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The exceptional oxidation of Ti6Al4V alloy with a pre-deposited silver layer

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Abstract:

For the first time, we discovered the exceptional oxidation phenomenon on Ti6Al4V alloy. A thin layer of silver was pre-deposited via PVD on a Ti6Al4V alloy surface before ceramic conversion treatment (CCT) based on thermal oxidation in air at 620°C. The pre-deposited silver particles accelerated the oxidation of the Ti6Al4V alloy by up to 50 times, and also helped to produce a thick compact surface oxide layer with a larger surface area compared to a non-silver pre-treated surface. However, silver had a less profound effect on the oxidation of other titanium alloys that didn't contain vanadium, additionally the silver particles tended to agglomerate on their surfaces, particularly for commercially pure titanium (CPTi). Systematic work examining the impact of vanadium found that vanadium together with silver played a critical role in activating oxygen and promoting its diffusion in the oxide layer, thus dramatically accelerating the oxidation of the vanadium-containing titanium alloys with a pre-deposited Ag layer in CCT. SEM/EDX, TEM, XRD and XPS analyses on the surface phase constituents and microstructure helped to explicate the rapid oxidation mechanism of pre-deposited silver on Ti6Al4V surfaces, and thus provide a new insight into modifying the titanium alloys surface efficiently.

Key words: Ti6Al4V, Oxidation, Ceramic conversion treatment, Silver

1. Introduction

Due to their chemical stability, high photoreactivity, optical transparency, broad-spectrum antibiosis and high refractive index, TiO₂-based materials have been broadly reported through an application-driven perspective: photocatalysis and hydrogen production, photovoltaic, anti-bacteria and biomedical devices, photochemical air and water treatments etc. [1, 2]. The addition of silver into titanium dioxide enhances its photocatalytic efficiency by assisting the formation of free radicals and strengthens the antimicrobial properties of the biomaterials like bone/dental implants [3-5]. Ag⁺ nanoparticles were also found to act as e⁻ traps to reduce the recombination rate of h⁺/e⁻ pairs in the TiO₂ thin films [6]. Hence, silver is commonly doped

into titanium oxide during processing the thin films/coatings [7] via reactive DC magnetron sputtering [8], ion beam assisted deposition [9] and sol-gel [10] etc.

A patented ceramic conversion treatment (CCT) has been developed in our group to improve the tribological performance of titanium and its alloys [11, 12]. We also found gold can catalyse the CCT process and make it more efficient [13], therefore, recently we tried to dope silver into titanium dioxide layer via CCT aiming at improving its efficiency and antibacterial properties in order for biomedical applications like implants [14]. A thin silver layer was pre-deposited on Ti6Al4V alloys' surface via PVD before CCT and then an extraordinary phenomenon was found: a thick (~5 μm), dense and adherent oxide layer was formed on the surface after only a 3-hour treatment at 620°C. The oxide layer formed is about 50 times thicker than that of the oxide layer (0.1-0.2 μm) formed under the same CCT conditions but without any pre-deposited silver layer; indeed, an oxide layer about 3.0 μm could be produced by conventional CCT (i.e., without pre-deposited silver layer) after a much longer period (80h). Silver nanoparticles are one of the catalyst most employed in oxidation reactions of alcohols but hardly reported on metals [15]. This exceptional acceleration in oxidation has fuelled our curiosity on the catalytic role of silver in the oxidation of the titanium alloys.

In this paper, we first compared the oxidation behaviour of the Ti6Al4V samples with or without a pre-deposited thin silver layer. Then, we tested different titanium alloys containing a varied amount of aluminium to examine if aluminium plays a role in the catalytic oxidation and if this is a common phenomenon. Following the findings, we inspected if vanadium could facilitate the oxidation of titanium, and then probed the joint action of vanadium/silver on the oxidation rate of CPTi. Finally, we concluded the contribution of Ag and V, and then systematically characterised the oxide layers via varied analytical techniques and elucidated the rapid oxidation mechanism based on the results to advance scientific understanding.

2. Experimental Methods

Both Ti6Al4V (grade 5) and CPTi (grade 2) bars (supplied by IMI Titanium Ltd.) were cut to coupons of 25.4 mm in diameter with a thickness of 4.5mm. Small pieces (5×5×1mm) were cut for thermogravimetric measurements. Samples of other alloys (Table 1) were cut to similar-sized coupons for comparative studies. All these samples were then ground progressively to 1200 grit before being ultrasonically cleaned in an acetone bath. Ceramic conversion treated samples were then cross-sectioned and mounted in conductive Bakelite. After grinding and polishing, they were etched in a Kroll's reagent to reveal their microstructure under SEM.

A 4-target Teer Coating Ltd Closed Field Unbalanced Magnetron Sputtering Ion Plater was used to deposit a thin Ag (50-80 nm), V (20-30nm) or V/Ag layer (90-110 nm) on one side of these samples at a current less than 1 A for a few minutes. Ceramic conversion treatments (CCT) were carried out in an Elite Thermal Systems Limited electric furnace, with a ramp rate of 8°C/min. The thermogravimetric test was carried out using a NETZSCH STA 449C with an alumina crucible to monitor the change of mass. The test includes a ramp period of 75 minutes to heat the sample at 8°C/minute, and then hold at 620°C for 15 hours (75-975 minutes). The detail of the CCTs and the corresponding sample codes can be seen in Table 1 (T is for Ti6Al4V alloy and C is for CPTi). For example, T-Ag620/3 denotes a Ti6Al4V(T) sample with a pre-deposited silver layer (Ag) which was CCTed at 620° for 3h, and C-620/3 denotes as a CPTi(C) sample without any pre-deposited layer was CCTed at 620° for 3h.

Table 1: Details of ceramic conversion treatments (CCT) and the corresponding sample code

Sample code	Pre-deposition	Temperature /°C	Time/ hour	Roughness (Ra, μm)	Oxide layer thickness (μm)
T-Ag	Ag	-	-	0.07-0.09	-
T-550/3	None	550	3	0.08-0.10	<<0.1
T-Ag550/3	Ag	550	3	0.18-0.19	~0.1
T-600/3	None	600	3	0.08-0.10	~0.1
T-Ag600/3	Ag	600	3	0.19-0.21	2.0-2.3
T-600/10	None	600	10	0.10-0.12	0.4-0.6
T-Ag600/10	Ag	600	10	0.23-0.27	10.0-12.0
T-620/3	None	620	3	0.09-0.11	0.1-0.2
T-Ag620/3	Ag	620	3	0.25-0.35	4.6-5.2
T-620/15	None	620	15	0.10-0.12	0.7-1.2
T-Ag620/15	Ag	620	15	0.42-0.45	14.0-16.0
T-620/80	None	620	80	0.15-0.18	2.4-3.8
T1-620/80	None	620	80	0.44-0.69	15-25
T-Ag620/80	None	620	80	0.69-1.34	40-45
C-Untreated	None	-	-	0.10-0.20	-
C-620/3	None	620	3	0.20-0.25	0.1-0.2
C-Ag620/3	Ag	620	3	0.38-0.42	0.6-0.8
C-V620/15	V	620	15	0.25-0.30	3.0-4.0
C-VAg620/15	V/Ag	620	15	0.63-0.68	7.0-7.5
C-620/15	None	620	15	0.20-0.28	0.6-1.0

The surface morphology, cross-sectional microstructure, and chemical compositions were analysed by a Jeol 7000 SEM equipped with an Oxford Inca energy-dispersive X-ray spectroscopy detector under 20 kV. High angle annular dark-field (HAADF) imaging and analysis were performed under scanning TEM (STEM) mode. TEM sample was prepared by focused ion beam (FIB) method using a FEI Quanta 3D instrument (Ga⁺ ion beam, 30 keV).

