanocolumnar and highly textured morphology of the coatings provides an important reduction in roughness by being sputtered off very

uniformly during TPN treatment – avoiding the ‘faceted’ selective etching of substrate grains, that is normally highly problematic in plasma diffusion treatment of many β-phased Ti-alloys.

On the other hand, the TiNb coating provided little or no positive effect in controlling the surface roughness for the Ti-64 substrate – also verified with AFM three-dimensional topographic maps, as seen in Fig. 11. It was also seen in Fig. 1 (b) and (d) that the surface topography of the TiNb-coated Ti-64 is very similar to that of uncoated Ti-64 after 8

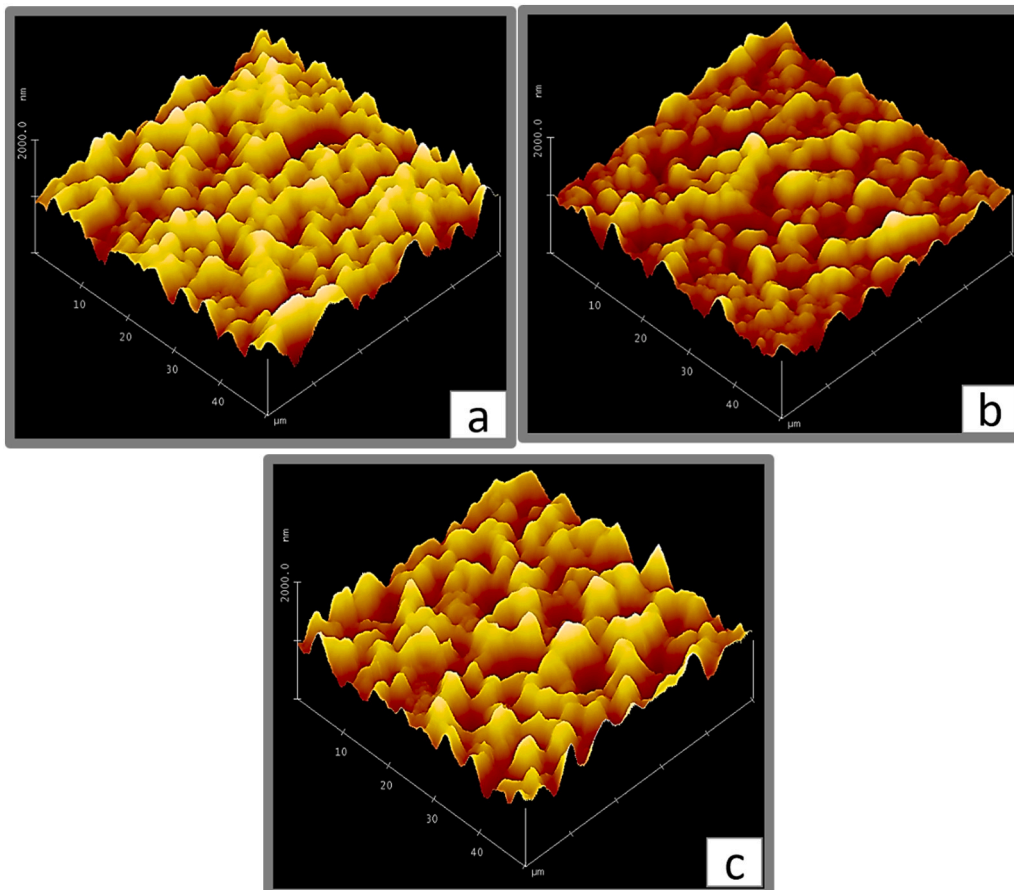


Fig. 11. AFM 3D topographic maps of (a) uncoated, (b) Ti-coated, (c) TiNb-coated Ti-64 substrates treated at 700 °C for 8 h (X-Y axis: 50 × 50 µm; Z axis: 0–2000 nm).

h of nitriding, which was unexpected. The cause may be related to the 8-hour process duration, which leads to the widespread formation of surface nitrides; this is not so pronounced as for uncoated Ti-64, but the surface nitride topography is measurably coarser. The nitride formation occurs more readily for both coatings on Ti-64 substrates – since the substrate blocks inward diffusion of nitrogen more strongly, compared to Ti-AVM.

