Fracture Toughness Of Nanoscale Zirconia Coatings On Titanium Substrates

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ABSTRACT: In the biomedical field, the surface modification of titanium aims to inhibit wear, reduce corrosion and ion release, and promote biocompatibility. Sol-gel-derived ceramic nanoscale coatings show promise due to their relative ease of production, ability to form a physically and chemically uniform coating over complex geometric shapes, and their potential to deliver exceptional mechanical properties due to their nanocrystalline structure. In this study zirconia coatings on titanium were investigated for their fracture toughness.
KEYWORDS: Thin Film, Fracture Toughness, Nanoscale, Zirconia, Sol-gel

1. INTRODUCTION

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 [Kirk, 1999 and Chen, 1994].

The properties of sol-gel zirconia coatings suggest they may be effective in relation to *in vivo* metal ion release and subsequent biological effects [Filiaggi et al., 1996]. Metal-based implants are used in load-bearing applications under which the response of the surface treatments to mechanical deformation is important. Delamination or perforation of a protective coating exposes the substrate to accelerated wear or corrosion, and the released coating particles may act to accelerate wear or provoke a negative host response [Kirk, 1999, Jaffe and Scott, 1996].

Phase-stabilised zirconia in the bulk form (Y-TZP) is an accepted bioinert implant material that suffers from long-term degradation of its mechanical properties [Kirk 1999]. Submicron thick sol-gel zirconia films crystallise directly into the tetragonal/cubic phases without the need to add phase stabilisers into the zirconia film [Atik *et al*. 1994, Atik and Aegerter 1992].

The anodisation of titanium involves the formation of a thin, compact oxide layer, which improves the wettability of the oxide film. This process involves the conversion of the rutile structure of the original titanium oxide into a mixed rutile and crystalline anatase structure.

2. MATERIALS

The titanium samples, commercially pure (CP), were anodised in a mixed phosphoric acid (H_3PO_4) sulphuric acid (H_2SO_4) solution. Three voltages were used, 25 volts, 50 volts and 75 volts for a period of twenty minutes. These voltages were based on the work of Arsov [Arsov 1985], Aladjem [Aladjem 1973], Delplancke and Winand [Delplancke and Winand 1988], and Blondeau [Blondeau *et al*.1997].

The experimental procedure and manufacture of the zirconia sol-gel is based on the previous work of Paterson *et al*. [Paterson *et al*. 1996, 1998], Anast *et al*. [Anast *et al*. 1992, 1993] and Torpy [Torpy 2003]. All titanium samples were ultrasonically cleaned in distilled water for a period of five minutes before drying in a 70°C oven for 20 minutes. The samples were then placed on a spin coater (Headway Research USA) and the solution was applied via a dropper onto the surface of the sample. The samples were then spun for 10 seconds at 2000 RPM. At this time, sol-gel was reapplied via the previous method and the samples were spun for a further 10 seconds. Zirconia-

coated samples underwent solution ageing for 24 hours at 70°C. Samples were then fired at 300°C for 24 hours, and finally fired for two hours at 550°C. The zirconia coatings were 70-100nm thick.

3. TEST METHOD

The tensile specimens for the micro-adhesion tester were made from 1mm thick commercially pure (CP) titanium plate (Titanium International), and were punched out using a flywheel punch and die set-up to produce specimens 3mm wide and a 12mm gauge length. These samples were then polished. The flat, "waisted" titanium samples were anodised and coated as indicated earlier, and were tested in tension at a rate of 0.005 mm/s using a specially designed high-stiffness small mechanical testing device positioned directly under the objective lens of an optical microscope (Zeiss Axioplan) at a fixed magnification of 200 times.

The set-up described above allowed the direct observation and recording of crack initiation and evolution, and debonding of the thin films on the titanium specimens. The applied load and the imposed displacement were recorded during the tests (every 2 seconds). Simultaneously, optical images of the coated surface were captured every 2 seconds using a MTI analog camera with image analysis software (Scion Image, NIH). After testing, the samples were imaged using a LEO SUPRA 55VP SEM.