To preserve surface features, the treated samples were deposited with a thin layer (~10 nm) of Au using an Olympus sputter coater before FIB process.

A powder diffractometer Inel EQUINOX 3000 (2C) X-ray diffraction (XRD) using Cu-K α radiation ($\lambda = 0.154056$ nm) was used to identify the phase constituents on the surface of the samples. The diffraction angle (2θ) was between 20.01 and 70.00° and the scanning step was 0.02° for counting times of 1 s at each step. X-ray photoelectron spectroscopy (XPS) was performed with monochromatic Al Ka (500 μ m, 15 kV/150 W) radiation to analyse the elemental valences of the surface oxides.

3. Results

3.1 Oxidation phenomena of silver pre-deposited Ti6Al4V

A thick and dense oxide layer (~5 μ m) was formed on the surface of the silver pre-deposited Ti6Al4V sample after a 3-hour CCT treatment at 620°C (Figure 1a, T-Ag620/3). The surface of the oxide layer is rough (Table 1) with some superficial rose-like features (Figure 1b, Inset picture is the silver pre-deposited surface before CCT). The oxide layer formed on T-Ag620/3 is about 50 times that formed on sample T620-3 under the same CCT conditions but without any pre-deposited layer (0.1-0.2 μ m, Figure 1d), and it is much thicker than the 3.0 μ m layer produced by a conventional CCT without any pre-deposition layers after 80 h (T-620/80, Figure 1c). Silver has had a dramatic effect on speeding the oxidation of Ti6Al4V alloy. Besides, we carried out an 80h CCT by putting a Ti6Al4V sample without any pre-deposition (T1-620/80) on the top of silver pre-deposited sample (T-Ag620/80) as schematically shown in Figure 2a. An oxide layer of 40-45 μ m was produced on sample T-Ag620/80 after CCT at 620°C for 80 hours (Figure 2b/c). In the meantime, an oxide layer of 15-25 μ m was generated on the surface of sample T1-620/80 sitting on the top of sample T-Ag620/80, which was far thicker than that (~3 μ m) of the sample T620/80 treated separately without the presence of silver. Silver was found in the oxide layer formed on the sample T-Ag620-80 (Figure 2c) but it was not detected in the oxide layer formed on the sample T1-620/80 (Figure 2d/e/f).

We pre-deposited a thin silver layer on CPTi surface and CCTed at 620°C for 3 hours to see if silver had the same effect. Surprisingly the sample C-Ag620/3 had an oxide layer of 0.6-0.8 μ m thick, which was only 3-5 times of the 0.1-0.2 μ m thick oxide layer on sample C-620/3 without a pre-deposited Ag layer (Figure 3a). Although Ag promoted the oxidation of Ti, it cannot account for the 50 times increase of the oxide layer formed in the same CCT conditions on the

Ag pre-deposited Ti6Al4V sample (T-Ag620/3). Furthermore, large silver agglomerates scattered on the sample C-Ag620/3 surface and led to a rougher surface as shown in Figure 3b and Table 1.

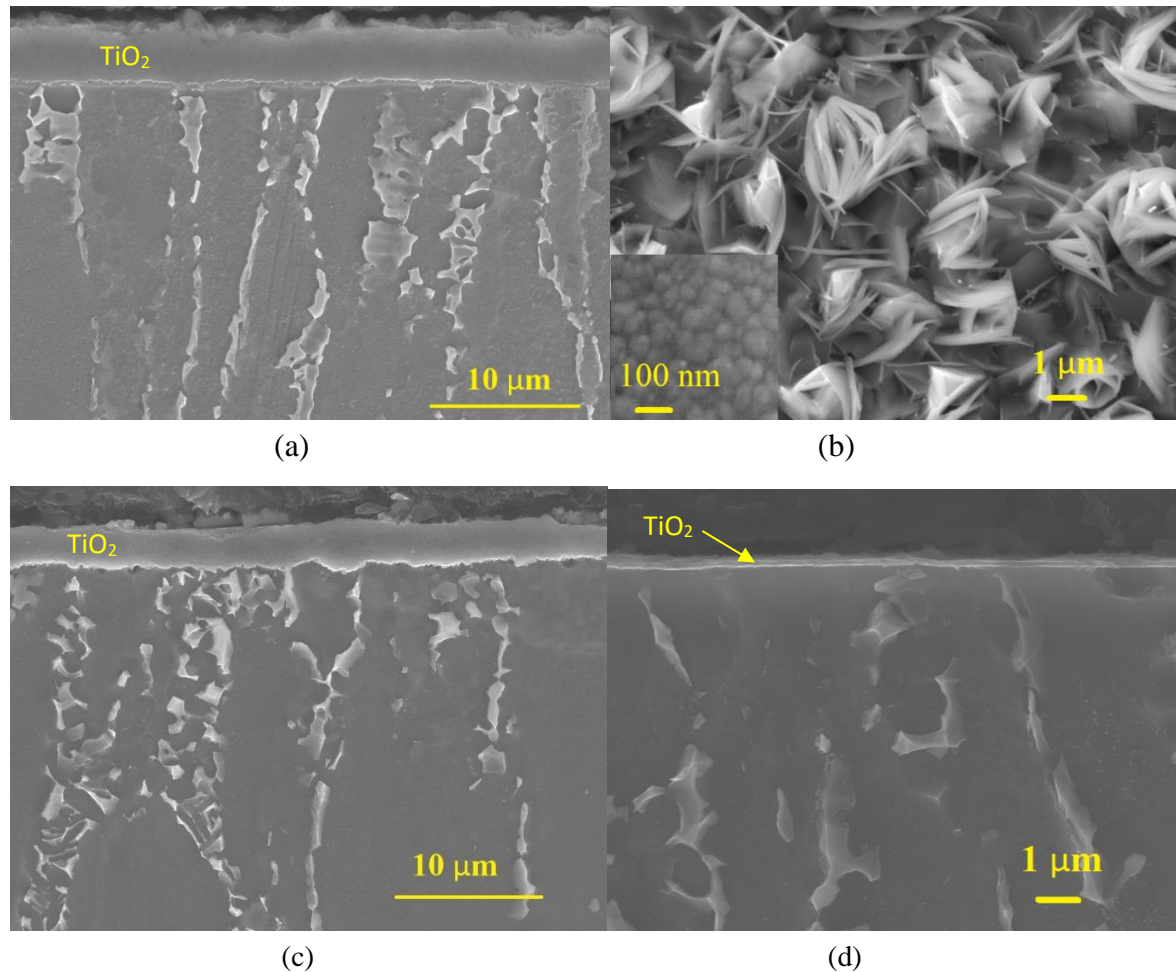


Figure 1: Ti6Al4V samples treated at 620°C: SEM image of silver pre-deposited sample T-Ag620/3 after 3-hour treatment (a) cross-sectional structure and (b) surface morphology, inset picture is the silver pre-deposited surface, TiO₂ layer formed on samples without any pre-deposition after (c) 80-hour (T-620/80) and (d) 3-hour (T-620/3).

