The Influence of Oxidized Interlayer on the Adhesion of Bioactive Cao-P_2o_5-Tio_2-Na_2o Glass Ceramic Coating to the Titanium Substrate

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Abstract

Titanium alloys are important bio materials which may also need to a bio compatible coating. To improve the Ti/glass-ceramic bonding is a challenging part of coating because the bonding properties play an important role in the long-term performance of medical implants. The purpose of this research is to improve the bonding strength of bioactive coating in the system of CaO-P_2O_5-Na_2O-TiO_2 using the formation of suitable oxidized layer and studying the effect of this interlayer on adhesion of coating. To achieve this goal, after surface modification, the surface of titanium samples was heat treated in 750 ˚c for 30, 60 and 90 min, to be oxidized. The results of Scanning Electron Microscopy (SEM) and Elemental concentration analysis by EDS and Atomic Force Microscopy (AFM) show that oxidized layer that was produced in 750˚c and 30 min. This oxidized interlayer has the best properties in comparison with two other samples and has the best adhesion to both substrate and coating.

Keywords: Titanium Alloys, Bioactive Coating, Oxidation, Heat Treatment, Bonding Strength.

1. Introduction

Commercially pure titanium (cpTi) is applied as a metallic material used in clinical fixed prosthetic implant because of its good biocompatibility and mechanical properties, high strength to weight ratio, low density and good corrosion resistance. But it is well known that, titanium and titanium alloys do not form good bonding with the bone by a chemical or biological interaction [1-3]. Insufficient adhesion to the bone, due to lack of a specific biological response from the living tissues, can progressively form a non-adherent fibrous capsule around the implant, leading, in some cases, to interfacial displacements, and clinical failure [4,5]. Several glass and glass-ceramic material are bioactive and can induce a biological bonding with both soft and hard tissues.

Titanium alloys can be coated with bioactive materials. The as obtained implants can offer several advantages, in term of the high mechanical properties of the metallic substrate combined with the bioactivity of the coating. But it is important that glass or glass-ceramic coating should be strongly bonded to a titanium substrate to achieve successful long-term clinical use. This titanium-glass or glass-ceramic bonding is influenced by the surface properties of the titanium substrate [6,7].

Glass ceramic which is coated directly onto commercially pure titanium adheres poorly. Oxidized interlayer can improve the adherence considerably and is recommended for bonding metal and glass-ceramic coatings. However, an excessive thick and non-adherent layer of titanium oxide formed on the surface may affect metal/ glass- ceramic bonding and can cause the failure of the coating [8-10].

The most crucial factor in the performance of the implant is the high strength bounding between interlayer and the coating material as well as the bonding of the interlayer to the substrate. For this reason, in This study the bond strength between a titanium substrate and phosphate base glass ceramic coating with modifying oxidized interlayer were evaluated and an adherent oxide layer was created on the titanium surface to improve the titanium/ glass-ceramic bonding by changing in heat treatment process.

2. Materials and Methods

2.1. Pre-Heat Treatment of Titanium

Commercially pure titanium was cut in the dimension of 20×60×0.5 mm. First; the titanium specimens were mechanically polished with 60 grit SiC abrasive paper to roughening the surface of the plates. The roughened substrates were ultrasonically rinsed in acetone for 60 min. Then, the samples merged in distilled water for 30 min, and then dried in the oven. Prior to the coating process to produce a glass ceramic coat, the specimens were heat treated on the temperature of 750˚C in the time intervals of 30(sample O_1), 60(sampleO_2) and 90(sampleO_3) min at a heating rate of 10˚C/min in the laboratory air, and then cooled to room temperature. The properties of the oxidized layers that were made from the controlled heat treatment process were detected using Scanning Electron Microscopy (SEM, Vega-T-scan), and Energy Dispersive Spectrometry (EDS) as well as Atomic Force Microscopy (AFM).

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2.2. Glass ceramic coating

The calcium phosphate invert glass was prepared with a composition of $45P_2O_5$-24CaO-28.5Na_2O-2.5TiO_2 in mole %. The mixture of starting materials, which were reagent grate $CaCO_3$, Na_2CO_3, TiO_2, P_2O_5 was completely mixed in a PET milling jar and then melted in an alumina crucible at 1100˚C for 0.5h. The melt was poured on the stainless-steel roller to produce the frit of glass. The fritted glass was pulverized to size of less than 40µm by using a zirconia ball mill. After pulverization, the glass powder was mixed with ethanol to make a slurry. Then the titanium substrates that were pre-heat treated in three different processes were dipped into the glass powder slurry described above and were dried at 100˚C. Finally, the samples were placed in an electric resistance furnace and held in the air at 800˚C for 1h and then, cool to room temperature in the furnace. Then adherence of the coating to the substrate and inter layer was examined qualitatively with shear stress test according to ASTM F1044-99 [11] as shown in Fig. 1.

