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EFFECT OF TiO_2 ADDITION ON BONDING STRENGTH OF $CaO-P_2O_5-Na_2O-TiO_2$ BIOACTIVE GLASS CERAMIC COATING

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Abstract: *The effect of titanium dioxide addition on bonding strength of $CaO-P_2O_5-Na_2O-TiO_2$ glass-ceramic system was investigated as a coating on titanium substrate. Thus, different amounts of TiO_2 (2, 3.5 and 5mol %) were added to the base glass batch composition. The prepared glaze slips were applied on the substrate by dip coating method, dried and then heat treated at various temperatures. After that, bonding strength of the glass- substrates was determined via shear stress testing method. The de-bonded interfaces were analyzed by scanning electron microscopy (SEM). According to these results, the 5 mol% TiO_2 containing coating showed the best bonding strength, comparing with the other coatings. The bioactivity of the coated samples was investigated by soaking them in simulated body fluid (SBF). The surface of the samples was studied using SEM and X-Ray microprobe and it was observed that an apatite layer was grown on their surface.*

Keywords: *Titanium, Bioactive Coating, Bonding Strength.*

1. INTRODUCTION

Pure titanium and titanium base alloys are widely used in several fields of bone substitution due to their good biocompatibility and mechanical properties, high strength to weight ratio, low density, and corrosion resistance [1- 3]. Many kinds of prosthetic implants have been developed for both orthopedic and dental applications. But it's well known that, when implanted, titanium and titanium alloys do not bond with the bone by a chemical or biological interaction, but simply by morphological connection to it [2 - 4]. Insufficient adhesion to the bone, due to the 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 [5, 6]. In this regard, several glass and glass-ceramic materials are bioactive and are able to induce a biological bonding with both soft and hard tissues [7, 8]. Titanium alloys can be coated by these materials. The resulted composite can offer several advantages, in terms of the high mechanical properties of the metallic substrate combined with the bioactivity of its coating, if the glass and/or glass-ceramic coating strongly bond to titanium substrate [7, 8, 9,10].

In this work, effect of various amounts of TiO_2 on bonding strength of P_2O_5-CaO-Na_2O-TiO_2 glass system to titanium substrate was investigated.

2. MATERIALS AND METHODS

The prepared nominal glass compositions are shown in table 1.

The starting materials which consist of pure (>99 wt.%) $CaCO_3$, Na_2CO_3, TiO_2, P_2O_5 were completely mixed with each other and then melted in an alumina crucible at 1100°C for 0.5 h. The melt was fritted by pouring between the rotating stainless steel rollers. Then, the fritted glasses were pulverized to the size of less than 53µm by using a planetary rapid mill. After that, the glass powder was mixed with ethanol to make slurry.

Then, commercial pure titanium was cut to the dimension of 25 × 75 × 0.5 mm and mechanically polished with 60 grit wet emery paper for roughening of its surface. The roughened

Table 1. The nominal composition of bioactive glasses

Sample name	Nominal glass composition (mol %)			
	P_2O_5	CaO	Na_2O	TiO_2
G1	47	30.5	20.5	2
G2	47	30.5	19	3.5
G3	47	30.5	17.5	5

substrates were then rinsed ultrasonically in acetone for 60 min. After that, the specimens were cleaned in distilled water for 30 min, and then dried in the oven. Prior to applying the glass coating, the specimens were oxidized in air atmosphere, at temperature 750 °C for 30 min and a heating rate of 10 °C/min. The specimens were then cooled in the kiln naturally to room temperature. Finally, they were immersed into the prepared slurry at a speed of 1.4 mm/s, dried at 100 °C and heat-treated at temperatures 750 °C and 800 °C,separeatly, for 1h and were cooled slowly to room temperature within the furnace.

