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AN INVESTIGATION OF SOL GEL COATED ZIRCONIA THIN FILMS ON ANODISED TITANIUM SUBSTRATE BY SECONDARY ION MASS SPECTROMETRY AND SCANNING ELECTRON MICROSCOPY

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ABSTRACT

Zirconia sol-gel-derived ceramic coatings have a variety of uses, due to their ease of production and ability to coat complex shapes. The sol-gel's nanocrystalline grain structure results in improved mechanical properties of the zirconia coating, which further aids their use in a variety of applications from thermal barrier coating to improved tribological properties on titanium substrates. Stabilised zirconia thin films were spin coated on anodised titanium substrates. The titanium was anodised in a dilute H_3PO_4/H_2SO_4 solution before spin coating with the zirconia sol gel. These films were then studied using secondary ion mass spectrometry (SIMS), to depth profile the elemental species through to the titanium substrate. In conjunction, scanning electron microscopy (SEM) and X-ray microanalysis were used to examine the craters formed by SIMS to gain an understanding of the diffusion gradient existing with the anodised titanium substrate and zirconia thin film.

1. INTRODUCTION

Titanium and its alloys are used in a wide range of applications from the biomedical field to the aircraft and aerospace industries this is in part due to the enhanced mechanical and chemical properties of titanium in addition to the excellent corrosion resistance and biocompatibility of the material [1,2]. Titanium has poor tribological properties for both unalloyed and common titanium alloys [3] but by coating the titanium with sol-gel derived zirconia results in a significant improvement in these properties [4,5].

Zirconia sol-gel-derived ceramic coatings have a variety of uses, due to their ease of production and ability to coat complex shapes. The sol-gel's nanocrystalline grain structure results in improved mechanical properties of the coating [6,7].

2. MATERIALS AND METHODS

The titanium alloy (Ti6Al4V) samples were machined from a titanium rod without lubricant and with a high speed steel (HSS) tool, and then polished on a Leco Auto polisher to a 1 micron finish, before the final polish in a vibratory polisher with alpha alumina grit to 0.5 micron finish. Samples were then degreased in Methyl Ethyl Ketone (MEK).

The titanium alloy samples were anodised in a dilute phosphoric and sulphuric solution. The samples were anodised at 75V for 30 minutes based on an earlier work [4]. Photo catalysis treatment consists of the treatment of the anatase layer with a UV wavelength of approximately 380nm for 1 hour. Exposing the catalyst to UV generates an excited state on the surface, which is able to initiate subsequent processes like redox reactions and molecular transformations. These samples were then coated with alkoxide-derived zirconia.

These coatings were applied by sol-gel spin coating methods, using techniques and protocols developed in an earlier work and were examined with Secondary ion mass spectroscopy [8, 9]. The samples were then imaged with a Zeiss SUPRA55VP, scanning electron microscope (SEM).

SIMS measurements were performed using a CAMECA IMS 5f secondary ion mass spectrometer. A Cs+ primary ion beam was used for depth profiling by rastering an area of $250 \times 250\mu m^2$ on the surface of the sample with a net impact energy of 3keV. To eliminate any edge effects the actual analysis area was dictated by aperture settings which restricted the measurement of positive secondary ions to a 100μm diameter circular area within the rastered region. The measurement of MCs+ molecular secondary ions, where M denotes the element of interest, was used for all samples as it can reduce the contribution of matrix effects on the SIMS results [10]. The depths of the SIMS craters were measured with an Alpha-step stylus profilometer to determine the average sputter rate of the analysis.

2.1 Secondary Mass Ion Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is a specialized analytical tool which combines high spatial resolution and high sensitivity. This technique uses a highly focused ion beam of caesium ions which 'sputters' material from a selected domain on the zirconia coated titanium surface. The 'secondary ions' which are ejected from this sample are passed through a mass spectrometer which separates the ion according to their mass/charge ratio: in effect providing a chemical analysis of a very small sampling volume [11].

2.2 Scanning Electron Microscopy

A Zeiss Supra 55 VP (variable pressure) scanning electron microscope was used to investigate the morphology of the coated samples. These types of field emission gun (FEG) microscopes can operate in conventional high vacuum mode, but can also be operated in low vacuum mode, thus allow imaging of electrically insulating materials in pristine condition. The samples were imaged using voltages (between 5 kV and 10kV) using the new in-lens secondary electron detector. These types of detectors provide high signal/noise images

3. RESULTS AND DISCUSSION

3.1 SEM of Zirconia Coated Ti6Al4V Samples

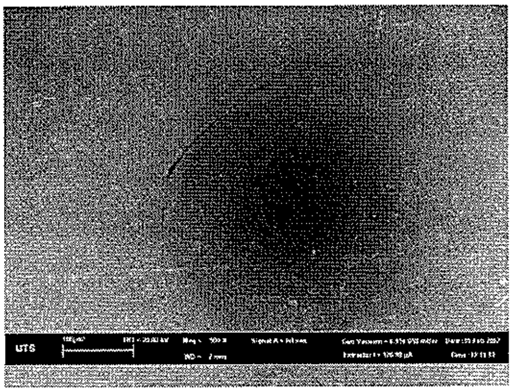

Figure 1 Ti6Al4V Alloy with zirconia coating showing SIMS sputtered area at low magnification with the scale at 100 microns.