The adhesion testing allowed for the calculation of the stress and strain at the initial cracking and initial debonding points, which were recorded during the tests. Using the equations from of Hu and Evans [Hu and Evans, 1989], Ignat [Ignat, 1996] and Beuth and Klingbeil [Beuth and Klingbeil, 1996], allowed for the calculation of the apparent fracture toughness and fracture energy of the film. In this case it is an apparent fracture toughness as residual stresses in the film have not been taken into account. As a result these apparent fracture toughness values appear somewhat higher than might be expected. Never-the-less fracture toughness trends can be observed and variations in processing assessed.

$$\lambda_f = \frac{\sigma_c^2 t}{E_f\left[n.g(a) + \frac{\sigma_c}{3T}\right]} \tag{1}$$

λ_f= fracture energy of film (Jm^{-2}) σ_c= critical stress for cracking g(a)= Constant from the tables of Hu & Evans, 1989

t= thickness of film E_f= Young's modulus of film E_s= Young's modulus of substrate

n= Dundas parameters = $\frac{E_f - E_s}{E_f + E_s}$ T= $\frac{\sigma_y}{\sqrt{3}}$ where σ_y=yield stress (from exp.)

and the apparent fracture toughness of the film from there

$$K = \left(\lambda_f E_f\right)^{1/2} \tag{2}$$

K= apparent film toughness

4. RESULTS

Apparent fracture toughness values are shown in Figure 1. The CP titanium sample yielded a fracture toughness value of 37.1 $MPa.m^{1/2}$. The 25V and 50V samples showed relatively close fracture toughness values of 44.5 $MPa.m^{1/2}$ and 45.2 $MPa.m^{1/2}$ respectively. The 75V sample was significantly lower at 26.9 $MPa.m^{1/2}$. The samples anodised at 50 volts were found to produce a more adherent and homogenous sol-gel coated surface after micro-adhesion. It should be noted that these are preliminary test results with further testing required to obtain statistical significance. None-the-less, careful control of the film deposition and testing variables should result in a

maximum 10 percent variation in fracture toughness values. As was stated earlier, these values are a higher than might be expected for zirconia. This is, in part, due to not measuring the residual stress in the film, but may also be due to the nanoscale nature of the coating. More rigorous characterisation of these films and their adhesion are to be discussed elsewhere

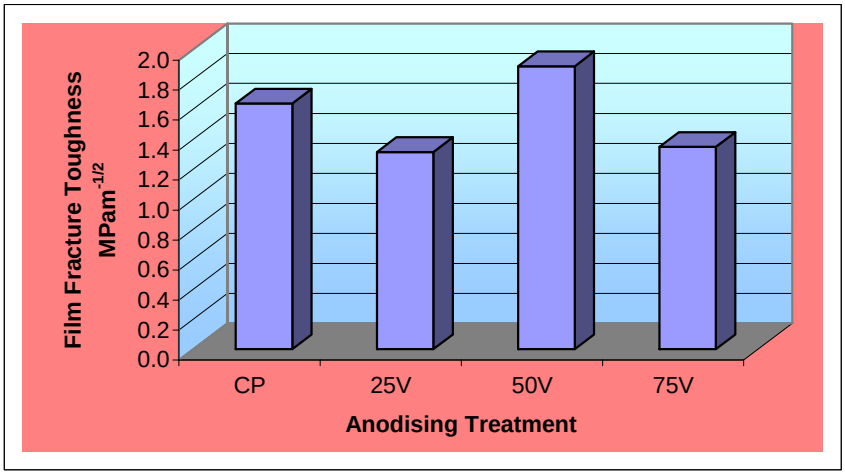

Figure 1 Apparent Film toughness – K_{Ic} – Zirconia coatings

5. DISCUSSION

It can be seen from the fracture toughness results that anodising the titanium surface prior to zirconia sol-gel coating can influence the fracture toughness of the resultant film. This can be associated with the increase in bonding between the film and the substrate. For the 50V anodised "precoat" an increase of 15. However on increasing to 75V pre-treatment an 18% decrease is observed. It is not clear at this stage why the 25V samples showed a lower fracture toughness but iis more than likely due to the phases formed.

The fracture toughness of the films would depend on the integrity of the film, the bonding to the substrate, interphases between coating and substrate and the nature of the substrate itself. The production of a homogeneous solution is necessary to ensure good mechanical properties for the film as well as protection of the substrate. No cracking of the coatings were observed for any of the preparation conditions.

X-ray diffraction analysis was carried out on the zirconia coated samples using $CuK_{\alpha 1}$ radiation and showed that the pattern produced is consistent with either the JC-PDS 24-1164 tetragonal form or the JC-PDS 27-997 cubic form (Figure 2) for all samples. Ben-Nissan *et al*. [Ben-Nissan et al., 1991], suggest that a strained tetragonal lattice is the more probable of the two alternatives.

