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BIOACTIVE RESPONSE ON TI ALLOY SURFACE INDUCED BY ANODICALLY BONDED BIOACTIVE GLASS

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Abstract. *The aim of this paper is to report the use of the anodic bonding technique to produce a modification to increase the bioactive response on titanium alloy surface by means of the bonding between a bioglass and titanium alloy. Ti alloy and bioactive glasses 52S4.6 and 45S5 were successfully bonded using anodic bonding technique for range of temperature and applied potential. Bioactive glass anodically bonded to Ti alloy results in a strong adhesion. Mechanical detachment can be performed and the fracture occurs in the glass and not at the interface. As a result small bioactive glass particles still bonded to Ti alloy surface spread to the bonding region. Bioactive in-vitro results revealed that after soaking in SBF, the Ti alloy submitted to anodic bonding and that was mechanically separated from bioglass prior to soaking in simulated body fluid solution were covered with a apatite layer in the bonding region indicating that anodic bonding technique is an effective way to produce a bioactive response on Ti alloy surface.*

Keywords: *Surface modification, titanium alloy, bioglass, bioactivity, anodic bonding*

1. INTRODUCTION

Titanium has been used in the production of dental implants and orthopaedic prostheses due to the low tendency to corrosion and good biocompatibility. Even so, the surface of titanium is not bioactive. Several surface treatments have been developed to make the surface of such metals bioactive (Liu, Chu and Ding, 2004). Plasma sprayed hydroxylapatite coatings can be used. However, bioactive glasses can be used as an alternative to hydroxylapatite. Among all bioactive materials, bioactive glasses show the best-known bioactive behaviour (Schrooten and Helsen, 2000; Fathi and Doostmohammadi, 2009). The use of anodic bonding technique of bioactive glasses and Ti alloy was investigated as a method to induce a bioactive response. A modified surface layer obtained on the Ti alloy after the application of the anodic bonding process was evaluated.

2. EXPERIMENTAL PROCEDURE

Titanium alloy (medical grade Ti-6Al-4V ELI) and two bioactive glasses close to 45S5 and 52S4.6 Bioglass® in chemical composition were used. To achieve the bonding a programmable dc power supply (Chroma 62012P-600-8) and a furnace (Qimis Q317M) were used. The bond was achieved applying the potential at temperatures ranging from 500 V to 600 V and 250 °C to 300 °C. A shear test was conducted to evaluate the bonding strength Results of this test are reported elsewhere (Szesz and Lepienski, 2017). After this procedure, it was noted there is a modified surface layer on Ti alloy surface as a result of the anodic bonding process.

Raman spectroscopy, energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and instrumented indentation techniques were used to evaluated the modified surface layer on the Ti alloy.

The bioactive response of Ti alloy modified surface was evaluated using simulated body fluid solution (SBF) where the samples were soaked at 37 °C for 14, 21 and 30 days. Apatite was identified by Raman spectroscopy and SEM.

3. RESULTS AND DISCUSSION

After the mechanical detachment of Ti alloy and bioglass previously anodically bonded, it was possible to observe a brown layer with small glass fragments still on Ti alloy surface. Figure 1 shows the SEM images and chemical mapping obtained by EDS of the Ti alloy specimen subjected to anodic bonding process and mechanically separated from the

bioglass specimen. Figure 1(c) indicates that Si is present in the modified layer as well as in small glass fragments. Thus, Si can be one of the main components of this layer. Raman spectra suggest that the modified layer can contain titanium silicide ($TiSi_2$) and titanium oxide (rutile).