The difference in catalysing effect of Ag in CCT of CPTi and Ti6Al4V alloy was naturally attributed to the difference in their chemical compositions. To verify if aluminium has played a role in the rapid oxidation of the Ag pre-deposited Ti6Al4V alloy, we deposited a thin layer of silver on some other titanium alloys containing different amounts of aluminium: a near α alloy (Ti6Al2Sn4Zr2Mo0.1Si), an $\alpha+\beta$ alloy (Ti4Al4Mo4Sn0.5Si), a low-cost beta alloy (Ti6.8Mo4.5Fe1.5Al) and a titanium aluminide (Ti44Al8Nb). Ceramic conversion treatments carried out at 620-850°C for 2 to 10 hours suggested that silver sped up their oxidation only to a moderate degree (Table S1). Similarly, pre-deposited silver on alloys like Ti6Al2Sn4Zr2Mo0.1Si and Ti44Al8Nb compounds tended to agglomerate to large particles on the surface (Figure S1). Only the vanadium-containing alloy, Ti6Al4V, exhibited the

exceptional acceleration phenomenon even it had a similar amount of Al to Ti6Al2Sn4Zr2Mo0.1Si alloy.

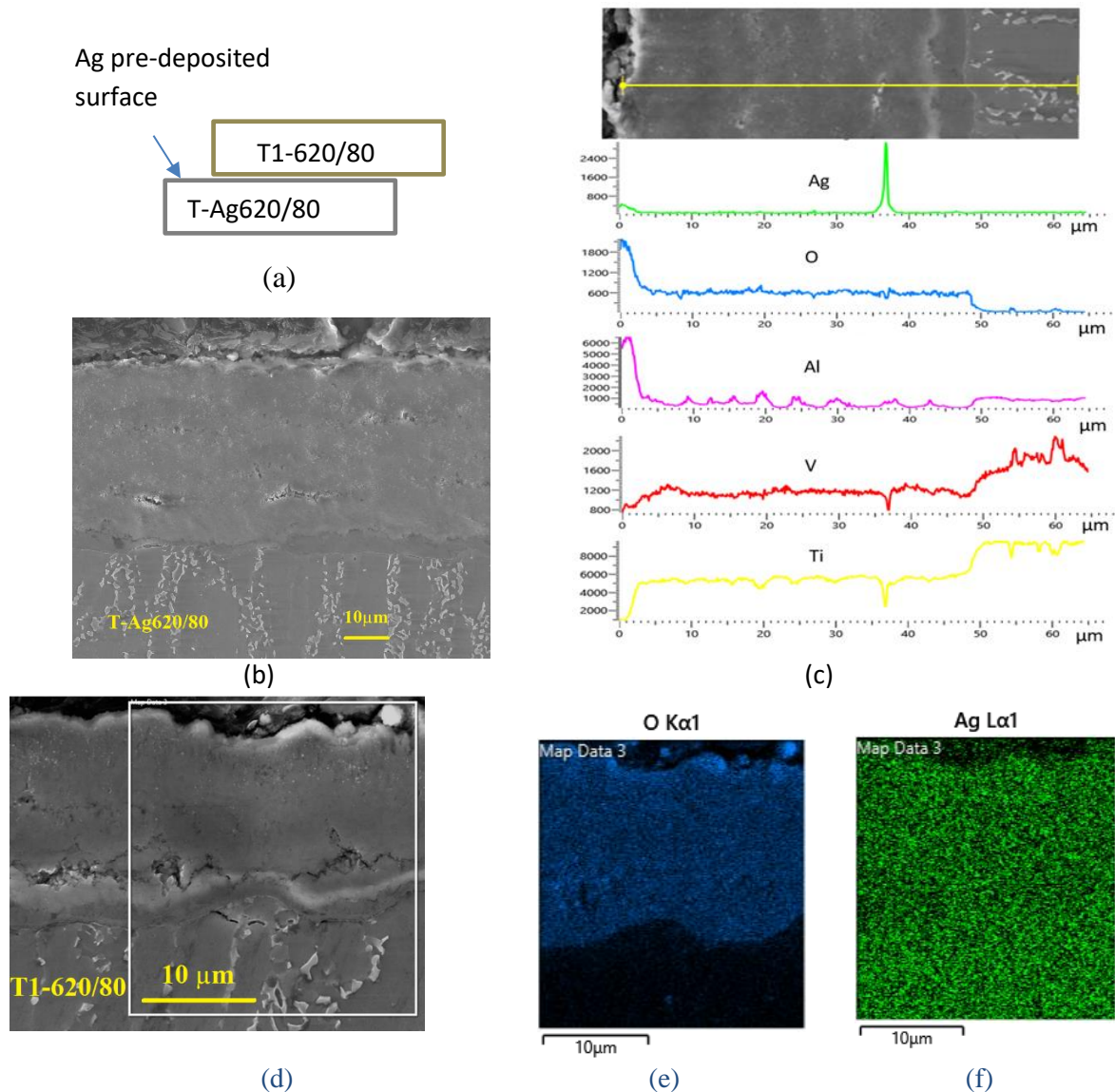


Figure 2: Special treatment (620°C/80h) of a sample without any pre-deposition (T1-620/80) on top of a silver pre-deposited sample (T-Ag620/80): (a) the configuration of two samples, (b) SEM view of the oxide layer on T-Ag620/80, (c) the cross-section elemental line scan of the oxide layer for T-Ag620/80, (d) oxide layer for sample T1-620/80 and (e/f) EDX elemental mapping of O and Ag.

To investigate if vanadium played an important role in promoting the oxidation of titanium alloys, we pre-deposited V or V/Ag layer on the surface of CPTi sample and used a thermogravimetric test (TGA) to monitor its weight change continuously in the process. We also include a Ti6Al4V sample pre-deposited with silver and CPTi and Ti6Al4V sample without any pre-deposition in the experiment. As shown in Figure 4. Both the CPTi and Ti6Al4V samples (C-620/15 and T-620/15) had a slow and steady weight increase in the ramp period (0-75 minutes) and the holding period and finished at about 100.15 % of their original weight (0.15% weight gain) after heating for 15 hours. Sample CPTi+V (C-V620/15) gained

weight slowly at the ramp period but it overtook CPTi and Ti6Al4V gradually and increased weight by 0.40% at the end of the process. Sample CPTi+VAg (C-VAg620/15) absorbed oxygen rapidly even in the 75 minutes ramp period and the weight gain was faster than the sample (Ti6Al4V+Ag) in the first three hours, which agreed with the measurement of the oxide thickness (Table 2). After three-hour CCT, it gained weight rather moderately until the end of the holding period with a 0.9% mass gain. Similarly, T-Ag620/15 put on weight rapidly before it reached 620°C, which continued during the dwelling period. The weight increase of 1.69% exceeded 10 times that of T-620/15, confirming that silver can accelerate the oxidation of Ti6Al4V alloy not only over a short period (3h) but also over a longer period (15h).