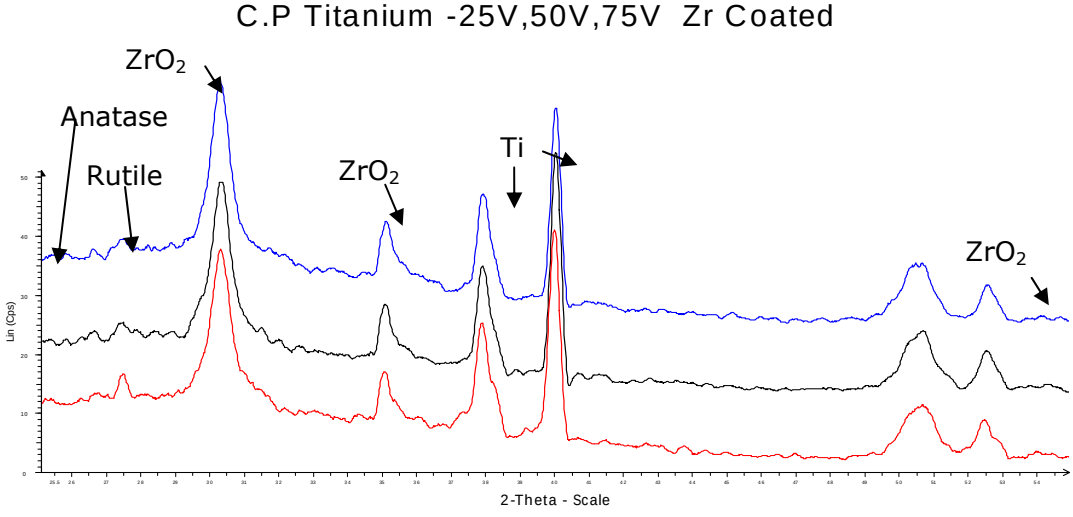

Figure 2. XRD patterns for the three zirconia coated films. a) 25V, b) 50V and c) 75V

As for the interphases, the actual anodised layers themselves decreased in toughness with increasing anodising voltage. The anodisation of the titanium samples produced oxide film thicknesses in agreement with the literature and the linear growth equation with the anodising solutions showing a linear growth of 2 nm per volt. As the thickness of the anodised layer increases it might be expected to decrease in toughness.

Secondly X-ray diffraction provides evidence of the amount of the rutile phase being reduced, (Figure 2) but show only small peak matches of the anatase structure pattern, indicating there is some evidence of the anatase structure being formed. This is in agreement with the literature [Arsov, 1975, 1985, Blondeau et al., 1977, Ask et al., 1990] . Arsov [Arsov, 1975,1985] and Blondeau *et al.* [Blondeau *et al.* 1977] argue that the rutile phase is converted to the anatase phase as the voltage is increased. Delplancke and Winand [Delplancke and Winand 1994], report that the oxide film formed with increasing voltage is a mixed oxide consisting of both anatase and rutile phases. Fracture toughness of the 75V anodised film does decrease [Roest, 2004] but as to whether this is due to increase in film thickness and/or phase development is not clear at this point. X-ray diffraction also suggested the development of titanium-zirconium-oxygen phases developing but this needs further work.

Bonding to the substrate was also found to be good for all films, as evidenced by the lack of spalling in all samples, (Figure 3). The pattern of fracture lines on the sample in Figure 3 have been observed before [Kirk et al., 1999 and Kirk and Pillar, 1999]. These authors state that these are through thickness cracks initiated at slip bands emerging from the substrate.

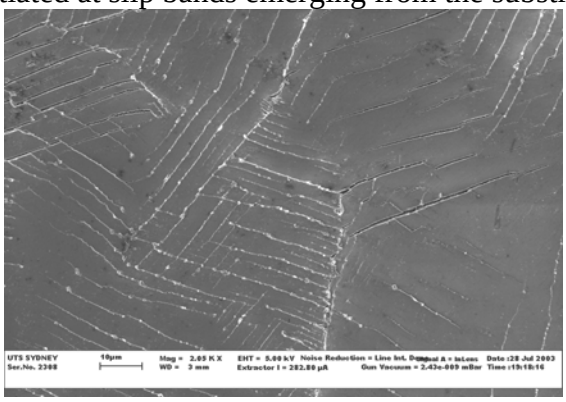

Figure 3. SEM of zirconia-coated - CP titanium sample, after micro-adhesion testing at 2K magnification of anodised

The test data allowed for calculation of the interfacial fracture energy (Eqn. 1). The 75V sample showed much lower interfacial fracture energy (Figure 4). These interfacial fracture energies were all less than or equal to the interfacial fracture energies for the interface between the titanium and the titanium oxide coating for all anodising conditions and suggests that the interfacial bonding between the zirconia and titania layer may be responsible for the observed results.

Another important aspect is the change in crack morphology for the tougher films. Figure 5 shows two SEM photographs. Figure 5(a) shows the crack path for an unanodised specimen and 5(b) for a 50V specimen. It can clearly be seen that the crack in the 50V specimen has a more tortuous path than former, as well as evidence of a higher level crack branching and the presence of crack bridging.