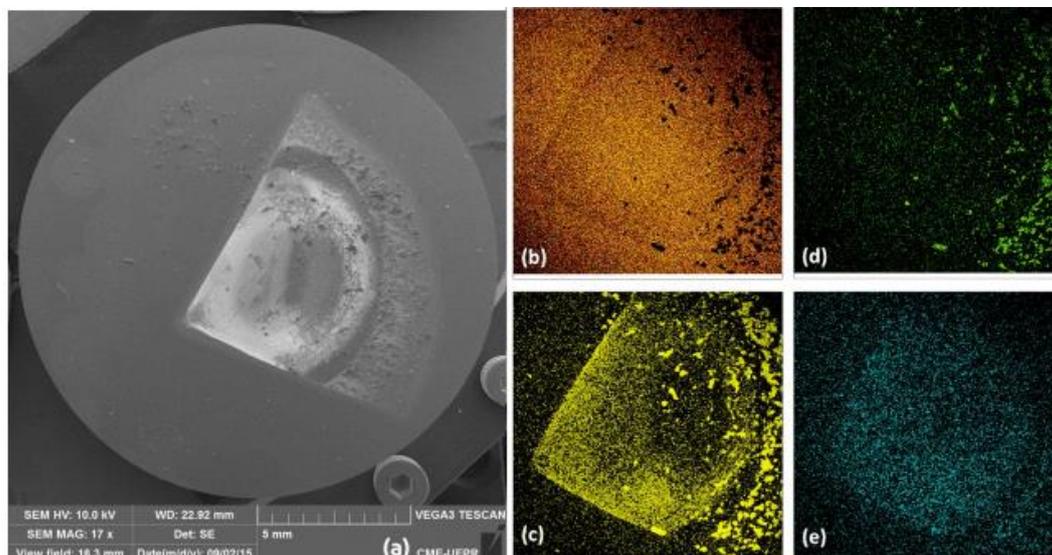


Figure 1. SEM images and chemical mapping obtained by EDS of the Ti alloy after mechanical detachment. (a) SEM image (17x). Chemical mapping (b) Ti (c) Si (d) Ca (e) P

Modified layer mechanical properties were obtained using instrumented indentation. Hardness and elastic modulus data are shown in figure 2. Data obtained for the Ti alloy substrate and typical values for bioglass are presented for comparison. Results indicate the modified layer has low hardness and elastic modulus when compared with bioglass. Furthermore, hardness and elastic modulus values get close for those of the Ti alloy substrate for increased contact depth. From this result is possible to infer that modified layer is thin, with thickness around 100-200 nm (Tsui and Pharr, 1999; Saha and Nix, 2002). Scratch test performed with increasing load on the modified layer results in no detachment or layer cracking. This result suggests that the modified layer has good adhesion with the substrate.

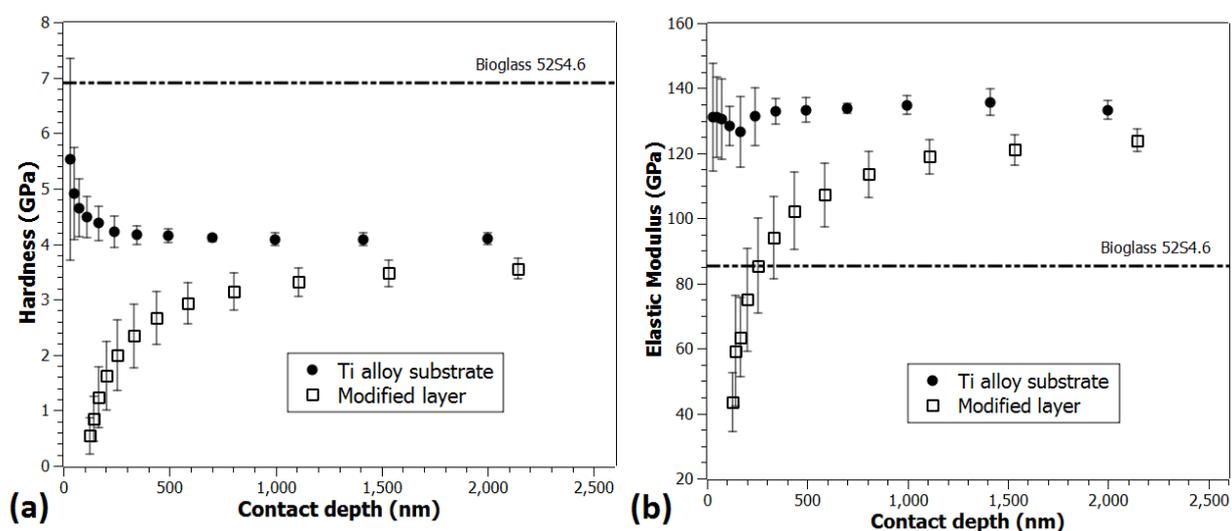


Figure 2. (a) Hardness and (b) elastic modulus profiles obtained for the modified layer

Analysis performed using SEM-EDS reveal that apatite was formed on the modified layer regardless the soaking period. However, as shown in figure 3, apatite was found over the modified layer only for samples submitted to anodic bonding with higher values of temperature or potential. Samples produced using the lowest values of these parameters exhibited apatite just in regions where remaining bioglass fragments were found.

