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RHEED characterisation of the near surface microstructure of Ti-O based biocompatible coatings

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Abstract. Mechanically polished, annealed, nitric acid treated and aged in boiling water after nitriding, commercially pure Ti substrates have been characterised using reflection high-energy electron diffraction (RHEED) and secondary electron imaging, in terms of their naturally formed or 'accelerated' oxide layers. Annealing induced crystallisation and transformation of anatase to the rutile phase and led to increased roughness, with localised fracture and balling up of the surface oxide layer as the time and temperature of annealing were increased. Nitric acid modification produced no influence on the anatase to rutile transformation, whilst further aging in boiling water induced an acceleration of this transformation. RHEED data acquired at differing accelerating voltages have indicated a Ti-O phase gradation within annealed sol-gel derived V modified TiO_2 layers deposited by spin coating onto Ti substrates.

1. Introduction

The success of Ti and Ti-based alloys for load bearing applications such as artificial implant biomaterials is due to the low elastic modulus combined with the natural formation of a surface oxide passivating layer. The oxide provides protection against metal ion release [1] and hence, there is interest in engineering thicker TiO_2 coatings using techniques such as the sol-gel method with the aim of further improving the material biocompatibility [2]. Recent work indicates that the biological cell response varies with the surface composition of modified Ti surfaces [3]. Nevertheless, it is not clear why the coating crystallinity influences this response, and in this context, the development and application of the surface sensitive technique of reflection high energy electron diffraction (RHEED) for the rapid characterisation of biomaterials could be beneficial [4]. RHEED provides a non-destructive, rapid, dynamical method of obtaining crystallographic information, taking the form of a half diffraction pattern produced following the interaction of an electron beam at glancing angle with the near surface microstructure of a material.

2. Experimental

The surfaces of mechanically polished, commercially pure Ti (cp-Ti) discs of 10 and 6 mm diameter and 1 mm thickness were annealed in air under conditions of 400°C for 30 min up to 700°C for 18 h; were treated in a 30% nitric acid bath for 10 min; and were aged in boiling

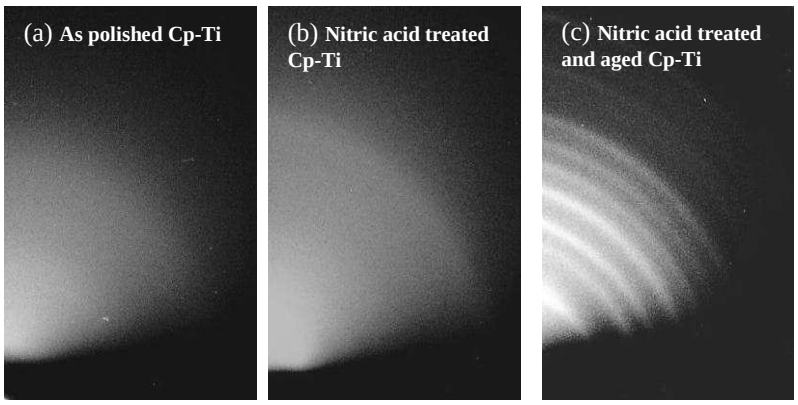

Figure 1. 80 kV RHEED diffraction patterns from cp-Ti specimens illustrating the surface microstructure following: (a) Mechanical polishing (amorphous); (b) nitric acid treatment (amorphous); and (c) immersion in boiling water following nitric acid treatment (indicative of the development of intermediate grain sized polycrystalline anatase-rutile TiO_2 (tetragonal)).