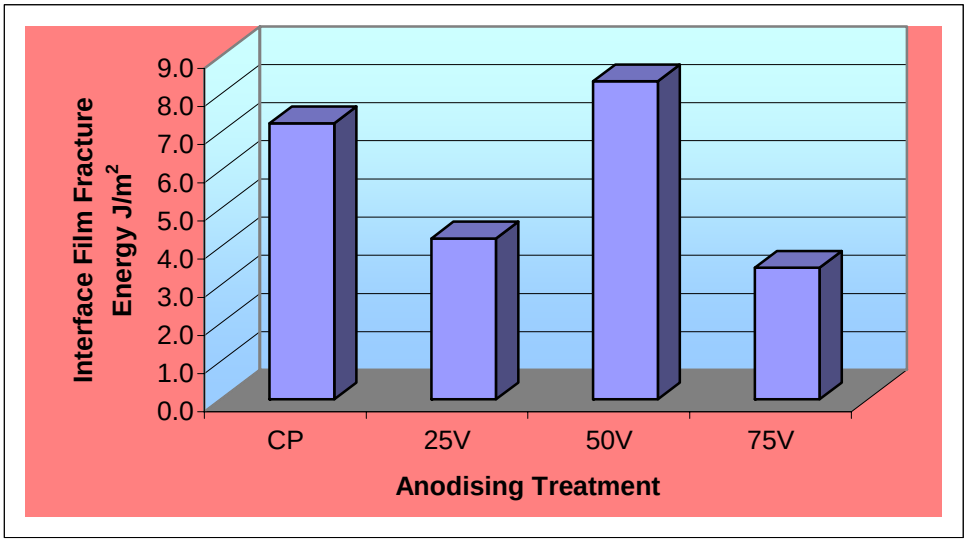

Figure 4 Interfacial fracture energy of the zirconia coatings.

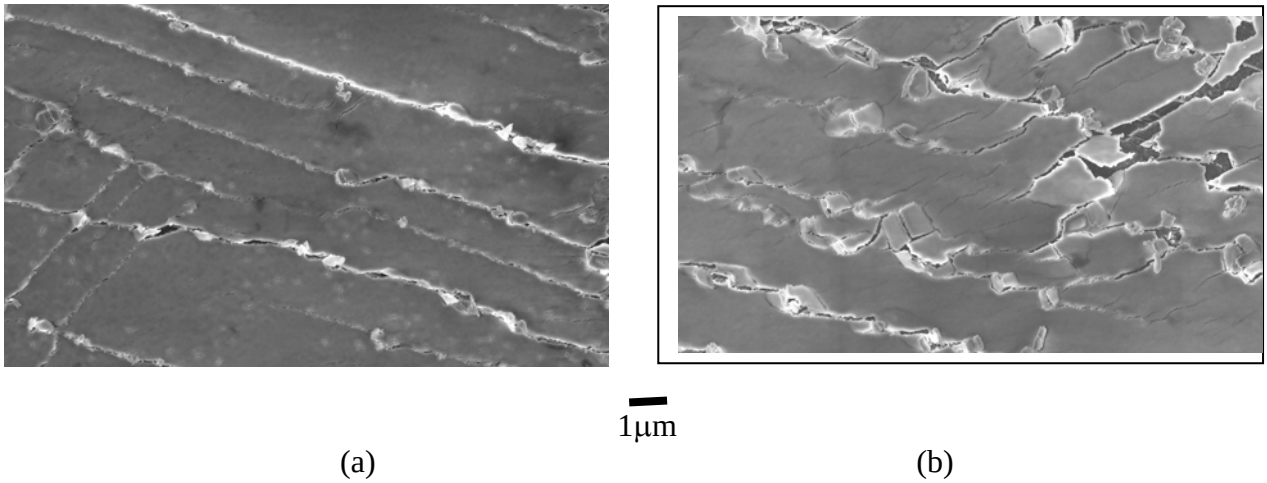

Figure 5. Comparison of the crack path morphology for (a) a specimen with no anodised coating and (b) the 50V anodised material.

6. CONCLUSIONS

The use of various thicknesses of anodised coating prior to the application of sol gel zirconia coating to the surface of CP titanium in some instances enhances the fracture toughness of the zirconia coating. It was also found that there is an optimum condition for this anodising, that being 50 volts for the anodising process. The reason for this is due to two factors;

- These conditions produce a homogeneous, adherent anodised layer that is not too thick and allows good stress transfer to the zirconia film.
- The mixture of rutile and anatase phases present in this anodised coating provide for good bonding between the anodised film and the zirconia coating. The growth of anatase grains at 75V may be detrimental the bonding of this thickness interlayer.

More work needs to be done to look at the nature and distribution of the phases within the anodised layer in order to determine the exact nature of the contribution to toughness as well as the effect of the anodised layer thickness. We are currently using finite element analysis to investigate this latter issue and hope to perform more experiments on the phase issue.

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