3.6. Micro-abrasion wear

The wear coefficient values for the uncoated, Ti-coated, and TiNb-coated Ti-64 and Ti-AVM substrates treated at 700 °C for 8 h can be seen in Fig. 12 – with 4-hour treatment wear data from Ref. [13] again included, for comparison. The increase in the thickness of the nitride (compound) layer and the more beneficial underlying diffusion zone – with its increased nitrogen concentration – may lead to the superior abrasive wear performance of the uncoated Ti-64 substrate. An approximate 18% reduction in wear rate, compared to untreated Ti-64, was also found after 8 h of TPN treatment which is better than the wear performance of the Ti- and TiNb-coated Ti-64 substrates after a 4-hour TPN700 process [13].

The uncoated Ti-AVM substrate showed a similar trend (with previous wear tests) on abrasive wear performance after 8-hour TPN700 process. The increased hardness (see Fig. 9) depending on the amount of nitrogen on the surface (30.9 at.% N dissolved inside β -Ti phase without any obvious formation of ceramic phases, (see Table 1) may be the reason to find superior abrasive wear performance for the uncoated Ti-AVM substrate after the 8-hour TPN700 treatment. If the nitriding temperature (which was chosen here as a suitable maximum of 700 °C) is increased more, the wear mechanism of the Ti-AVM alloy can be different depending on its α to β transus temperature. Moreover, the nitriding time can be increased to see the effect on wear performance but, in this condition, the surface roughness value (the biggest value was found for this sample – which was 0.161 μm after 8-hour TPN700) could be more detrimental to wear behaviour, notwithstanding any substrate grain growth that might reduce core strength.

Cassar et al. [11] reported that Ti-15Mo – which is another example of a larger-grained, metastable β -Ti alloy – has an Ra value of about 0.34 μm after 4 h of TPN treatment at 700 °C. This value is almost two times larger than that which was found in the present study, and approaches the limit of what is typically considered as being acceptable for tribological bearing applications; i.e. when considering the ‘plasticity index’ for adequate performance in bearing design, less than 0.6 (and preferably 0.3 to 0.4) μm Ra is often considered as a ‘safe’ practical upper

boundary for the surface asperities to remain under predominantly elastic loading [29]. It was also reported previously that a PVD Ti-coated Ti-15Mo substrate facilitated a significant decrease in the final surface roughness after TPN treatment – and that this was consequently the main factor in decreasing the wear coefficient under micro-abrasion testing [11,23].

The PVD Ti- and TiNb-coated Ti-64 substrates showed better wear performance than the uncoated Ti-64 substrate after an 8-hour TPN700 treatment. The remaining surface coating layers contain more nitrogen in their near-surface led to better wear properties. The EDX results (Table 1) support the idea that the PVD pre-coated substrates have more nitrogen at their surfaces after the 8-hour TPN700 process. The surface coatings provided lower post-nitriding surface roughness values, with the exception of Ti-Nb coatings on a Ti-64 substrate. However, it is notable that the wear coefficient value of the TiNb-coated Ti-64 substrate is slightly lower than that of the Ti-coated Ti-64 substrate, despite the higher roughness of the former. This suggests that the anticipated negative effects of surface roughening on wear performance were to some extent counteracted by a superior nitriding efficiency from the TiNb coating. However, as a result, the Ti-coated and TiNb-coated Ti-64 substrates all exhibit fairly similar wear performance, overall. This suggests that the thickness of the PVD surface coatings should be selected carefully. If the TiNb coating thickness had been chosen to be, say, 3 μm (rather than 5 μm), the final properties might be more fully optimised, because the residual thickness of the TiNb coating in the present work is still quite high after the 8-hour TPN700 process. The remaining coating thicknesses also affects the micro-abrasion wear test results (the selected 100 ball revolutions produced about 2-micron crater depth which is greater than any of the remaining coating thicknesses). So, the later stages of the wear test will be influenced slightly by the (nitrided) substrate behaviour – which might in reality be either slightly superior, or inferior, to the coating layer wear resistance, depending on the individual sample parameters.