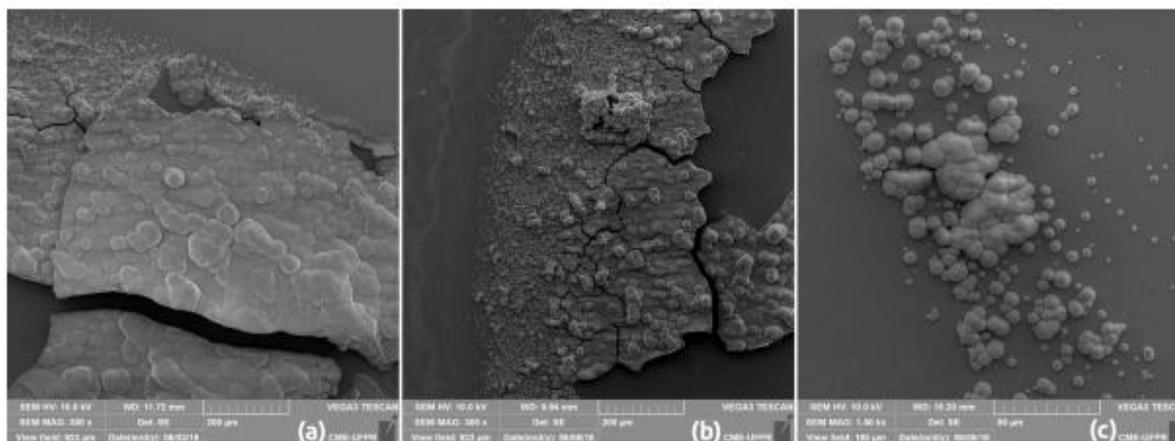


Figure 3. SEM images after 30 days in SBF. Anodic bonding performed at (a) 300 °C; 600 V (b) 250 °C; 600 V and (c) 300 °C; 500 V.

Glass-to-metal seal, as well as anodic bonding, rely on chemical reactions at the interface between metal and glass to bond these materials. However, these reactions should be kept to a minimum level in order to obtain high quality seals, once the interface compounds obtained presents different elastic behavior and different thermal expansion coefficient of those of metal and glass (Donald *et al.*, 2011). On the other hand, the bioactivity test herein performed indicates that the modified layer formed as a product of interfacial reactions during the anodic bonding process has the ability to form apatite *in vitro*. Results of Raman spectroscopy suggests that the modified layer is composed by titanium silicide and rutile. *In vivo* results reported by Kitsugi *et al.* (Kitsugi *et al.*, 1996) demonstrates that titanium implants coated with titanium silicide can promote the osteointegration. Thus, if desired, anodic bonding parameters can be choose in order to promote the formation of the modified layer to obtain a bioactive surface at the cost of do not rely on the permanent bonding between bioglass and Ti alloy.

4. CONCLUSIONS

A good anodic bonding of bioglass to the Ti alloy was obtained. Mechanical detachment of bioglass from Ti alloy results in regions with a surface modification of Ti alloy and presence of small bioglass particles well bonded to Ti alloy. Immersion in SBF indicate that the surface modified and the bioglass particles bonded by anodic bonding can be used to induce bioactivity on Ti alloy.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Donald, I. W., Mallinson, P. M., Metcalfe, B. L., Gerrard, L. a. and Fernie, J. a. (2011) 'Recent developments in the preparation, characterization and applications of glass- and glass-ceramic-to-metal seals and coatings', *Journal of Materials Science*, 46(7), pp. 1975–2000. doi: 10.1007/s10853-010-5095-y.
- Fathi, M. H. and Doostmohammadi, a. (2009) 'Bioactive glass nanopowder and bioglass coating for biocompatibility improvement of metallic implant', *Journal of Materials Processing Technology*, 209(3), pp. 1385–1391. doi: 10.1016/j.jmatprotec.2008.03.051.
- Kitsugi, T., Nakamura, T., Oka, M., Yan, W. Q., Goto, T., Shibuya, T., Kokubo, T. and Miyaji, S. (1996) 'Bone bonding behavior of titanium and its alloys when coated with titanium oxide (TiO₂) and titanium silicate (Ti₅Si₃).', *Journal of biomedical materials research*, 32(2), pp. 149–56. doi: 10.1002/(SICI)1097-4636(199610)32:2<149::AID-JBM1>3.0.CO;2-T.
- Liu, X., Chu, P. and Ding, C. (2004) 'Surface modification of titanium, titanium alloys, and related materials for biomedical applications', *Materials Science and Engineering: R: Reports*, 47(3–4), pp. 49–121. doi: 10.1016/j.mser.2004.11.001.
- Saha, R. and Nix, W. D. (2002) 'Effects of the substrate on the determination of thin film mechanical properties by nanoindentation', *Acta Materialia*, 50(1), pp. 23–38. doi: 10.1016/S1359-6454(01)00328-7.

Schrooten, J. and Helsen, J. . (2000) ‘Adhesion of bioactive glass coating to Ti6Al4V oral implant’, *Biomaterials*, 21(14), pp. 1461–1469. doi: 10.1016/S0142-9612(00)00027-2.

Szesz, E. M. and Lepienski, C. M. (2017) ‘Anodic bonding of titanium alloy with bioactive glass’, *Journal of Non-Crystalline Solids*, 471, pp. 19–27. doi: 10.1016/j.jnoncrysol.2017.04.038.

Tsui, T. Y. and Pharr, G. M. (1999) ‘Substrate effects on nanoindentation mechanical property measurement of soft films on hard substrates’, *Journal of Materials Research*, 14(1), pp. 292–301. doi: 10.1557/JMR.1999.0042.

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