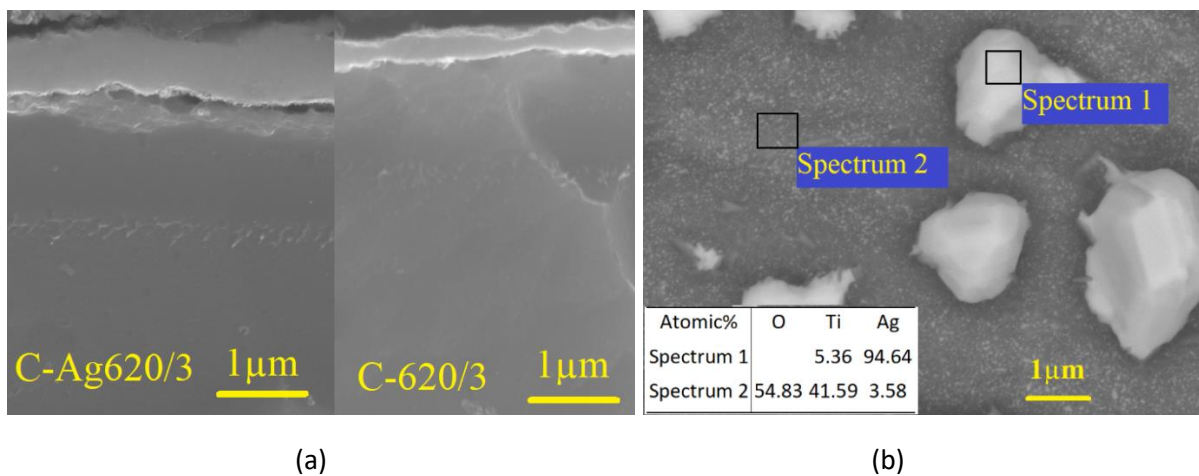


Figure 3: SEM analysis of the CPTi samples treated at 620°C for 3hours: (a) sample C-Ag620/3 with Ag pre-deposited layer versus sample C-620/3 without pre-deposited layer, (b) BEI image of the surface of sample C-Ag620/3 and the relevant composition identified by EDX.

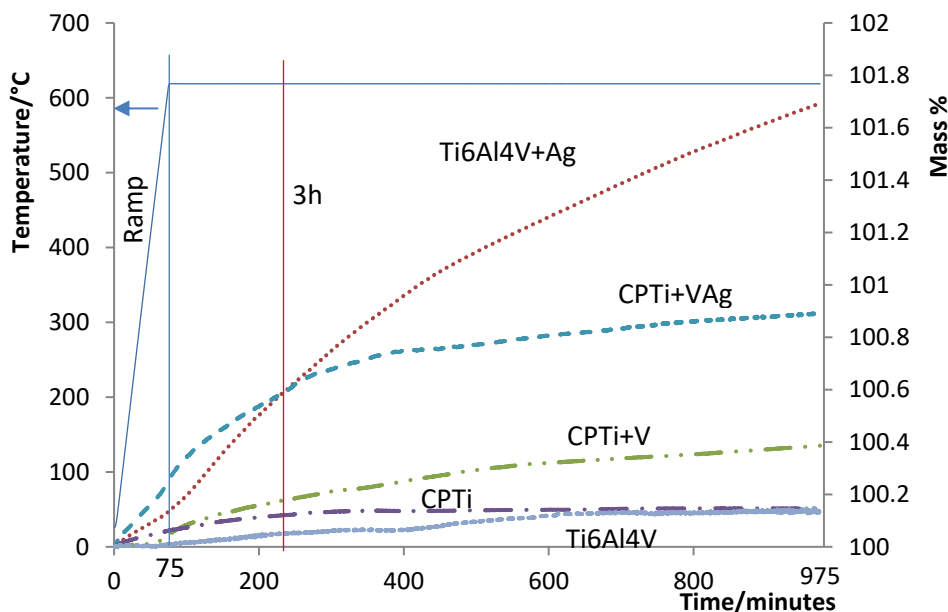


Figure 4: Mass gain of CPTi and Ti6Al4V samples (5×5×1mm thick disc) with or without different pre-deposited metal layer as a function of the oxidation temperature and time