The effects of the PVD Ti and TiNb metallic coatings which were pre-deposited onto the Ti-AVM substrate were different from the nitriding behaviour of the uncoated Ti-AVM substrate after the 8-hour TPN700 process. Although the surface roughness values (Fig. 10) were decreased by the effect of pre-depositing a surface coating, the abrasive wear performance of the Ti- and TiNb-coated Ti-AVM substrates was actually somewhat worse than the uncoated ones – despite the dramatic reductions in post-treatment surface roughness imparted by the coatings. The abrasive wear performance of the coated Ti-AVM substrates was decreased by the formation of a thin nitride layer (that breaks up under the abrasion test and creates additional, hard wear debris) which was

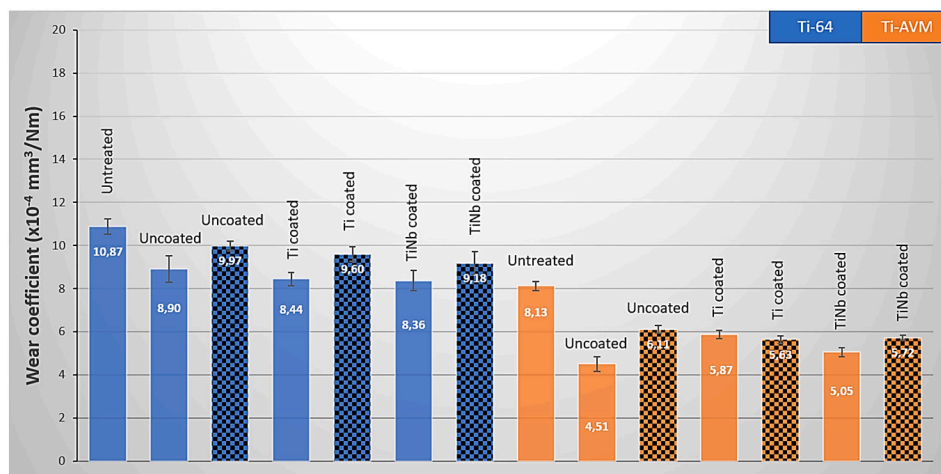


Fig. 12. Wear coefficients of uncoated Ti-64 and Ti-AVM surfaces subjected to 4-hour (pattern-filled [13]) and 8-hour (plain coloured) TPN700 treatments (a 25 mm diameter SAE52100 bearing steel ball was used with 0.1 N applied load for 100 revolutions). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

thought to accelerate the wear, in combination with the lower load-bearing capacity of the β -alloy substrate. As TiNb-coated Ti-AVM is found to be harder than Ti-coated Ti-AVM after the 8-hour TPN700 process – and due also to the different microstructures of the Ti and TiNb coatings (Fig. 2e and f) – the abrasive wear performance of the Ti-coated Ti-AVM substrate was found to be inferior, compared to TiNb-coated Ti-AVM substrate. The thin (and brittle) nitride layer (Fig. 2g) formed on Ti-coated Ti-AVM could be broken in the early stages of the abrasion test (compared to the TiNb coating on a Ti-AVM substrate). Our conclusion is therefore, that the wear performance of the diffusion/coating system depends critically on the substrate type, surface coating material (and its thickness) and the diffusion treatment time.

4. Conclusions

- Two titanium alloys: namely, a predominantly HCP α -phased Ti-6Al-4V alloy, and a predominantly BCC β -phased Ti-4Al-10V-22Mo, were successfully pre-coated with α -Ti and β -TiNb PVD coatings nominally 5 μ m thick, then Triode Plasma Nitrided for 8 h at a low (700 °C) treatment temperature – to assess the potential of such coatings to improve the nitriding response.
- All coatings partially survived the nitriding treatment, providing significant reductions in surface roughening – particularly of the larger-grained BCC alloy. However, although the coatings marginally improved the micro-abrasion wear behaviour of the HCP alloy, the BCC alloy did not benefit from coating – most likely due to the combination of a thin hardened surface layer, with a lack of underlying load support from the substrate. This would lead to break-up of the surface layer, amplifying the abrasion effect.
- The “sputter-off” percentage removal of the pre-deposited PVD metallic coatings showed that both coating types survived proportionately longer when they were deposited on the HCP substrate – suggesting that the diffusion kinetics of the substrate itself play a role in the rate of coating sputter removal during plasma treatment. Furthermore, the TiNb alloy coating survived proportionately better than pure Ti, on both substrates.
- EDX mapping of the uncoated Ti-6Al-4V after TPN treatment showed not only nitrogen interstitial diffusion but also local partitioning of both Al and V – leading to the formation of tetragonal Ti-Al intermetallic and orthorhombic α'' martensite phases beneath the Ti₂N-containing surface layer.
- It can be concluded overall, that, although the surface roughness of TPN-treated Ti-alloys (and particularly large-grained β -alloys) can be controlled very well by a PVD metallic coating pre-treatment, wear performance enhancement by such pre-coating/nitriding – although showing potential – depends very strongly on substrate composition, coating type/thickness, and treatment strategy/parameters, with many challenges remaining.