3. Result and Discussion

3.1. Characterization of Pre-Oxidized Titanium

Fig. 2, 3 and 4 shows the results of SEM examinations of the cross section of titanium plates that were heat treated on the 750˚C for 30, 60 and 90 min. Observations indicate that the thickness of the oxidized layer was increased with increasing time from sample O_1 to sample O_3. In addition, the color of oxidized layer, in different part of the oxide was varied. The EDS analysis of the cross section of the oxide layer show that the composition of the oxide is varying from the interface to surface of oxidized layer; in O_2 and O_3, quantity of the titanium/oxygen ratio were decreased with increasing distance from the interface. It seemed that with increasing the time of heat treatment, the cohesion of the oxide was decreased and in the interface.

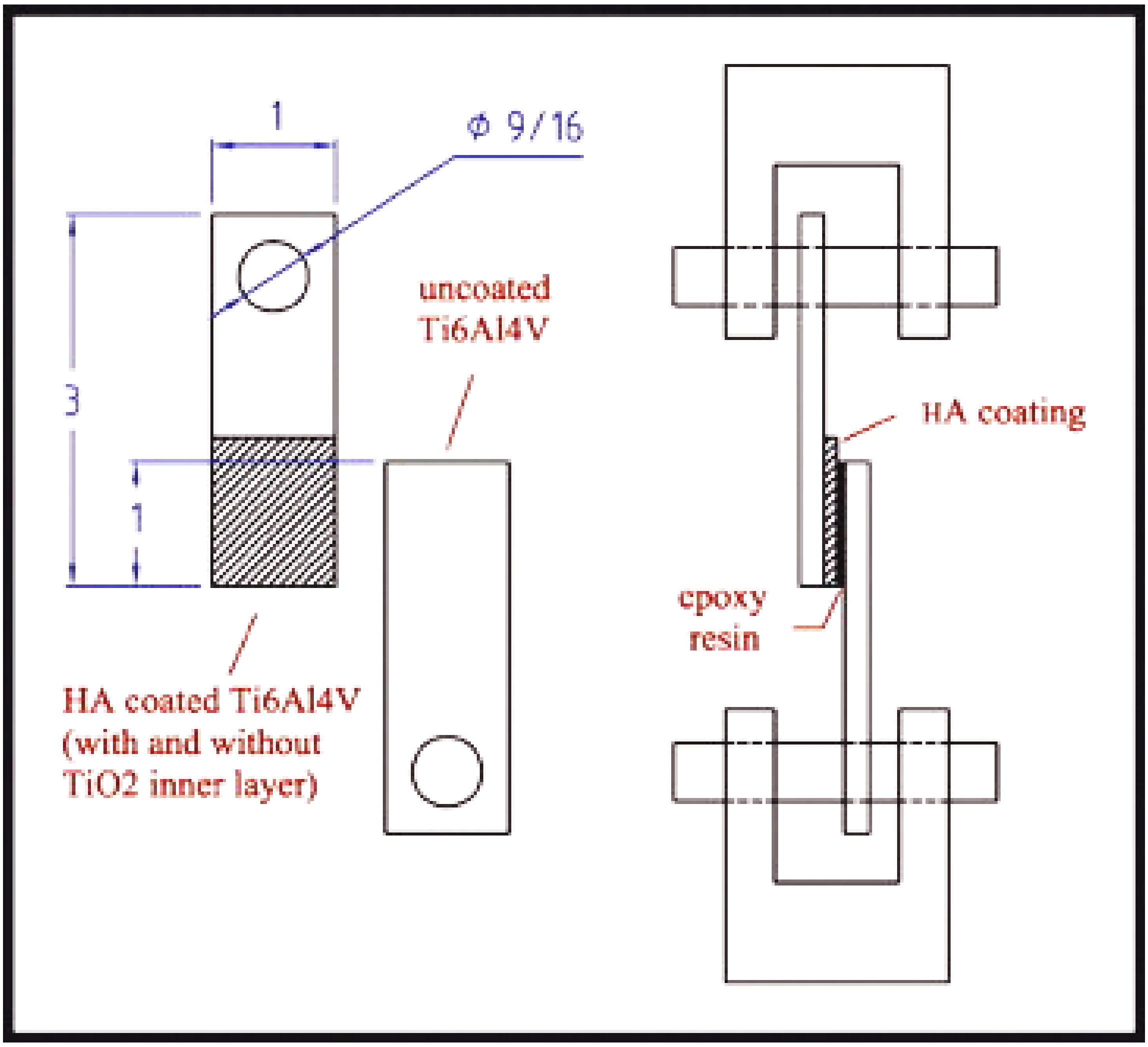

Fig. 1. Schematic diagram of the mechanical testing apparatus and samples (1 unit=1 in=25.40 mm) [11].

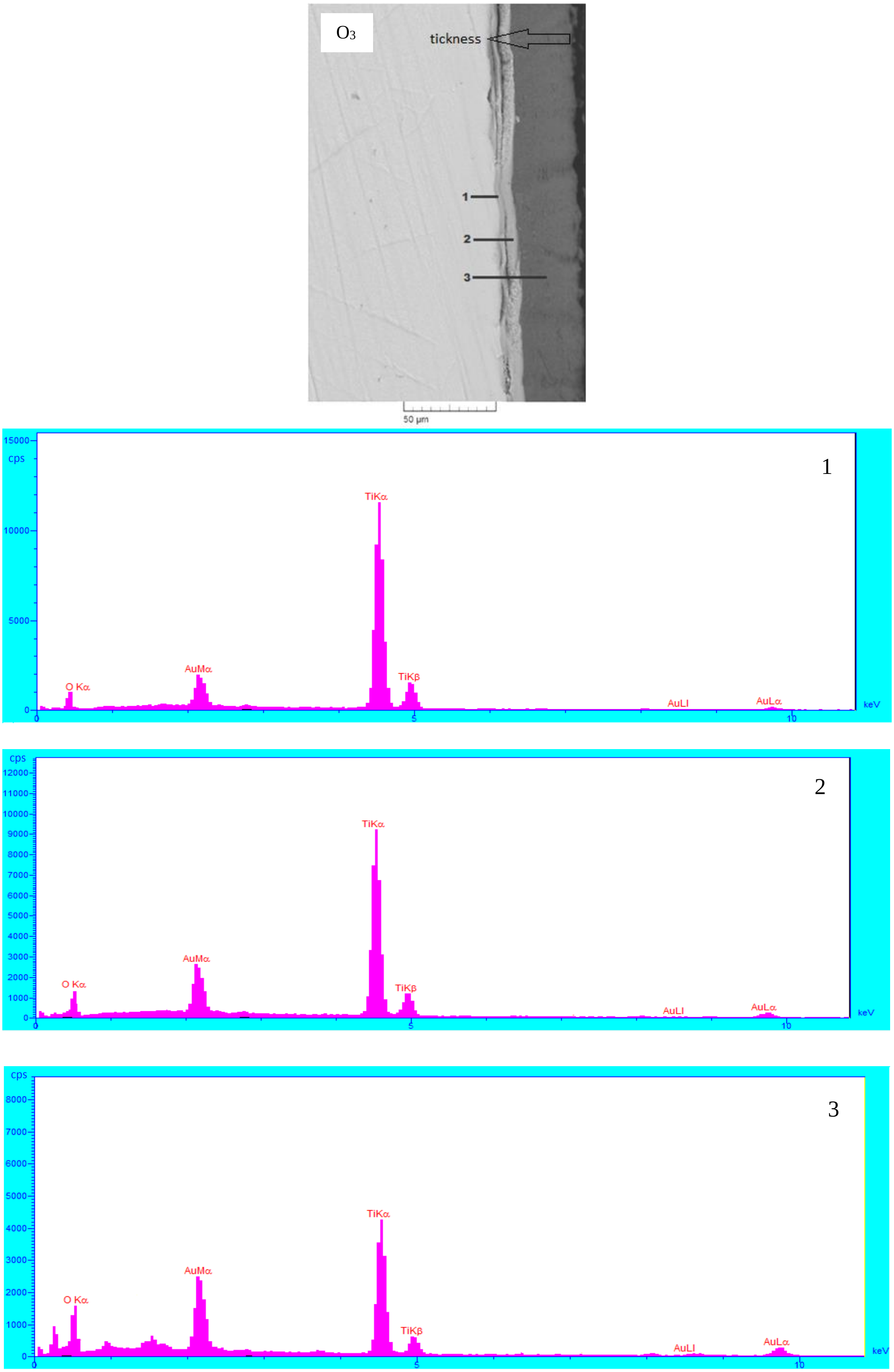

Fig. 2. SEM and EDS of O_3, that heat treated at 750°C and 90 min.