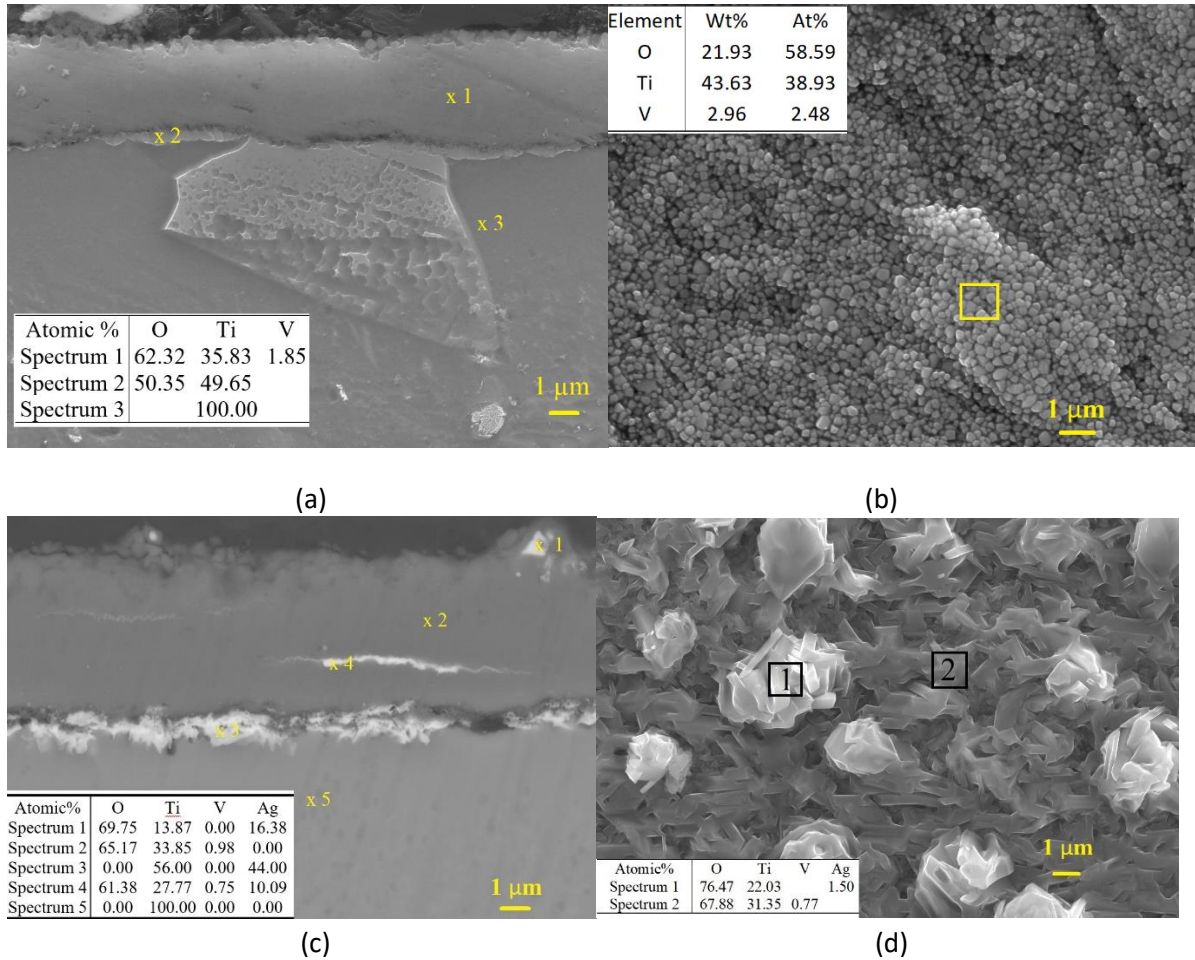


Figure 5: Cross-sectional and surface images and the elemental information of (a/b) sample C-V620/15 with a vanadium pre-deposited layer and (c/d) sample C-VAg620/15 with a V/Ag pre-deposited layer.

Observations on the surface and cross-sectional images of the vanadium pre-deposited CPTi sample (C-V620/15) suggested that the vanadium distributed evenly in the oxide layer after 15 hours CCT, and the oxygen content was slightly lower than the stoichiometric TiO_2 , indicating an oxide of non-stoichiometric TiO_{2-x} (Figure 5a/b). The compositions detected from Spectrum 2 at the interface of the oxide layer and the substrate (Figure 5a) implied that TiO titanium oxide formed there. As shown in Figure 5b, very fine particles were formed on the surface. The oxide layer is 3-4 μm thick which was much thicker than that (0.5-0.8 μm) of C-620/15 as listed in Table 2.

Table 2: Thickness (μm) of the oxide layer after CCTed at 620 $^{\circ}C$

	2h	3h	8h	15h	80h
Ti6Al4V	-	0.1-0.2	-	0.7-1.2	2.4-3.8
Ti6Al4V+Ag	1.6-2.1	4.6-5.2	-	14-16	40-45
CPTi	-	0.1-0.2	0.5-0.8	0.6-1.0	2.0-2.3
CPTi+Ag	-	0.6-0.8	-	-	-
CPTi+V	-	1.5-2.5	-	3.0-4.0	-
CPTi+V/Ag	1.9-2.7	4.0-5.0	6.8-7.2	7.0-7.5	-

As shown in Table 2, V/Ag pre-deposited CPTi sample (C-VAg620/15) can produce an even thicker oxide layer of 7.0-7.5 μm than that (3-4 μm) formed on V pre-deposited CPTi sample (C-V620/15). Vanadium distributed evenly in the oxide layer after 15 hours CCT (Figure 5c), and the oxygen content was slightly lower than the amount required for the stoichiometric TiO_2 . The O/Ti ratio of the oxide layers formed on C-VAg620/15 (1.93) is higher than that (1.74) when formed on C-V620/15 (Figure 5c/d). Silver-rich rose-flower pattern was formed on the surface of V/Ag pre-deposited CPTi, which is similar to that on the surface of Ti6Al4V sample (Figure 1b).

3.2 Characterisations of the oxides formed at different conditions

In order to investigate the initial reaction, CCTs were carried out at 550°C, 600°C and 620°C for 3 hours for the Ti6Al4V sample with or without a pre-deposited silver layer. Observations on the treated surfaces revealed no clear change to the surface of samples T-550/3, T-600/3 and T-620/3 without any pre-deposited layer. No oxide peak was detected from the surface of T-620/3 and the peaks of the α -Ti phase shifted towards a lower angle suggesting high oxygen solid solution in sample T620-3, while rutile is the dominating phase on the surface of T-620/80 after a longer treatment (80 h) as shown in Figure 6.

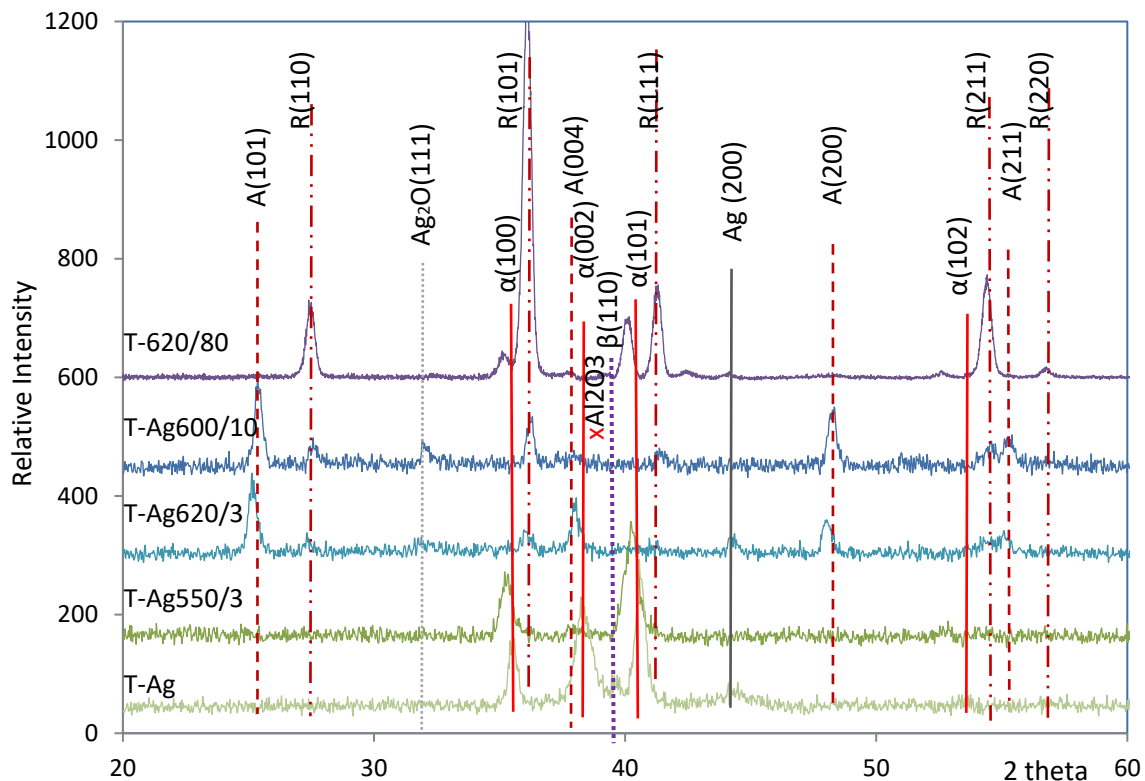
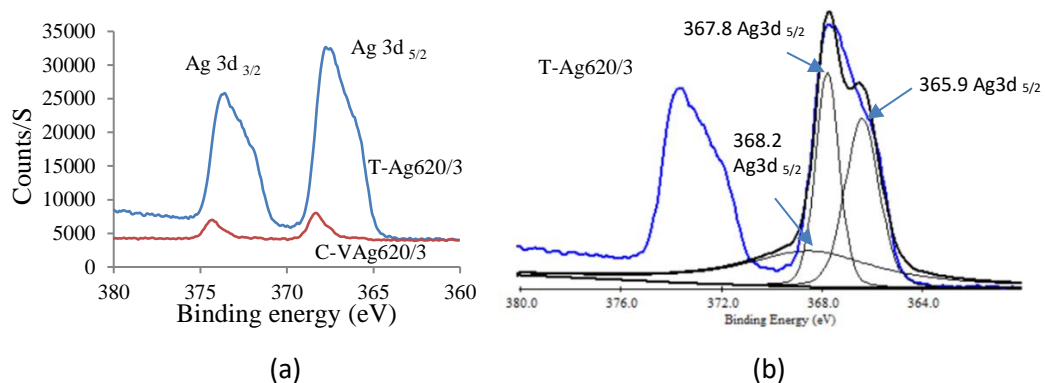