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.

References

- [1] M. Peters, C. Leyens, *Titanium and titanium alloys: fundamentals and applications*, Wiley, 2003.
- [2] U. Wiklund, I.M. Hutchings, Investigation of surface treatments for galling protection of titanium alloys, *Wear* 251 (1) (2001) 1034–1041, [https://doi.org/10.1016/S0043-1648\(01\)00730-X](https://doi.org/10.1016/S0043-1648(01)00730-X).

- [3] J. Meneve, K. Vercammen, E. Dekempeneer, J. Smeets, Thin tribological coatings: magic or design? *Surf. Coat. Technol.* 94–95 (Oct. 1997) 476–482, [https://doi.org/10.1016/S0257-8972\(97\)00430-1](https://doi.org/10.1016/S0257-8972(97)00430-1).
- [4] G. Cassar, S. Banfield, J.C. Avelar-Batista Wilson, J. Housden, A. Matthews, A. Leyland, Micro-abrasion wear testing of triode plasma diffusion and duplex treated Ti-6Al-4V alloy, *Wear* 274 (2012) 377–387, <https://doi.org/10.1016/j.wear.2011.10.002>.
- [5] F. Siahjani, E. Atar, H. Cimenoglu, Structural changes on the surface of alloy Ti6Al7Nb under gas nitriding, *Met. Sci. Heat Treat.* 58 (3) (2016) 170–174, <https://doi.org/10.1007/s11041-016-9983-x>.
- [6] S. Mridha, T.N. Baker, Effects of nitrogen gas flow rates on the microstructure and properties of laser-nitrided IMI318 titanium alloy (Ti-4V-6Al), *J. Mater. Process. Technol.* 77 (1–3) (May 1998) 115–121, [https://doi.org/10.1016/S0924-0136\(97\)00408-1](https://doi.org/10.1016/S0924-0136(97)00408-1).
- [7] A. Grill, Ion beam nitriding of titanium and titanium alloy, *Vacuum* 33 (6) (Jun. 1983) 333–337, [https://doi.org/10.1016/0042-207X\(83\)90102-1](https://doi.org/10.1016/0042-207X(83)90102-1).
- [8] A. Leyland, K.S. Fancey, A. Matthews, Plasma nitriding in a low pressure triode discharge to provide improvements in adhesion and load support for wear resistant coatings, *Surf. Eng.* 7 (3) (1991) 207–215.
- [9] A. Matthews, A. Leyland, Hybrid techniques in surface engineering, *Surf. Coat. Technol.* 71 (2) (Mar. 1995) 88–92, [https://doi.org/10.1016/0257-8972\(94\)01004-3](https://doi.org/10.1016/0257-8972(94)01004-3).
- [10] A. Matthews, A. Leyland, The future of plasma-based surface engineering techniques in tribology (keynote), in: *World Tribology Congress 42029*, 2005, pp. 297–298.
- [11] G. Cassar, A. Matthews, A. Leyland, Triode plasma diffusion treatment of titanium alloys, *Surf. Coat. Technol.* 212 (2012) 20–31, <https://doi.org/10.1016/j.surfcoat.2012.09.006>.
- [12] B. Attard, A. Matthews, A. Leyland, G. Cassar, Enhanced surface performance of Ti-6Al-4V alloy using a novel duplex process combining PVD-Al coating and triode plasma oxidation, *Surf. Coat. Technol.* 257 (2014) 154–164, <https://doi.org/10.1016/j.surfcoat.2014.07.083>.
- [13] G. Yumusak, A. Leyland, A. Matthews, The effect of pre-deposited titanium-based PVD metallic thin films on the nitrogen diffusion efficiency and wear behaviour of nitrided Ti alloys, *Surf. Coat. Technol.* (2020) 125545, <https://doi.org/10.1016/j.surfcoat.2020.125545>.
- [14] V. Fouquet, L. Pichon, M. Drouet, A. Straboni, Plasma assisted nitridation of Ti-6Al-4V, *Appl. Surf. Sci.* 221 (1–4) (Jan. 2004) 248–258, [https://doi.org/10.1016/S0169-4332\(03\)00889-4](https://doi.org/10.1016/S0169-4332(03)00889-4).