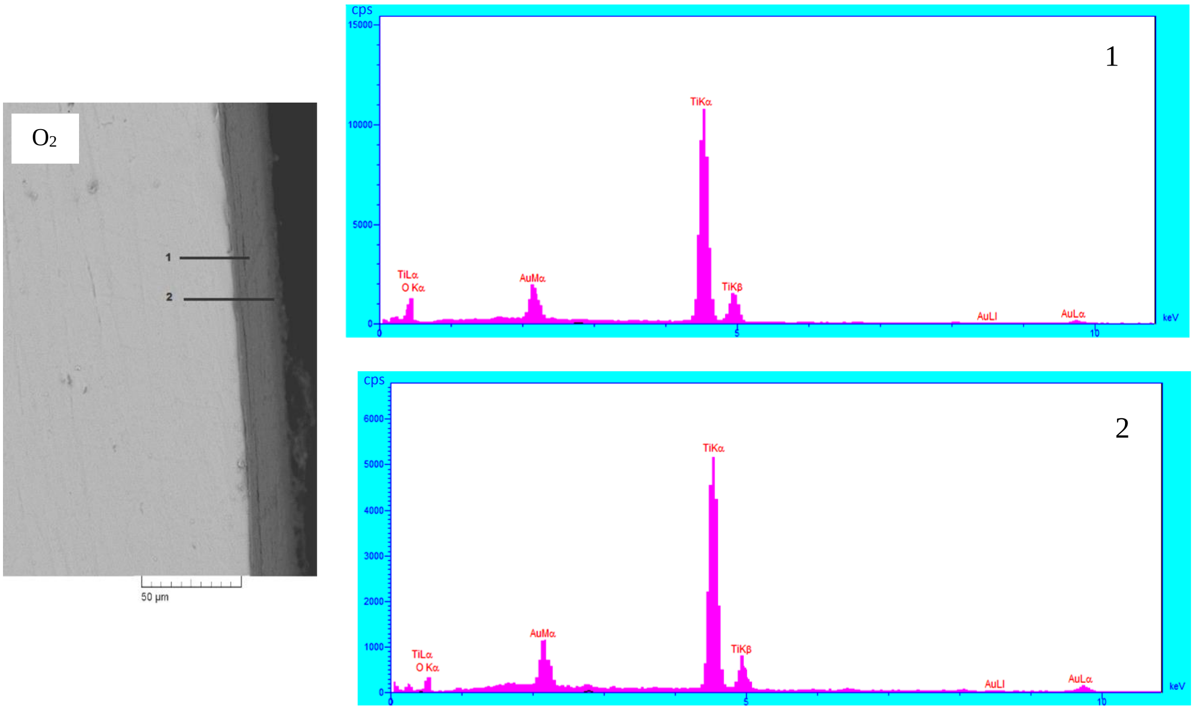

Fig. 3. SEM and EDS of O_2, that heat treated at 750˚C and 60 min.

