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Inst. Phys. Conf. Ser. ***168*** *(2001) pp 381-384*
Electron Microscopy & Analysis Conference, EMAG 2001, Dundee

Microstructural characterisation of biocompatible sol-gel derived vanadium-aluminium doped TiO_2 on Ti substrates

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ABSTRACT: Sol-gel derived pure titania is compared with vanadium and / or aluminium modified titania deposited by spin coating on pure titanium substrates annealed at 300°C and 650°C. Reflection high-energy electron diffraction indicated the presence of anatase from the surface layers of samples annealed at 300°C with a transition to rutile with increasing annealing temperature and addition of vanadium. Cross-sectional transmission electron microscopy indicated a gradation of Ti-O phases through the layer with the dominant presence of rutile. Aluminium was found to inhibit grain growth while vanadium promoted crystallisation.

1. INTRODUCTION

Titanium and titanium alloys naturally exhibit a thin but adherent titanium oxide passivating surface that provides good corrosion and wear resistance (Pouilleau et al. 1997). These properties are particularly enhanced for titanium alloys such as TiAlV when used as a biomedical implant material as compared with conventional stainless steel and cobalt based alloys (Long and Rack 1998). There is interest in engineering thicker TiO_2 coatings that may improve the material biocompatibility depending on the oxide chemical composition, thickness, topography, roughness, microstructure and polycrystallinity (Casaletto et al. 2001). The effect of the interaction of Ti with the implant environment, allowing the release of metal ions that might otherwise contaminate living tissue, may be reduced in the presence of a passivating TiO_2 layer and even more so as the engineered coating is increased in thickness (Woodman et al. 1984, Lausmaa 1996). By way of example, coatings of nanocrystalline titania and alumina are particularly favoured by osteoblasts (Webster et al. 1999, Webster et al. 2000). Hence, it is of great interest to control the titania stability (Gouma et al. 1999, Byun et al. 1997, Hengerer et al. 2000), since anatase which is one of the unstable phases of TiO_2 can have a nanocrystalline form at low temperature. Sol-gel, one of the most promising, easy and cheap preparation techniques for high quality thin films, is widely applied in synthetic implants (Haddow et al. 1996, Xu et al. 1998). As part of a larger research program, there is evidence to suggest that additions of vanadium to TiO_2 promote the formation of the more stable rutile phase, while additions of aluminium act to lower the extent of polycrystallinity. The microstructural development of vanadium and aluminium doped TiO_2 is investigated using a combination of reflection high-energy electron diffraction (RHEED) and transmission electron microscopy (TEM).

2. EXPERIMENTAL

Preparation of the TiO_2 sol-gel modifications by evaporation of aqueous colloidal sols was followed by deposition of titania thin film coatings (up to 200nm thickness) onto 10mm diameter pure titanium discs using a custom-built spin coater controlled by an EMC TOP-5200 syringe pump.

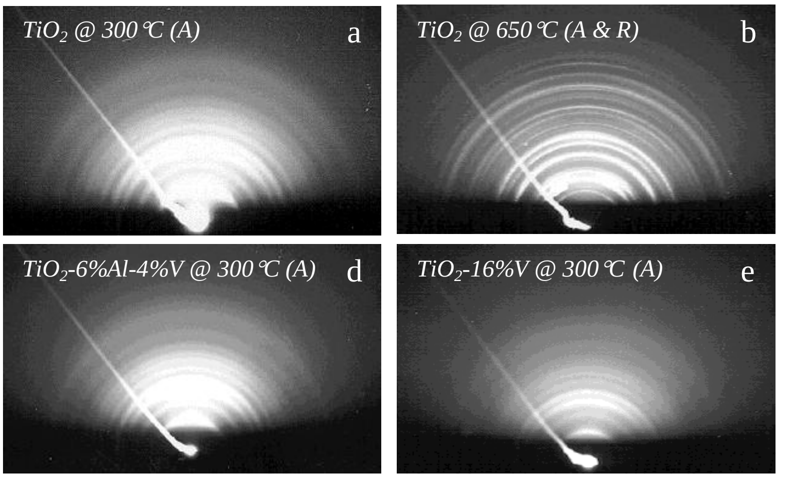


Figure 1. RHEED patterns from unmodified and vanadium and / or aluminium modified TiO_2/Ti samples; (1a-1e) 80kV (1f) 200kV (acquired with a different camera length).