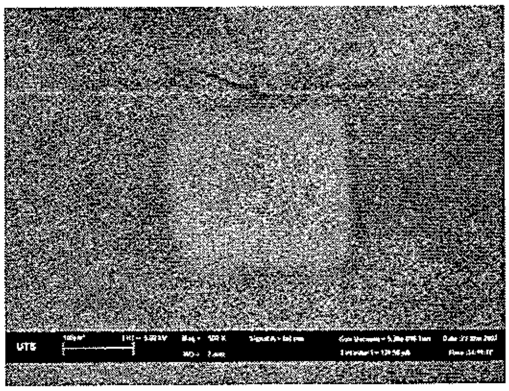

Figure 2 Anodised Ti6Al4V alloy with zirconia coating showing SIMS sputtered area at low magnification with the scale at 100 microns.

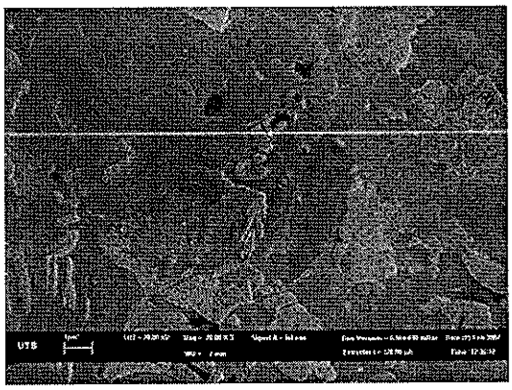

Figure 3 Ti6Al4V alloy with zirconia coating showing floor of SIMS sputtered area at high magnification with the scale at 1 micron.

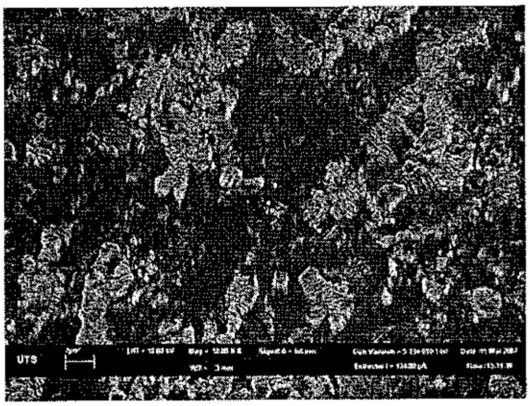

Figure 4 Anodised Ti6Al4V alloy with zirconia coating showing floor of SIMS sputtered area at high magnification with the scale at 2 microns.

Figure 5 Anodised Ti6Al4V alloy with zirconia coating showing floor of SIMS sputtered area at high magnification with the scale at 1 micron.

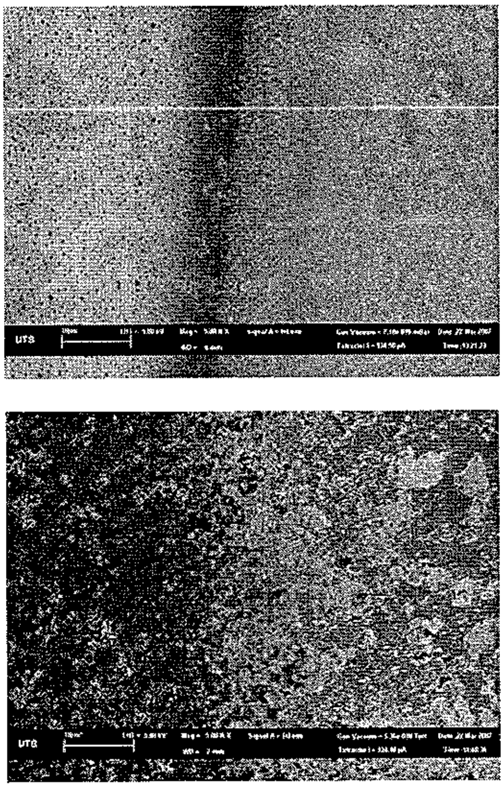

Figure 6 Ti6Al4V alloy and anodised Ti6Al4V alloy with zirconia coatings showing the interface boundary of the SIMS sputtered area with the scale at 10 microns.