Figure 6: Phase evolution under different treatment conditions for Ti6Al4V samples with and without pre-deposited silver. A: anatase (JCPDS:84-1286), R: rutile (JCPDS: 86-0147), α : α titanium (JCPDS: 44-1294), β : β titanium (JCPDS: 44-1288) and Ag_2O (JCPDS: 76-1393).

For silver pre-deposited sample, when treated at 550°C, the silver layer tended to coalesce on the surface of T-Ag550/3, oxides started to form but with a very limited amount. When increasing the treatment temperature to 600°C, after 3 hours, a thick surface oxide layer (2.0-2.3µm in Table 1) was formed on the surface (T-Ag600/3) with evenly spread rose flower-like features on the surface. The oxygen content in the oxide layer (T-Ag600/3) was slightly lower than the stoichiometric composition of TiO₂, indicating an oxygen-deficient TiO_{2-x} layer formed on the surface and it comprised of anatase and rutile phases. At 620°C, after 3-hour treatment (T-Ag620/3), the oxide layer is about 5µm thick, and the surface is composed of a mixture of anatase and rutile phase with a weak trace of Ag₂O (Figure 1 and Figure 6).

The elemental valences of the oxidised surface were analysed by high-resolution X-ray photoelectron spectroscopy (XPS) as shown in Figure 7. Three Ag-3d_{3/2} peaks of 368.2, 367.8eV and 365.9 eV on the surface of sample T-Ag620/3 (Figure 7a/b) are corresponding to Ag⁰, Ag⁺ and Ag²⁺ indicating that silver has been partially oxidised [16, 17]. For V/Ag pre-deposited CPTi sample, both the Ag-3d_{3/2} and 3d_{5/2} peaks shift slightly to Ag⁰ (368.2eV) binding energy position [18]. Titanium peaks of Ti2p_{3/2} suggest that a mixture of anatase and rutile phase coexist on the surface of T-Ag620/3 (Figure S2). However, a peak of 458.68 is linked to anatase on the surface of the sample C-VAg620/3.

As shown in Figure 7c, the peaks of 530.5 and 531.9 (T-Ag620/3) correspond to the lattice oxygen and non-lattice oxygen (i.e. oxygen vacancy) [18]. The binding energy peaks at 516.38 eV (IV 2p_{3/2}) and 517.28 eV (V 2p_{3/2}) are linked to vanadium oxides (VO₂ and V₂O₅) for sample C-VAg620/3 (Figure 7d). However, there is no vanadium peak was detected for the sample T-Ag620/3.



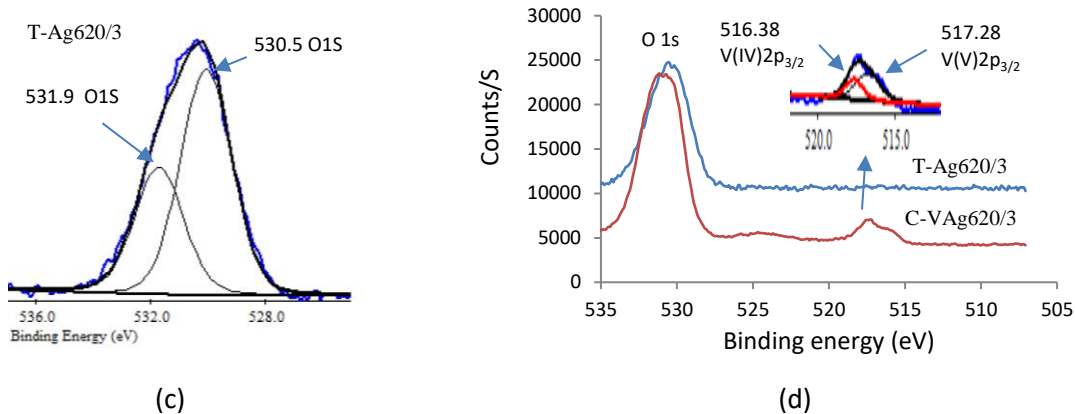
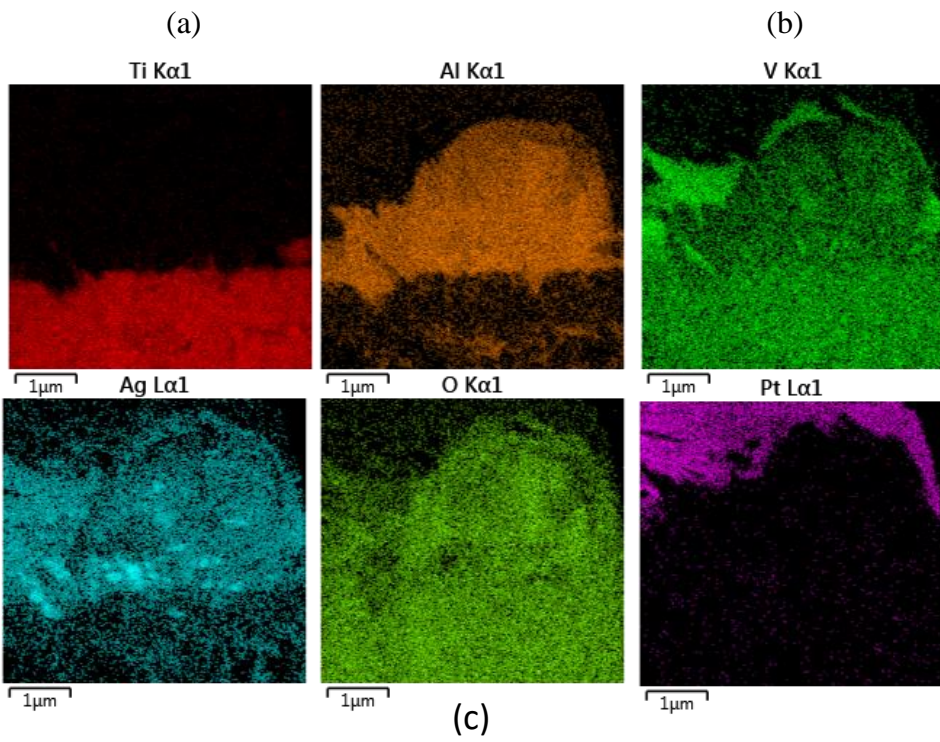
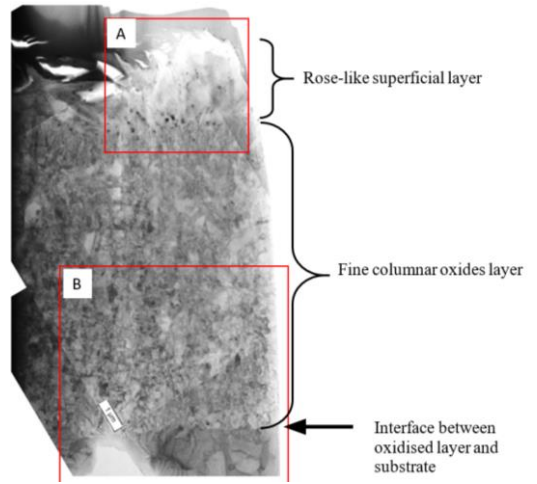
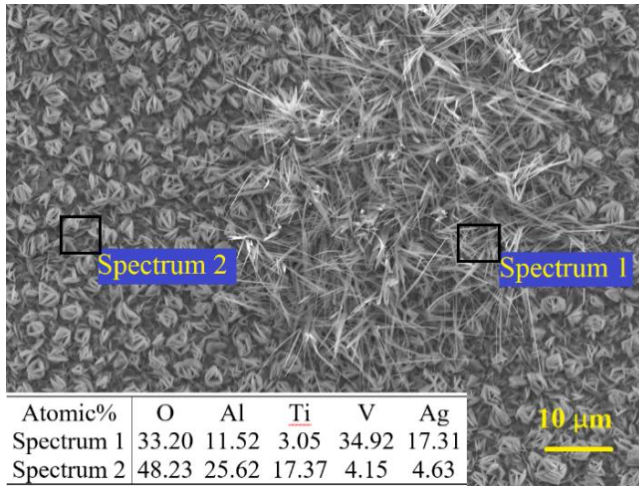