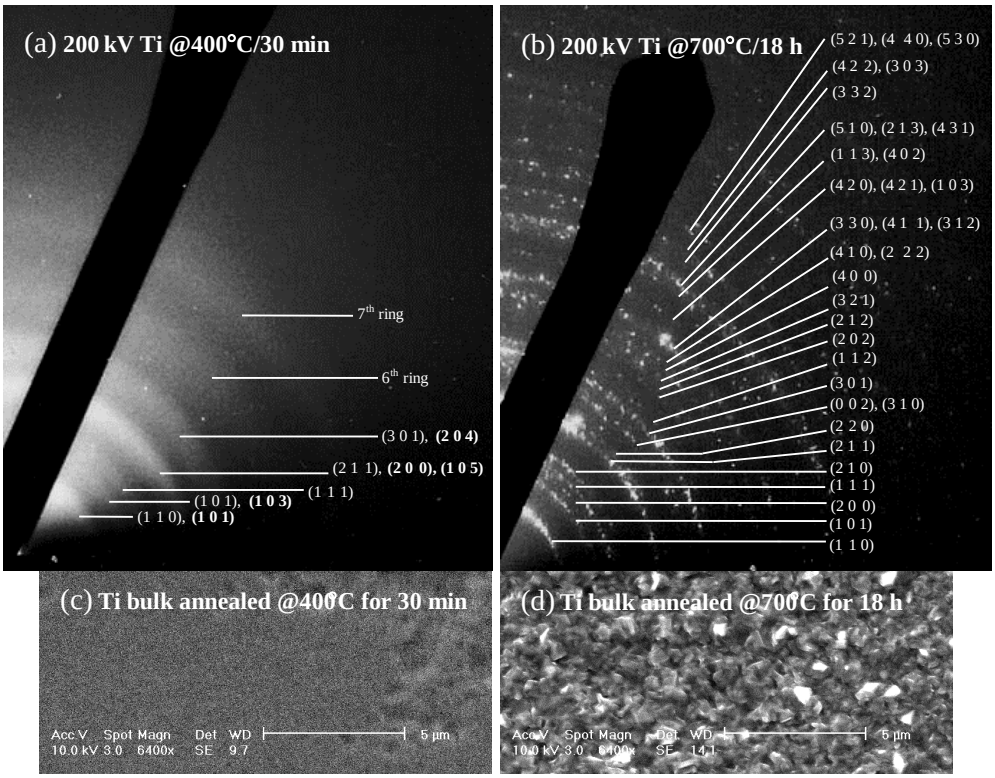

Figure 2: 200 kV RHEED polycrystalline diffraction patterns from a cp-Ti sample annealed at (a) 400°C in air for 30 min and (b) 700°C in air for 18 h, with the assignment of d_{hkl} Miller indices. (c,d) show the corresponding SE images from these samples acquired at 10 kV. Fig. 2a is consistent with the development of fairly small grains of polycrystalline anatase-rutile TiO_2 (tetragonal), with anatase being more dominant, and there is also the possibility of some TiO (hexagonal); Fig. 2b is consistent with the development of larger grained polycrystalline rutile TiO_2 (tetragonal). (Assignments in normal font: rutile TiO_2 (tetragonal); bold font: anatase TiO_2 (tetragonal).)

double distilled water for 24 h subsequent to a nitric acid treatment. Vanadium modified titania sol-gels were produced by the evaporation of an aqueous colloidal sol and deposited onto 10 mm diameter cp-Ti discs by spin coating, using a custom-built spin coater controlled by an EMC TOP-5200 syringe pump. The 16wt.%V modified titania sol-gel sample reported on here was heat-treated in air at 300°C for 18 h. All the sample heat treatments were performed using a Vecstar 91e tube furnace. Topographical and morphological information on the samples was

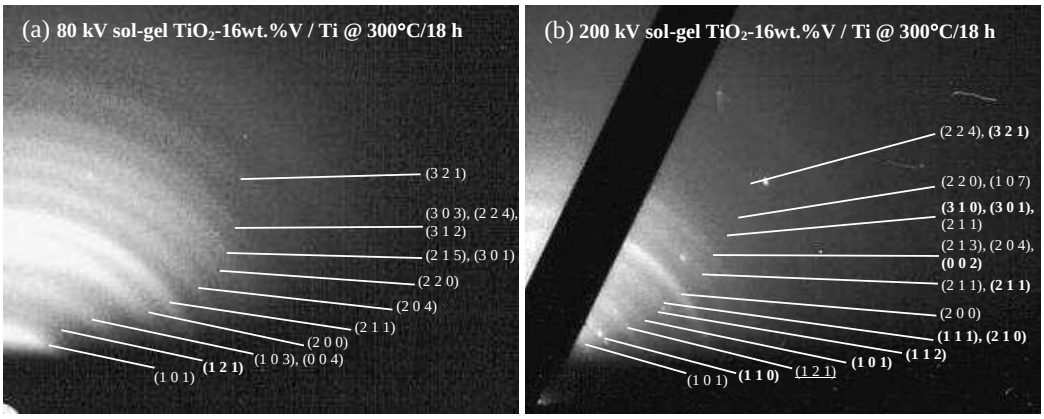

Figure 3. (a) 80 kV and (b) 200 kV RHEED patterns from a sol-gel TiO_2-16wt.%V / Ti sample annealed at 300°C in air for 18 h, illustrating some differences in the surface microstructure. Fig. 3a is consistent with the development of fine grains of polycrystalline TiO_2-anatase (tetragonal) with the possibility of some TiO_2-brookite (orthorhombic). Fig. 3b is consistent with grains of polycrystalline TiO_2-anatase (tetragonal), some TiO_2-rutile (tetragonal) with the possibility of some TiO_2-brookite (orthorhombic), TiO (hexagonal) and V (cubic). (Assignments in italic font: anatase TiO_2 (tetragonal); bold font: rutile TiO_2 (tetragonal); normal font: TiO (hexagonal); underlined font: brookite TiO_2 (orthorhombic).)

obtained using a Philips XL30 FEG-ESEM operated in high vacuum mode at 10 kV. Sub-projector RHEED stages inserted within either a Jeol 2000fx or a Philips 410 TEM operated at 200 and 80 kV, respectively, were used for near surface study of the specimens positioned vertically in the microscope column. The RHEED patterns were calibrated using a particulate Au sample that produced polycrystalline rings and a crystalline GaN specimen.