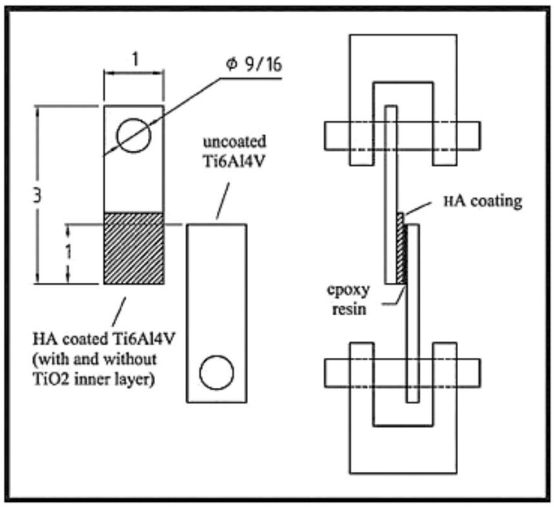

Fig. 1. Schematic diagram of the mechanical testing apparatus and samples (1 unit=1 in=25.40 mm) [11].

The precipitated crystalline phase in the glass coating layer was examined by X-ray diffraction (XRD, Jeol JDX-8030) and their microstructures were investigated by scanning electron microscopy (SEM, Cambridge – S 360).

The bonding strength of the glass ceramic coatings was measured using a modified shear stress method of ASTM F1044-99 [11]. The schematic drawing of the mechanical testing apparatus and samples are given in fig. 1.

To investigate the bioactivity of the resulted glass-ceramic coatings, the optimum one was soaked in SBF solution for 7 and 14 days at 37 °C, respectively. After that, the surface was examined by microprobe analysis and observed by SEM.

3. RESULTS AND DISCUSSIONS

As it was mentioned previously, the adhesive strength of the coating layer was examined quantitatively by using shear test. The results showed that the glass ceramic coating layers obtained by heating at 750°C were easily peeled off indicated a weak bonding had been existed between the glass layer and the substrate. However, the layers obtained by heating at 800°C showed conversely a strong bonding and did not easily fail and peeling off.

The shear bonding strengths of various coating layers are shown in table 2. Based on these results, the shear bonding strength has been increased with increasing of TiO_2.

Table 2. Mean and standard deviation (SD) of bond strength values

Sample	Bond strength ± SD (MPa)
Ti/G_1	7.95±0.3143
Ti/G_2	11.09333±0.585748
Ti/G_3	12.79667±0.433628

Fig. 2 shows the SEM micrographs of various substrates- coating interfaces, fractured by applying of shear test. The remaining coating is obviously increased with increasing the amount of TiO_2 in the glass. It is important to note that residual glass ceramic adhere to the titanium surface after fracture, as shown in fig. 2, indicating a mixed mode of cohesive and interfacial fractures. The cohesive fracture was possibly due to separation of the ceramic material from the substrate, while the interfacial fracture was due to exfoliation of the glass ceramic coating from the oxide layer bonded to the substrate and/or de-bonding of the oxide layer of the titanium substrate.

Fig. 3 shows the cross sectional view of titanium substrate- coating G3 interface. It is hard to determine the definite separated layer in the interface of titanium and glass ceramic around the substrate, the partial melting of glass and produced crystals, were contacted with a thin oxide layer formed with pre heated process, resulting in the fine glass ceramic/ metal joining.

Improvement of bonding strength of the substrate-coating layer, which was observed with increasing the amount of TiO_2 in the glass layer,

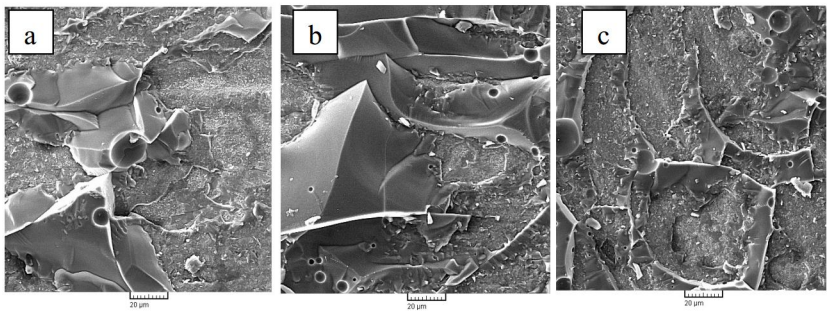

Fig. 2. SEM fracture photograph of the surface of titanium substrate after shear test .a) sample Ti/G_1, b) sample Ti/G_2, c) sample Ti/G_3.