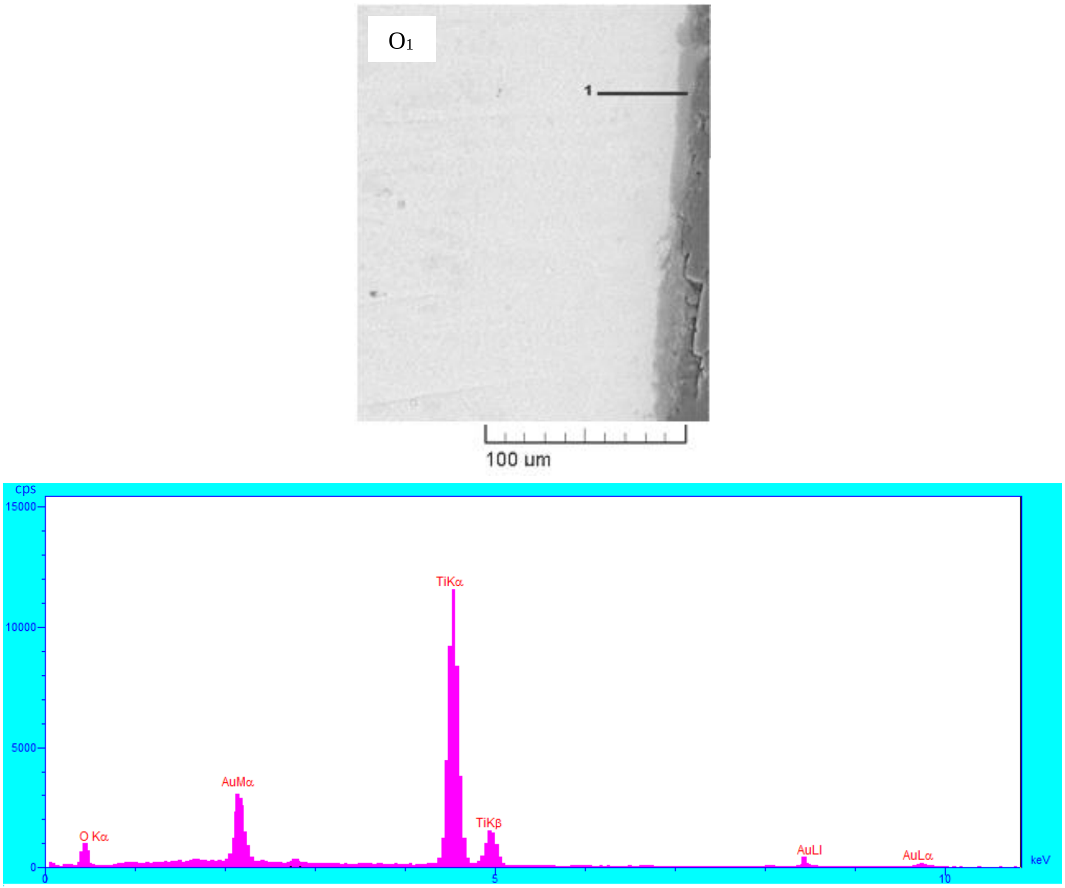

Fig. 4. SEM and EDS of O_1, that heat treated at 750˚C and 30 min.

Increasing in bonding strength of the glass ceramic coating, although was resulted from suitable bonding and reaction between interlayer and coating. Fig. 5. shows AFM results of titanium surface after (Fig. 5a) and before (Fig. 5b) oxidation process.
The heat treated surface appeared to be somewhat rough, possibly due to refinement of the microstructure [8-11].

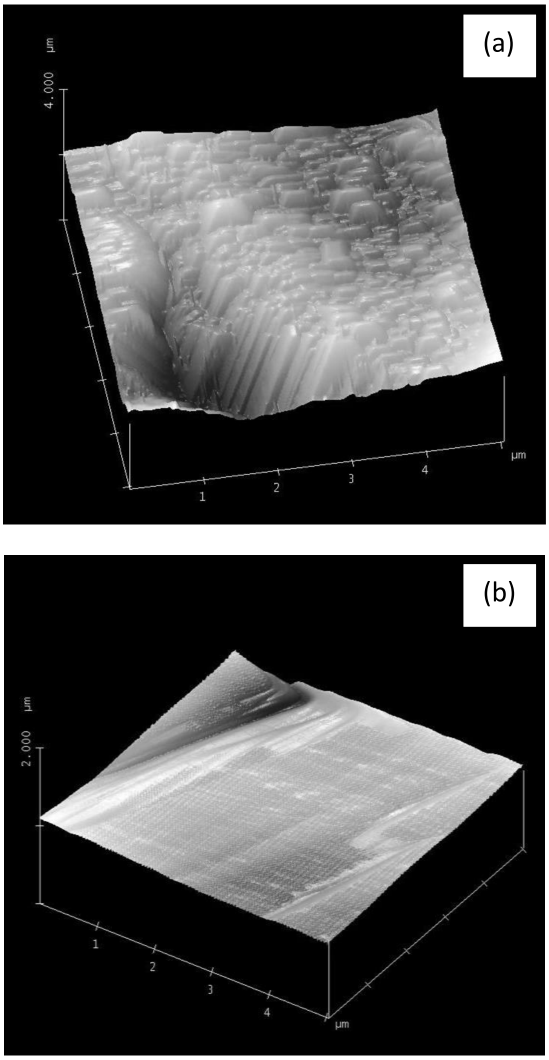

Fig. 5. AFM of titanium surface before and after oxidation. a) as-oxidized sample and b) grounded sample before oxidation

Before obtaining to chemical bonding, the surface roughness caused the formation of mechanical bonding in metal/glass ceramic systems and had positive effects on the increase in the bond strength [3].