Figure 7: The elemental valences on the silver pre-deposited Ti6Al4V sample T-Ag620/3 and V/Ag pre-deposited CPTi sample C-VAg620/3 surface analysed by high resolution X-ray photoelectron spectroscopy (XPS): (a)Ag, (b)Ag peak fit for T-Ag620/3, (c) O peak fit for T-Ag620/3, (d) V and O with inset of V peak fit for C-VAg620/3

As seen in Figure 8a, after 10-hour CCT at 600°C (T-Ag600/10), rose-pattern features appeared on the surface with some clusters of needle-like fibres rich in vanadium content, which is similar to $\text{AgV}_6\text{O}_{15}$ [16]. It is noticed that the needle-like fibres only appeared on the surface with a thick pre-deposited silver layer (>100 nm) for a relatively long CCT time (i.e., 10 hours). EDX analysis on different parts of the oxide layer suggested that the rose-pattern features were rich in aluminium together with a moderate amount of silver and vanadium as indicated by spectrum 2 in Figure 8a. As shown in Table 1, the 10-hour treatment at 600 °C (T-Ag600/10) resulted in a thick oxide layer (~10 μm) consisting of a rose-like superficial layer and fine columnar oxide layer (Figure 8b). The superficial layer was rich in Ag and Al including the fibre clusters on the surface where highly enriched with vanadium (~35%) can be identified in the surface EDX (Spectrum 1 in Figure 8a). Al_2O_3 may co-exist with TiO_2 as a minor peak of Al_2O_3 can be identified in XRD (Figure 6) and a high amount of aluminium can be seen in spectrum 2 in Figure 8a and elemental mapping in Figure 8c. In the meantime, silver has a higher amount in this superficial layer with a more oxidative condition, as Ag_2O peak was stronger while Ag (200) peak significantly weakened (Figure 6). The main part of the fine columnar oxide layer (Figure 8b/d) contained a mixture of anatase and rutile TiO_2 and the anatase became more dominated as revealed by XRD (Figure 6). The mixture of anatase and rutile was further confirmed by XRD analysis on the sample after removing the superficial surface oxide layer (A in Figure 8b). Traces of silver can still be seen near to the interface indicating that silver might have promoted the outward diffusion of titanium (Figure 8d).



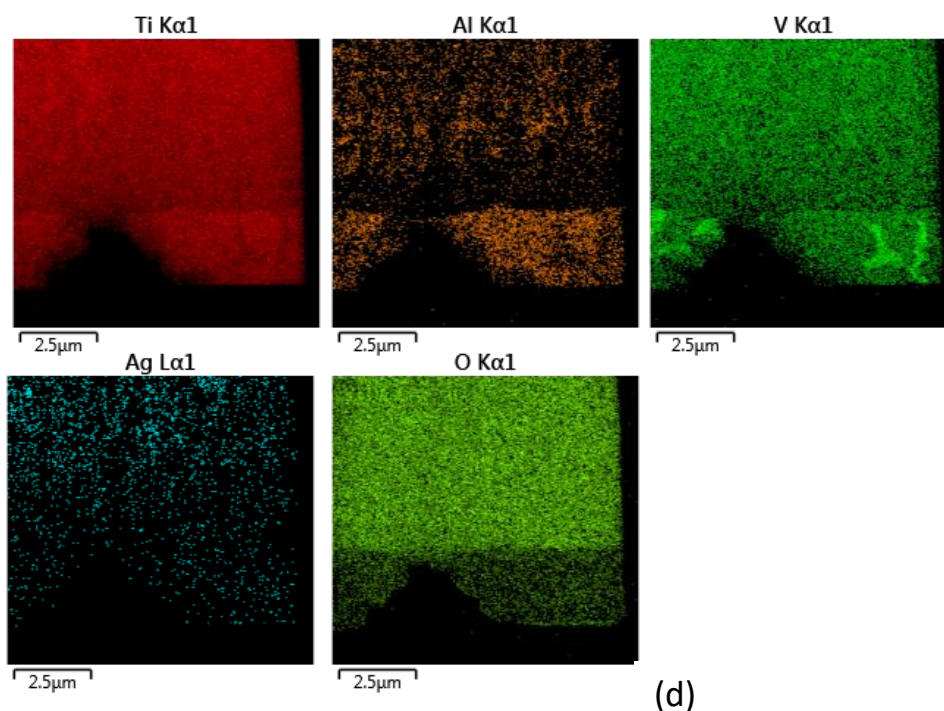


Figure 8: The oxide layer formed on the silver pre-deposited Ti6Al4V sample after 600°C/10-hour treatment (T-Ag600/10): (a) Surface morphology and composition comparison by SEM/EDX, (b) TEM Cross-sectional image of the oxide layer, and STEM/EDX mapping of (c) top side of the oxide layer from area A, and (d) the interface area of the oxide/substrate from area B.

4. Discussion

Traditional ceramic conversion treatment of titanium-based alloys is a lengthy thermal oxidation at controlled environment, i.e. a 3 μm thick oxide layer need a treatment of 80 hours at 620°C [19]. By pre-depositing a thin silver layer on Ti6Al4V alloy, the oxidation can be dramatically accelerated, and a thick ceramic layer (3-5μm) can be formed in just 2-3 hours at 620°C. Therefore, it is important to discuss the mechanism of rapid oxidation of Ti6Al4V with the assistance of the pre-deposited silver to advance scientific understanding.