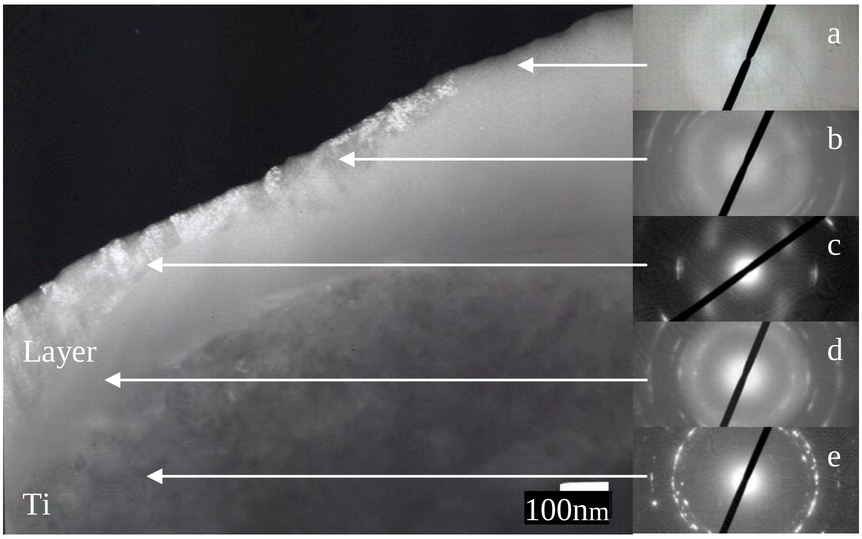
The following samples were examined: unmodified TiO_2, TiO_2-12wt.%Al, TiO_2-6wt.%Al-4wt.%V and TiO_2-16wt.%V annealed at 300°C; in addition to unmodified titania and TiO_2-16wt.%V samples annealed at 650°C. Heat treatment took place in air for 18 hours using a Vecstar 91e tube furnace. Cross-sectional samples were prepared by sequential mechanical polishing and argon ion milling for examination using a JEOL 2000FX II TEM operated at 200kV. The associated titania electron diffraction patterns were indexed with reference to a standard titanium specimen used for instrument calibration. Samples were also studied using RHEED within either the 2000FX TEM or a Philips 410 TEM operated at 80kV, with specimens being held vertically on a RHEED stage positioned immediately below the projector lens. Accelerated electrons undergo glancing angle diffraction at the layer surface. The samples were tilted so that the shadow edge was positioned close to the primary beam to access near surface diffraction information.

3. RESULTS AND DISCUSSION

Figures 1a to 1f show RHEED patterns for a range of annealed unmodified and V-Al modified TiO_2 coatings. The crystallographic phase of all the layers annealed at 300°C was indentified as being anatase. However, unmodified TiO_2 annealed at 650°C revealed a transition to a mixed phase of anatase and rutile, while TiO_2–16wt.%V annealed at 650°C transformed to rutile. RHEED patterns from the TiO_2 and TiO_2-6wt.%Al-4wt.%V annealed at 300°C also exhibited slight blurring of the diffraction rings implying that the size of the grains is relatively small. Conversely, the 12wt.%Al and the 16wt.%V TiO_2 modifications, also annealed at 300°C displayed more well defined polycrystalline rings indicating a distribution of comparatively larger particles. Following heat treatment at 650°C the unmodified TiO_2 and the TiO_2-16wt.%V specimens additionally showed tentative evidence of preferred orientation. The sequence of more well defined polycrystallinity and increased spottiness of the diffraction rings signifies that a high vanadium modification is responsible for lowering the rutile phase transition point with a corresponding increase in TiO_2 grain size.

More detailed TEM investigation was carried out on the TiO_2-12wt.%Al and TiO_2-16wt.%V samples annealed at 300 and 650°C respectively (Figures 2 and 3). The associated diffraction patterns acquired throughout both layers indicated the presence of titanium and a gradation of several other Ti-O based phases. Rutile was the most dominant phase identified in both samples.

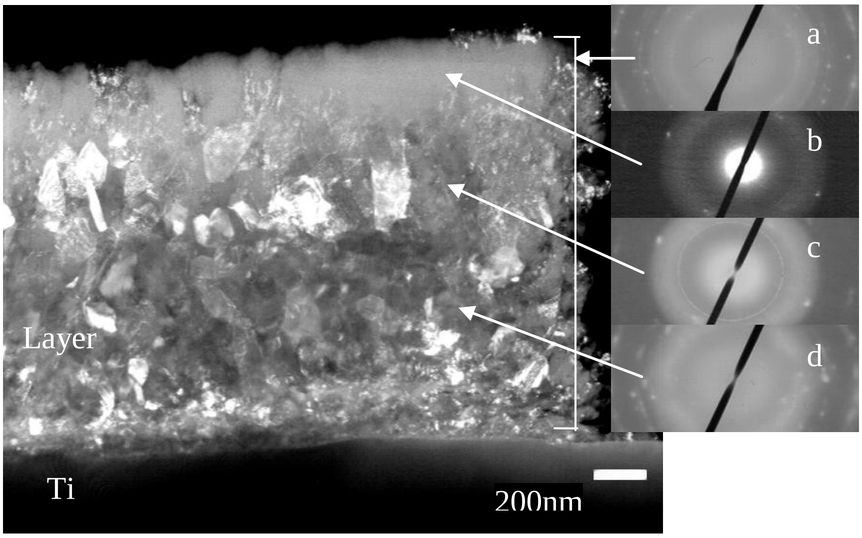
It is of interest to note that the 12wt.%Al layer exhibited a transition from very small columnar grain polycrystallinity at the surface through to an amorphous (α-TiO_2) layer beneath, in turn leading through to the polycrystalline titanium substrate, i.e. nucleation occurs at the surface and crystallisation of the amorphous sol-gel deposit proceeds towards the substrate. Conversely, for the 16wt.%V-TiO_2, the coating exhibits regions of amorphous material at the top surface with a larger grained polycrystalline phase in contact with the Ti substrate. The implication in this case is that nucleation has occurred at the TiO_2/Ti interface and crystallisation has proceeded towards the sol-gel