3.2. Bond Strength

In this study, bonding strength of the samples that coating with phosphate base glass- ceramic, was measured using a shear stress method that modified ASTM F1044-99 [11]. The number of specimens for each subgroup was five. Table 1. represents the result of shear stress for each group of samples.

Table 1. Bonding strength of coating on different pre-heat treatment samples.

Sample code	Bond strength ±SD
Nonoxide layer	2.730± 0.353
O_1	8.296± 0.325
O_2	4.133± 0.436
O_3	3.397± 0.523

Although, the results show that bonding strength was increased in the samples that heat treated before coating of glass ceramic, but, observations indicate that with increasing the time of oxidation, bonding strength of the coating was decreased. It seems that, increasing the time of oxidation, adversely affected the bond strength and weakened the cohesion of coating, possibly due to the excessive thick layer of titanium oxide formed on the titanium surface. In addition, increase of oxygen caused the formation of the layer that has the poorly adherent and non-compact structure that was made the coating with not acceptable properties. [8]

3.3. Characterization of Titanium/ Glass Ceramic Interface

In general, the metal/ glass ceramic bonding is due to the mechanical interlocking between glass ceramic and metal and chemical bonding across the metal/ glass ceramic interface. Mechanically polished cross sectional morphologies of the sample O_1 that was coated with glass ceramic, are shown in Fig. 6. the glass ceramic appeared dense and well bonded to the substrate that was oxidized in 750˚C for 30 min. It could be induced that adherent oxide could be formed at this heat treatment condition. Observations indicate that good bonding was formed at the interface of glass ceramic and substrate and it is very hard to determine the intimate place of the interface of titanium/oxidized layer/glass ceramic coating.

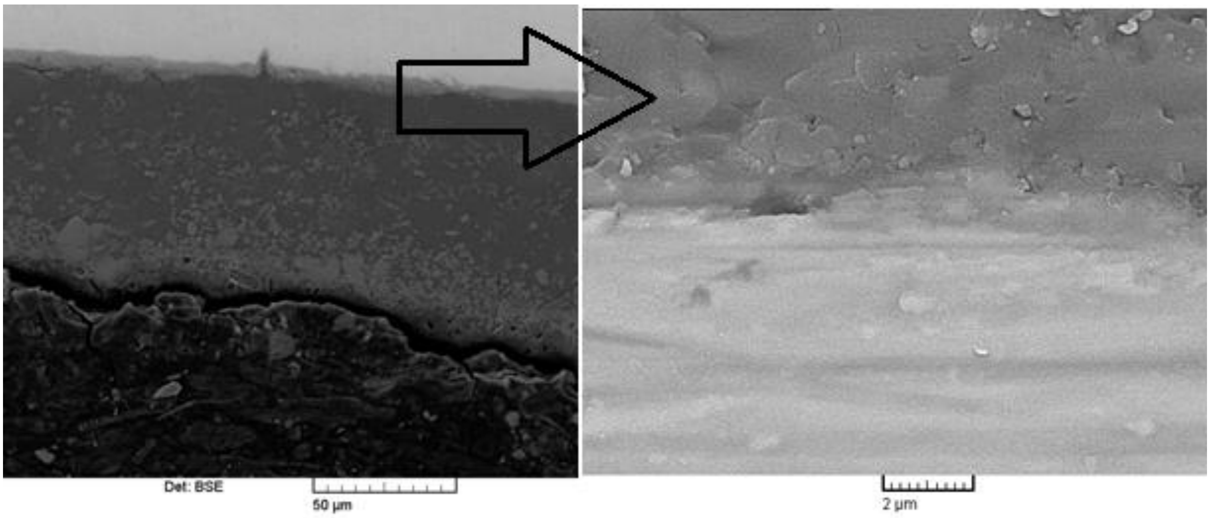

Fig. 6. The glass ceramic appeared dense and well bonded to the substrate that was oxidized in 750˚C for 30 min.

4. Conclusions

1. Pre-heat treatment of titanium in the air, affect titanium oxide formation and result in higher titanium / glass ceramic bond strength. SEM and EDS revealed that increasing the period of pre-heating, decrease the bonding strength of oxidized layer.
2. A pre-oxidizing process at the temperature of 750˚C for 30 min could achieve the significantly higher bond strength in comparing with another heat treatment process and fracture analysis demonstrated that considerable amount of glass ceramic remained on the titanium surface.
3. The titanium specimens pre-heat treated at an appropriate temperature may form a dense, protective, adherent oxide layer on surface that provides the ability to resist fracture.

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