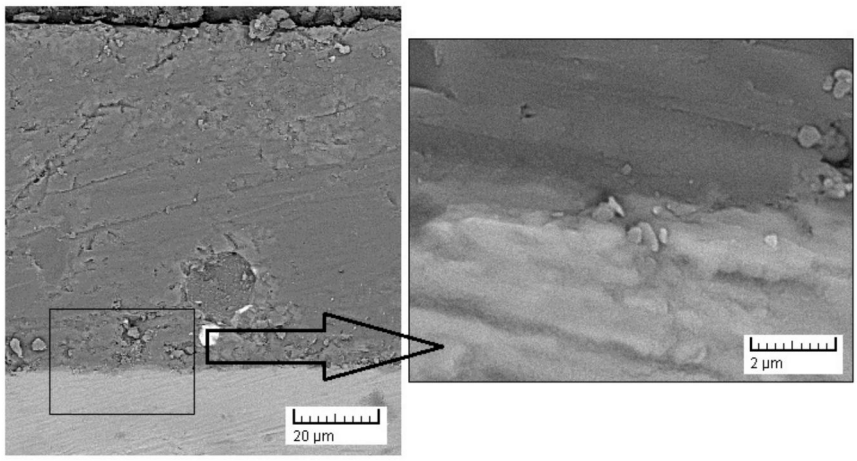

Fig. 3. SEM micrograph of mechanically polished cross section of the titanium/ glass ceramic system.

Table 3. coefficient of thermal expansion of some oxides [14]

Oxide	Thermal expansion coefficient(1/°C)
CaO	5.0×10^{-7}
P_2O_5	2.0×10^{-7}
Na_2O	10.0×10^{-7}
TiO_2	4.1×10^{-7}

may have different reasons. The thermal expansion of glass ceramics G_1 and G_3 that were prepared by heating at 800°C was measured by dilatometric method. Thermal expansions of them were 12.1783×10^{-6} °C $^{-1}$ and 11.7441×10^{-6}°C $^{-1}$, respectively. The thermal expansion of titanium substrate metal is between 9.6×10^{-6} °C^{-1} and 10.6×10^{-6} °C^{-1} [7] and interlayer TiO_2 is about 8.16×10^{-6} °C^{-1}[13]. Since the thermal expansions of the used coatings are larger than titanium substrate, it is possible that the coatings experience crazing during cooling. Small amount addition of titanium dioxide will improve the crazing resistant and decrease the thermal expansion coefficient of the coating layer. On the other hand, addition of sodium oxide in a glass will increase its thermal expansion coefficient (Table 3) [14,15]. Therefore, it should be concluded that substituting of Na_2O by an equal amount of TiO_2, could improve the crack resistance of the coating.

Fig. 4 shows the line scan chemical analysis of the cross sectional view of the glazed specimen. As it can be seen there exists a compositionally gradient zone of ≈5μm in thickness between the glass-ceramic layer and the substrate. Accordingly, the titanium amount decreases with increasing the distance from the substrate. Calcium, sodium and phosphor amounts show an opposite trend and their amounts increase with moving out from the substrate. These compositional changes make an interfacial layer, with an intermediate thermal expansion which will decrease the thermal expansion mismatch of substrate and coating parts

In addition, TiO_2 can increase the young's and shear modules and also the mechanical strength of the glass coating. It is believed that titanium ions are able to form structural units of TiO_5 or TiO_4 group and strengthening the glass network when its amounts reach to 0.5%mol. An initial