3. Results and discussion

The RHEED patterns from the as-polished cp-Ti sample presented in Figure 1a and the annealed cp-Ti samples of Figures 2a,b indicate a transformation of the outer surface layer with processing. The initial amorphous microstructure, evident after mechanical polishing (Fig. 1a), is replaced by nanocrystalline anatase TiO_2 particles (Fig. 2a), which in turn provide the nucleation sites for the formation of a few, initially small rutile TiO_2 grains (Fig. 2b), as the temperature and time of annealing are increased. Full rutilisation is apparent at 700°C annealing for 18 h, with the development of relatively large grains. The observation of some slight preferred orientation in a direction normal to the surface of the heat treated samples is characteristic of alignment of some of the grain growth within the film following the anatase to rutile transition. The related secondary electron (SE) images of the annealed specimens (Figures 2c,d) indicate uniform layer contrast at low annealing temperatures, which is consistent with the RHEED observations and the concept of uniform coverage of nanocrystalline TiO_2 anatase particles at this stage. SE imaging also reveals a rough, porous, large-grained layer for the sample annealed at 700°C. This layer seems to have balled-up and become broken due to the process of densification. The additional presence of flake-like polygonal shaped features is commensurate with RHEED supporting the observation of rutile grain growth.

The amorphous surface structure evident from the RHEED pattern of the nitric acid treated cp-Ti sample (Figure 1b) suggests that this modification has had no influence on the surface microstructure, being similar to that of the mechanically polished sample (Figure 1a). The early formation of polycrystalline anatase, however, at the surface of the cp-Ti sample aged in boiling water after nitric acid treatment (Figure 1c) is considered to be due to the presence of the

hydrogen-anodic environment that must have initiated the anatase to rutile transformation at such a low temperature of 100°C.

In the attempt to investigate the extent of applicability of the RHEED technique at differing accelerating voltages, diffraction patterns from the surface of a sol-gel TiO_2-16wt.%V / Ti sample annealed at 300°C in air for 18 h were compared at 80 and 200 kV, respectively (Figures 3a,b). Both RHEED patterns are dominated by the anatase TiO_2 phase, nevertheless, it is only at 200 kV (Figure 3b) where there is an additional indication of the formation of some rutile TiO_2 phase. The sequence of intensities and the location of the polycrystalline rings for different RHEED voltages allow these different assignments for Figures 3a,b, being clearly dissimilar, in addition to the poorer definition of the 80 kV rings as compared with those obtained at 200 kV. Hence, it is suggested that a variable voltage RHEED technique might be able to provide tentative insight into the depth distributions of certain microstructures. Thus, a sub-surface oxide phase gradation is indicated from these RHEED patterns, and this is consistent with cross-sectional TEM observations reported on previously [5]. The development of a graded microstructure is probably related to the initial oxidation / amorphisation of the Ti substrate when exposed to the atmosphere prior to the sol-gel deposition, combined with further oxidation during sol-gel processing.

4. Summary

The development of the surface oxide layer of bulk Ti samples under different surface treatments has been investigated using the combined characterisation techniques of RHEED and SE imaging. RHEED results from annealed cp-Ti specimens demonstrate the transformation of the anatase to the rutile phase of TiO_2, as the annealing time and temperature are increased. SE observations reveal fracture and balling up of the oxide layer surfaces and void development, due to densification of the surface. Nitric acid treatments and mechanical polishing introduce amorphous surface oxide layers. Specimens aged in boiling water after nitric acid treatment exhibit much lower anatase to rutile transformation temperatures compared to the annealed samples. 80 and 200 kV RHEED results indicate several significant differences in the near surface microstructure of a 16wt.%V modified TiO_2 sample deposited by spin coating onto a Ti substrate, implying that depth crystallographic profiling of the surface becomes possible to investigate graded oxide layers at the near sample surface.

5. Acknowledgments

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6. References

[1] M Long and H J Rack, 1998 Biomaterials **19** 1621-1639

[2] M P Casaletto, G M Ingo, S Kaciulis, G Mattogno, L Pandolfi and G Scavia, 2001 Appl. Surface Science **172** 167-177

[3] J Ryhanen, E Niemi, W Serlo, E Niemela, P Sandvik, H Pernu and T Salo, 1997 Journal of Biomedical Materials Research **35**(4) 451-457

[4] B Kasemo and J Lausmaa, 1988 'Biomaterials from a surface science perspective' in Surface characterization of Biomaterials (ed. B.D. Ratner; Elsevier Science)

[5] S Marlafeka, F Allison, D M Grant, P G Harrison and P D Brown 2001 Inst. Phys. Conf. Ser. No. **168** 381 – 384