TiO_2-12%Al@300℃

a. Ti+α-TiO_2+rutile
b. Ti+α-TiO_2+rutile
c. Ti+rutile
d. Ti+α-TiO_2+rutile
e. Ti+TiO_2-(hex)

Figure 2. Dark field image of TiO_2-12wt.%Al annealed at 300°C showing amorphous to crystalline transition.



TiO_2-16%V@650℃

a. α-TiO_2+rutile+TiO-(hex), [whole layer]
b. Ti+α-TiO_2 +rutile+anatase
c. Ti+α-TiO_2+rutile
d. Ti+α-TiO_2+rutile

Figure 3. Dark field image of TiO_2-16wt.%V annealed at 650°C showing columnar mixed phase grains.

deposit surface. It is noted that there is evidence from other annealed systems such as amorphous Si for either surface or interface nucleated grain growth (Shimiju and Ishihara 1995, Saki et al. 1991).

TEM images from the TiO_2-6wt.%Al-4wt.%V and TiO_2-16wt.%V samples annealed at 300°C are shown in Figures 4 and 5, respectively. For the case of the mixed Al-V modification, a very complicated microstructure has developed similar to the case of the 12wt.%Al modification, with a predominant columnar rutile phase on amorphous TiO_2 on a polycrystalline Ti substrate. The 16wt.%V sample annealed at 300°C shows complete polycrystallinity through the entire anatase / rutile phase layer but with a significantly smaller grain size as compared with the equivalent sample annealed at 650°C (Figure 3). The increased annealing temperature results in approximately a doubling of the oxide layer.

RHEED data is very sensitive to the top few atomic layers with a large ~ $1mm^2$ sampling surface area. The implication from this part of the study is a transition from anatase to rutile with increasing annealing temperature and vanadium addition. However, cross-sectional TEM provides more depth information indicating a greater presence of rutile within all the layers examined. Graded Ti-O layers were found for the case of Al and Al-V modifications, indicating that the presence of aluminium acts to lower the rate of crystallisation, while the presence of vanadium clearly accentuates crystallisation.

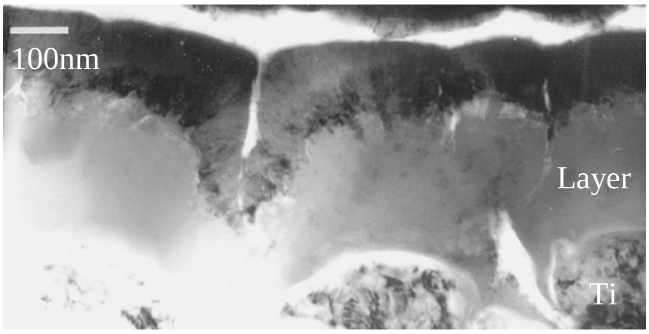


Figure 4. Bright field TEM image of TiO_2-6wt.%Al/4wt.%V annealed at 300°C showing an amorphous to crystalline transition

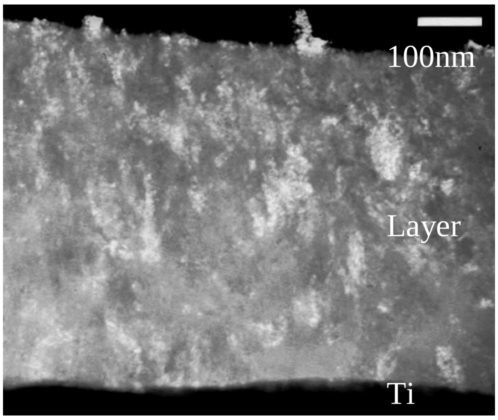


Figure 5. Dark field TEM image of TiO_2-16wt.%V annealed at 300°C showing small mixed anatase-rutile grains.

4. CONCLUSIONS

RHEED investigation of sol-gel derived vanadium-aluminium modified titania on titanium substrates indicated the presence of an anatase microstructure from the top few atomic layers of samples annealed at 300°C. At higher annealing temperatures (650°C) a transition to a mixed anatase / rutile phase was observed for unmodified TiO_2, while the addition of vanadium promotes a transformation to the stable rutile phase. However, when observed in cross-section by TEM, the majority of the layers revealed a dominant rutile phase throughout the layer. The addition of aluminium was found to inhibit the extent of crystallisation.

5. ACKNOWLEDGMENTS

This work was supported under EPSRC contract GR/M74603 and GR/L55209.

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