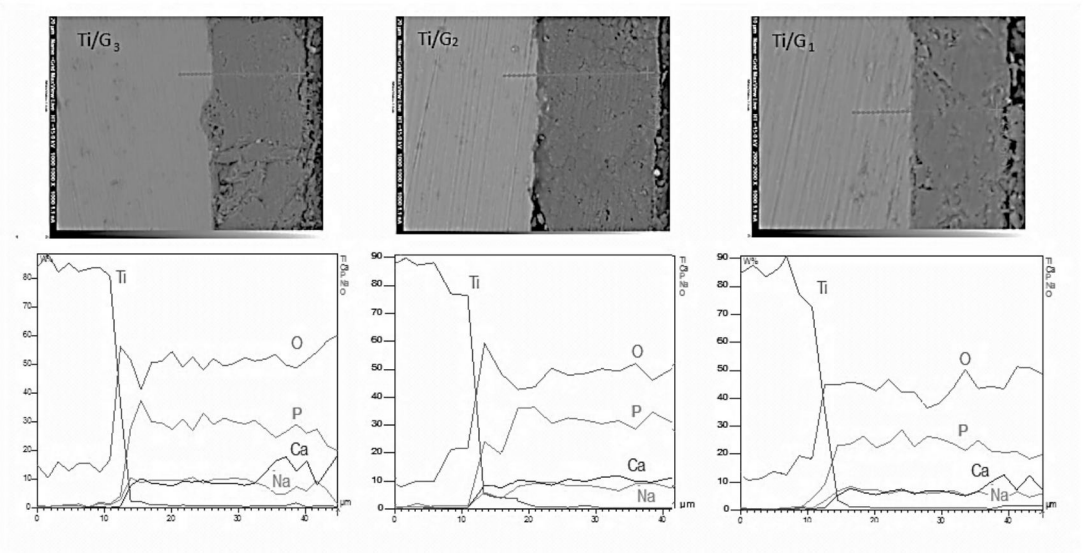

Fig. 4. Elemental concentration analysis by EDS along the indicated line in SEM photo.

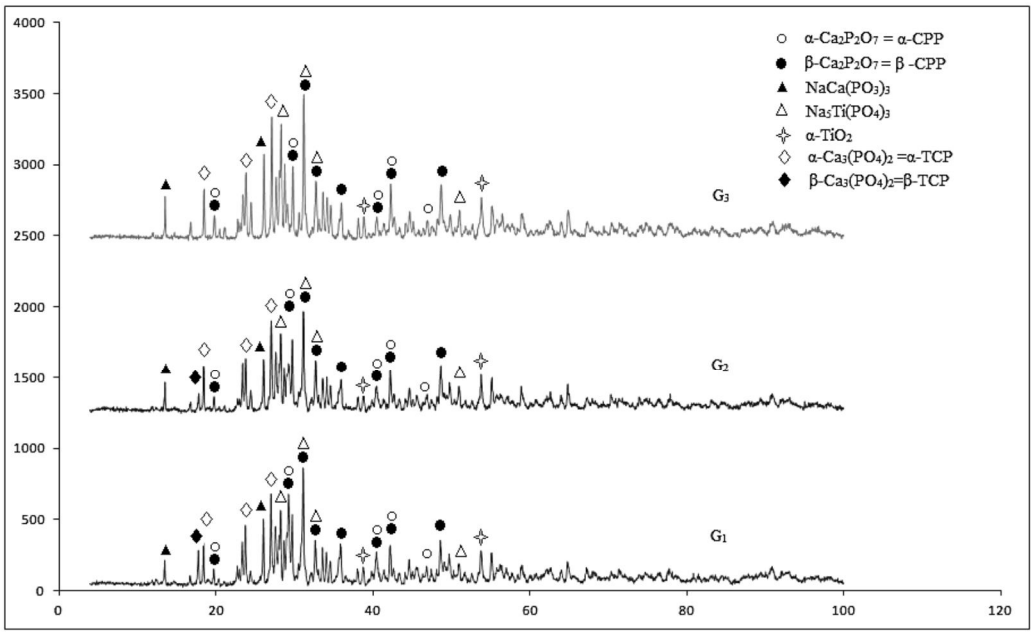

Fig. 5. XRD pattern of the glass ceramic after heat treatment.