The SEM micrographs in figures 1 and 2 show the sputtered area of the SIMS instrument which is roughly 250 microns x 250 microns resulting from a primary beam current of 10nA and a acquisition time of 1827 seconds for the Ti6Al4V alloy and an acquisition time of 4959 seconds for the anodised Ti6Al4V alloy sample. The increased time for the anodised sample is due to the additional thickness of the anodised layer of TiO_2 which is approximately 150nm thick.

The coating of zirconia on both the anodised and Ti6Al4V samples as shown in figures 4 and 5 demonstrates the good adhesion of the coating as no cracking or buckling of the coating is evident at the interface boundary after the use of the SIMS sputtering; any stress or poor adhesion would have been evident at these areas

Figures 3 and 4 show the interior of the sputtered area which is the pure Ti6Al4V alloy after sputtering in both samples in which the alpha and beta phases appear in the grain structure, the alpha phase appears as a whitish columnar type microstructure while the beta phase as a greyish matrix this was verified by using the SEM-EDS. It is also evident in the anodised sample the coarser nature of the grain structure which may in part be due to the increased SIMS acquisition time needed to penetrate the TiO_2 layer.

Figure 5 shows a high magnification image of the floor of the SIMS sputtered area which shows clearly the alpha and beta grain microstructure of the Ti6Al4V sample after sputtering.

Figure 6 shows the interface boundary area on both the anodised and Ti6Al4V samples, the Ti6Al4V sample has a much more clearly defined boundary with a degree of porosity in both the zirconia coating and the interface layer over a 10 micron area. The anodised sample shows a less well defined boundary area in addition to a significantly smaller degree of porosity in both the coating and interface areas although the zirconia coating does appear to be significantly rougher in appearance which is in part due to the rougher surface of the grown anodic oxide layer formed by anodising at 75V. This results in an increase of the film thickness on the titanium substrate from 5-7nm to 150nm for the anodised layer of TiO_2 [4,5].

Using energy dispersive spectroscopy (EDS) attached to the Zeiss Supra 55 VP SEM we were able to detect zirconia on the areas outside of the SIMS sputtered area that confirmed its presence on both the anodised and Ti6Al4V samples but within the sputtered areas of both samples no zirconia was detected but the presence of titanium, vanadium, aluminium and oxygen as the SIMS sputtering had destroyed the coating and penetrated through the anodised layer to expose the base material in the case of both samples is Ti6Al4V base material.

Figure 7 shows the SIMS depth profile for the 75V anodised sample and this gives an overview of the elemental variations as the SIMS sputters for the corresponding time period allowing for a depth profile of the sample to be graphed and using previous work [4,5] in which the zirconia coating was found to be approximately 100nm thick. The SIMS detected ever decreasing amounts of zirconia up to the depth of 200nm well into the existing layer of TiO_2 indicating that some degree of diffusion has occurred although this needs to be further verified to check that it is not simply some penetration of the zirconia coating into the TiO_2 layer by mechanical means such as porosity of the anodised TiO_2 layer.

The SIMS in figure 7 also showed the presence of some phosphorus and sulphur in the anodised sample and this is due to minute amounts being incorporated into the anodic film as it is being formed during the anodisation process.

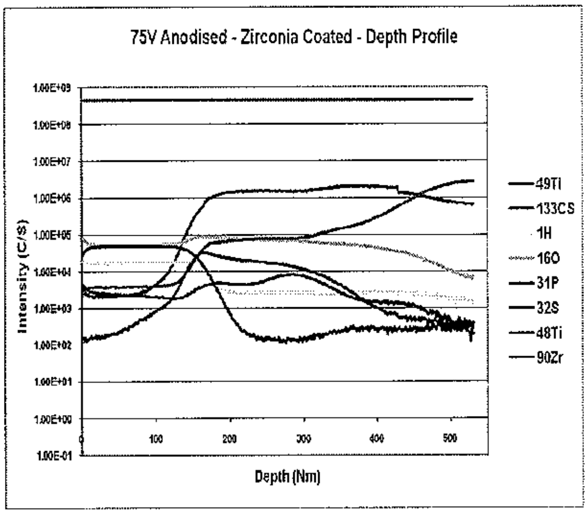

Figure 7 SIMS depth profile of anodised Ti6Al4V sample (75V) showing the elements existing in this sample through to a depth of 500nm.

4. CONCLUSION

The zirconia coatings on both the anodised and Ti6Al4V samples demonstrated good adhesion and were successfully applied by the sol gel technique. The SIMS results also showed that the zirconia diffused a significant degree into the interface layer, but this needs further studies to verify it. Further work into the interface also needs to be undertaken to see if a diffusion gradient can be x ray mapped to further validate the SIMS results.

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