- [15] S.L.R. Da Silva, L.O. Kerber, L. Amaral, C.A. Dos Santos, X-ray diffraction measurements of plasma-nitrided Ti-6Al-4V, *Surf. Coat. Technol.* 116 (1999) 342–346.
- [16] F. Yildiz, A.F. Yetim, A. Alsan, A. Çelik, Plasma nitriding behavior of Ti6Al4V orthopedic alloy, *Surf. Coat. Technol.* 202 (11) (2008) 2471–2476, <https://doi.org/10.1016/j.surfcoat.2007.08.004>.
- [17] A. Zhecheva, S. Malinov, I. Katzarov, W. Sha, Modelling of kinetics of nitriding titanium alloys, *Surf. Eng.* 22 (6) (2006) 452–454.
- [18] A. Zhecheva, S. Malinov, W. Sha, Surface gas nitriding of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08 Si alloys, *Z. Met.* 94 (1) (2003) 19–24.
- [19] G. Cassar, S. Banfield, J.C.A.-B. Wilson, J. Housden, A. Matthews, A. Leyland, Impact wear resistance of plasma diffusion treated and duplex treated/PVD-coated Ti-6Al-4V alloy, *Surf. Coat. Technol.* 206 (10) (2012) 2645–2654, <https://doi.org/10.1016/j.surfcoat.2011.10.054>.
- [20] H. Shibata, K. Tokaji, T. Ogawa, C. Hori, The effect of gas nitriding on fatigue behaviour in titanium alloys, *Int. J. Fatigue* 16 (6) (Aug. 1994) 370–376, [https://doi.org/10.1016/0142-1123\(94\)90448-0](https://doi.org/10.1016/0142-1123(94)90448-0).
- [21] J. Morgiel, T. Wierzczoń, New estimate of phase sequence in diffusive layer formed on plasma nitrided Ti-6Al-4V alloy, *Surf. Coat. Technol.* 259 (2014) 473–482, <https://doi.org/10.1016/j.surfcoat.2014.10.043>.
- [22] T. Bacci, G. Pradelli, B. Tesi, C. Gianoglio, C. Badini, Surface engineering and chemical characterization in ion-nitrided titanium and titanium alloys, *J. Mater. Sci.* 25 (10) (Oct. 1990) 4309–4314, <https://doi.org/10.1007/BF00581089>.
- [23] G. Cassar, Improvement in the tribological characteristics of titanium alloys using duplex intensified plasma treatments, PhD Thesis, The University of Sheffield, 2011.
- [24] K.L. Rutherford, I.M. Hutchings, A micro-abrasive wear test, with particular application to coated systems, *Surf. Coat. Technol.* 79 (1–3) (1996) 231–239.
- [25] R. Maas, M. Koch, N.R. Harris, N.M. White, A.G.R. Evans, Thick-film printing of PZT onto silicon, *Mater. Lett.* 31 (1) (1997) 109–112, [https://doi.org/10.1016/S0167-577X\(96\)00249-2](https://doi.org/10.1016/S0167-577X(96)00249-2).
- [26] R.J. Wasilewski, G.L. Kehl, Diffusion of nitrogen and oxygen in titanium, *J. Inst. Met.* 83 (1954).
- [27] J.P. Bars, E. Etchessahar, J. Debuigne, Kinetics, diffusion and morphology of titanium nitriding using high-temperature nitrogen-mechanical and structural-properties of solid Ti-alpha-nitrogen solutions, *J. Less-Common Met.* 52 (1) (1977) 51–76.
- [28] G. Yumusak, Evaluating the Effect of Titanium-based PVD Metallic Thin Films on Nitrogen Diffusion Efficiency in Duplex Plasma Diffusion/Coating Systems (PhD Thesis), The University of Sheffield, 2019.
- [29] J.A. Greenwood, J.B.P. Williamson, Contact of nominally flat surfaces, *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* 295 (1442) (1966) 300–319.