When Ti6Al4V alloy is exposed to air, oxygen molecules are adsorbed on the surface and they are gradually dissociated into oxygen atoms as the temperature rises. The dissociated oxygen atoms reacts with the activated titanium surfaces to form titanium oxides, and the oxidation process occurs through the inwards diffusion of oxygen anion and the outwards diffusion of titanium cation through the titanium oxides layer [20]. However, once a barrier titanium oxide layer formes on the surface, the growth of the oxide layer is dominated by inward oxygen anion – diffusion process, which generally results in slow progress. In the meantime, aluminium is left or ejected to the surface and gradually produces an Al₂O₃ layer, which can impede the further titanium oxidation. However, Becker found that the addition of a small

amount of V (1.4 wt%) in TiAl compounds can prevent the formation of the continuous Al₂O₃ barrier and thus increase the oxidation rate [21]. However, the oxidation of Ti6Al4V alloy is only marginally different from CPTi alloys at current test range (Table 1) due to the balanced promotion of vanadium and impeding effect of aluminium [22].

Pre-deposited silver particles on the surface of Ti6Al4V are between 50-150 nm as shown in the inset picture of Figure 1b. When exposed to air at elevated temperatures, silver can absorb up to twenty-two times its volume of oxygen [23, 24] and it can react with oxygen to form AgO or Ag₂O in the following reversible reactions [18, 25]:



At temperature of 300°C and above, both AgO and Ag₂O decompose to Ag and oxygen atoms, which greatly increase the oxygen dissociation on the surface. As a transition metal, silver has multi oxidation states Ag⁺ and Ag²⁺ as shown in the XPS analysis (Figure 8a), which is essential for an effective catalyst. The existing of dopants (Ag) can lower the energy for the conversion of oxygen anions by providing extra electrons, and thus increase the absorption and facilitate the diffusion of oxygen through the vacancies [26]. Large silver agglomerates can be found on the surface of the silver pre-deposited CPTi samples like C-Ag620/3 in Figure 3b, which is similar to a report that silver nanoparticles deposited on quartz glass by magnetron sputtering tends to agglomerate especially at 600°C [27]. The agglomerates significantly reduced the activation effect, and thus led to a less effective acceleration of the oxidation on CPTi samples (Figure 3). In contrast, the agglomerates on the surface of Ti6Al4V samples are much smaller especially for long time treated samples and they commonly existed as a mixture of Ag/Al/O/V (Figure 2 and Figure 8). Silver particles are also sparsely distributed in the oxide layer as shown in Figure 2c and Figure 8c/d, which might be due to silver layer were broke down by the growing oxides or the diffusion of silver particles through the TiO₂ layer as reported by Kulczyk-Malecka [28]. Further investigation on the V/Ag pre-deposited CPTi sample found that silver existed at the interface of the oxide layer and the substrate when a thick V/Ag layer (>100 nm) was pre-deposited (Figure 5c), suggesting that titanium atoms can diffuse through it. Therefore, silver might promote the outward diffusion of titanium atoms and facilitate reaction with oxygen, and thus generate a thick oxide layer, which explains why sample T-Ag620/80 has a much thicker oxide layer than that of T1-620/80h (Figure 2). However, the accelerated oxidation became less profound if the pre-deposited silver layer was

too thick, i.e. >100 nm, because a thick silver layer which might hinder the diffusion of oxygen and titanium (Figure S3). The positive catalysing effects of silver were also found in the anodic spark deposition of titanium, as adding silver species can produce an anatase layer of 5.6-5.9 μm thick instead of 2.9 μm without the addition of silver [29].

As shown in Figure 4/Figure 5a/b, vanadium can also accelerate the oxidation of titanium and generate a thick oxide layer. Vanadium is a strong oxidizing agent because of its multi-oxidation states as evidenced in Figure 8c. It was found by other researchers that a thin V layer on top of evaporated Zr films can lower the oxidation activation temperature of zirconium, promote the boundary diffusion of the captured oxygen from the surface to the bulk of the films and generate a much thicker zirconium oxide layer [30, 31]. Furthermore, after annealing at 350°C for 1 hour, the oxygen diffusion length was 885 nm in vanadium layer verse only about 4 nm in zirconium layer. Due to the similarity of titanium to zirconium, vanadium is expected to resemble the effect in titanium and its alloy. Thongtem and co-workers revealed that Ti-(0.5-20.0)wt.%V had a faster oxidation rate in the air than Ti-36.0wt%Al at 1100-1300 °K [32]. Vanadium was noticed to be able to promote oxygen adsorption at the interface of titanium particles [33] and vanadium doping can promote the formation of spherical nano-TiO₂ particles with sizes ranging from 70–120 nm [34]. The doped V ions occupied the Ti⁴⁺ site and homogeneously distributed in the vanadium doped titanium dioxide and resulted in an anatase TiO₂ structure [35]. The presence of vanadium solutes accelerated the diffusivity of oxygen through titanium due to the presence of metastable interstitial sites. A reduction in site energy at metastable sites could reduce barriers for transition into the site, increasing the total transition rate across the site, and led to an increase in oxygen diffusivity. Multiple V neighbours might have conferred exponentially more acceleration in a small region [36]. In the meantime, we found a thicker pre-deposited vanadium layer or a higher V/Ag ratio in the pre-deposited V/Ag layer can both increase the oxide layer thickness on CPTi at the same CCT conditions.

In short, with the activation and catalysis of the pre-deposited silver, oxygen molecules are easily adsorbed/dissociated and form oxygen atoms/anions on the surface of Ti6Al4V. Meanwhile, silver can promote the outward diffusion of titanium atoms and make them more favourable to combine with the oxygen anions to form titanium oxides. The retaining silver in the oxide layer plays a sustaining activation role in promoting CCT process. Although aluminium solutes had an impeding effect on the diffusion of oxygen, vanadium solutes accelerated the diffusivity of oxygen through titanium due to the existence of metastable interstitial sites [36]. Vanadium can be released after titanium oxide formation and produce

multiple V neighbours in the oxide layer. This not only further activate the oxygen absorption, but also accelerates the diffusion of oxygen atoms/anions exponentially to reach the reaction front at the interface of oxide and substrate, where they meet with the outward diffused titanium atoms promoted by silver, thus producing a much thicker oxide layer [26].

5. Conclusions

In this work, we investigated the oxidation behaviour of Ti6Al4V and other titanium alloys with or without a pre-deposited thin silver layer. The following conclusions can be reached:

- A pre-deposited thin silver layer on the surface of Ti6Al4V alloy can accelerate its oxidation significantly at temperatures of 600 °C and 620°C and produce a compact titanium dioxide layer up to 50 times thicker than that formed under the same oxidation conditions without silver.
- The accelerated oxidation role of Ag for CPTi and other titanium alloys containing no vanadium is relative less significant.
- Vanadium can promote the oxidation of CPTi, and together with Ag this acceleration is more profound.
- The rapid oxidation of Ti6Al4V is due to the activation of the oxygen on the surface by Ag and V, and the facilitated diffusion in the oxide layer.

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