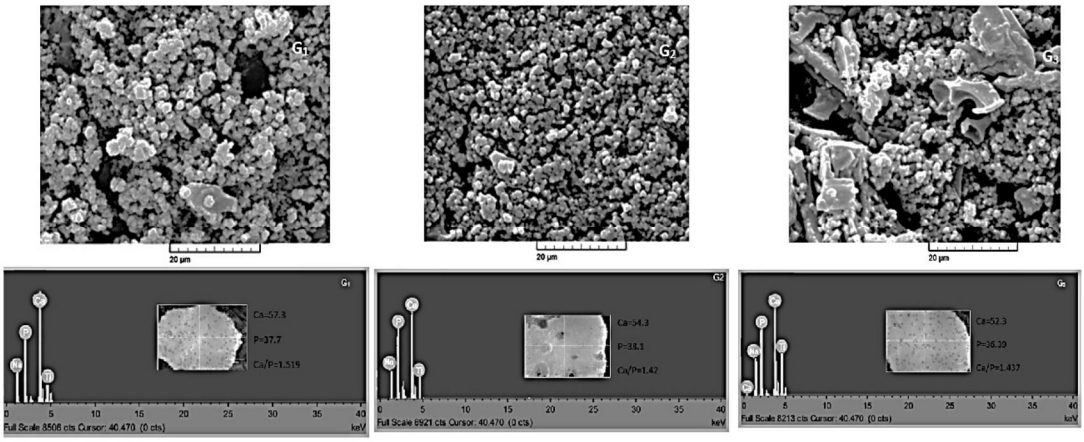

Fig. 6. SEM and microprobe analysis of the glass ceramic coatings surface after 10 days.

introduction of the intermediate oxides, namely TiO_2, leads to breaking of P-O-P bonds phosphate network and formation of terminal oxygens [16, 17]. Thus, the Ti^{+4} ions are connected to PO_4 tetrahedral through non bridging oxygens (NBO). Further addition of TiO_2 leads to creation of ionic cross linking between non bridging oxygens of two different chains; thereby reinforcing the glass structure and affects the mechanical strength of the coating. The metallic ions with small ionic radius and high electrical charge contribute to formation of stronger P-O-M bonds in the P_2O_5-CaO-Na_2O-MO glass system. Several modifying ions such as (M) Fe^{3+}, Al^{3+}, Zn^{2+} and Ti^{4+} have been used for reinforcement of the glass system. Among them Ti^{4+} has been found to be very effective in this regard [16].

Fig. 5 shows the XRD pattern of the glass

ceramic after heat treatment. Based on the result, $Ca_2P_2O_7$ (CPP) and $Ca_3(PO_4)_2$ (TCP) have been precipitated during heat-treatment in the glass layer.

The concentration of the elements was analyzed using X-Ray microprobe (EPMA). Fig.6 shows the SEM photograph of the coating and the electron probe micro analysis (EPMA) of the glass-ceramic surface after soaking in SBF.

According to EPMA, new phase or phases has or have precipitated on the glass surface layer during the soaking into SBF, which its Ca/P ratio is about 1.4 to 1.5 [18]. This precipitant is considered to be calcium phosphate phase such as HA. Therefore, it can be considered the glass-ceramic layer as a bioactive layer which can be used in a living body.

4. CONCLUSIONS

It was found that bonding strength of calcium phosphate glass ceramic - titanium substrate could be increased with increasing of its TiO_2. The interfacial layer was strong as a compositionally gradient layer was developed automatically on the substrate during the heating procedure. In the other hand, increasing the amount of TiO_2 within the glass was strengthened the structure of glass ceramic and increased the force that is needed for fracture of glass ceramic coating. TCP and CPP phases were precipitated in the glass ceramic coating layer. During soaking in SBF, HA was precipitated on the surface of the coating. This phenomenon makes the use of titanium, as a bioactive specimen, in living body possible.

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