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The effect of bond coat on mechanical properties of plasma sprayed bioglass-titanium coatings

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Abstract

Bioglass, known as 45S5 (45% SiO_2, 6% P_2O_5, 24.5% CaO and 24.5% Na_2O all in weight percent), was plasma sprayed onto a titanium substrate with and without Amdry 6250 (60% Al_2O_3 40% TiO_2) as bond coating layer. Mechanical properties were evaluated in accordance with the ASTM C633 method and scanning electron microscopy was used for the microstructural characterization. Results indicated that it is possible to coat bioglass on titanium substrate by utilizing similar conditions used for hydroxyapatite. Application of bond coat layer in the plasma spraying of (45S5) bioglass on titanium substrate has increased the bonding strength about three times. The adhesive bonding observed at the bioglass metal interface turned into cohesive bonding by application of the bond coating layer. It has been observed that there is a uniform coating layer with a thickness of 110 and 80 μm depending on coating type with a little amount of porosity.

Keywords: Bioglass; Plasma spray coating; Bond coat layer; Titanium

1. Introduction

Bioglasses are silicate glasses containing sodium, calcium and phosphate as main components [1]. Although having excellent bioactivity performance, the mechanical properties of bioactive glasses are not enough to be used for load-bearing applications due to their limited content of network formers. This problem can be solved by combining glass with a tougher phase such as metal or polymer to produce a composite or coating on a surface [2]. For this purpose various coating techniques have been introduced such as dip coating, electrophoretic deposition, hot isostatic pressing, flame spraying and plasma spraying [3]. Chern et al determined mechanical properties of bioglass and bioglass–HA (50–50%) coatings. ASTM C633-79 adhesion test which is designed to characterize plasma sprayed coatings specifically were used and the results were compared to HA coatings. The bonding strength was found to be 33.0±4.3, 39.1±5.0, 52.0±11.7 MPa for bioglass, bioglass–HA and HA coatings respectively [4]. In another research by Ding et al., bioglasses basically containing SiO_2, Na_2O, CaO and P_2O_5 studied for the plasma spray application. Bioglass composition has been mixed to 5–25 wt.% HA powder and then coating was subjected to ASTM C633-79. The bonding strength values were varied between 49.6 and 63.6 MPa. The highest bond strength was obtained with the monolithic HA (63.6 MPa). It was observed that the glass addition to HA decreased the bonding strength [5]. Coating of bioactive glass powder on different substrate such as Ti6Al4V core implants and standard ASTM test samples were also carried out by Schrooten et al. The purpose was to develop a bioactive glass coated dental implant by an economically feasible technique called reactive plasma spraying [6].

Bond coatings are already used widely in many industrial plasma spray applications. They have specific functions; because the substrate and the main coating have different coefficients of thermal expansion, bond coating layer should be used to provide a good thermal expansion match between these two different layer [7–9]; on the other hand, bond coating layers are always thinner than the main coatings. Bond coating applications for developing mechanical properties of bioglass coating

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are very limited. In one of the studies, a layer of titanium was used as bond coat on which glass powders with particle size ranging from 45 to 125 μm were applied. The pure Ti bond coat was used to ensure adherence between the substrate and the bioactive glass top coating. It has been reported that after the plasma-spraying process, the bioactive glass coating had preserved the amorphous structure without the formation of a crystalline phase 10.

The purpose of this study was to find out the effect of bond coat application on mechanical properties and microstructural characteristics of bioglass plasma-sprayed coating on titanium.

2. Materials and method

2.1. Preparation of glass and plasma spray coating procedure

Bioglass, known as 45S5 (45% SiO_2, 6% P_2O_5, 24.5% CaO and 24.5% Na_2O all in weight percent) was prepared by melting in Heraeus K1700/I high temperature oven at 1400–1450–1500 °C for 4 h and then quenched in water to produce a powder form. Wet chemical analysis has been carried out to determine composition of glass depending on remelting temperature (Table 1). It was observed that chemical composition is similar to that in literature for all remelting temperature [2] and no alkali losses occurred specifically at high temperature experiments.

Powders produced were subjected to grinding by blade milling to produce suitable particle size for plasma spray applications, the size distribution of particles, after milling are given in Table 2. Scanning electron microscopy studies showed that the particles have sharp cornered morphology (Fig. 1). The powder used for bond coating was commercial Amdry 6250 (60 wt.% Al_2O_3–40 wt.% TiO_2, particle size 25 + 5 μm), hardened pure titanium (IMI Titanium Ltd, USA, R_a = 19 ± 0.3 μm) was used as substrate suggested by ASTM F67-89 6RZ.

For producing bioglass coating without bond layer, powder fraction between −212 and 63 μm was plasma sprayed directly on sand blasted and cleaned titanium substrates. In the second stage, which is the coating of bioglass on bond layer; Al_2O_3 TiO_2 powder was plasma sprayed on sand blasted and cleaned titanium substrates and then bioglass was sprayed by employing similar conditions as in coating without bond layer. The plasma spray process parameters were similar to hydroxyapatite coating procedure stated in the literature (Table 3) [11]. It has been observed that bioglass powder fraction used in the coating process showed better flowing characteristics than the HA powders coated under the same conditions [12].

3. Microstructural characterization

Microstructural characterization was carried out by Jeol JSM T330 scanning electron microscope. Secondary electron image was used to evaluate coating surface. Characteristic plasma coating microstructure was observed on both coating surfaces (Fig. 2). Cross sectional investigation of coating were carried out as follows: (a) Bioglass–substrate interface by back-scattered electron image; a homogeneous coating layer were

Table 1
Sieve analysis results of bioglass powders

+355 μm	−355 + 300 μm	−300 + 212 μm	−212 + 150 μm	−150 + 63 μm	−63 + 38 μm	−38 + pan
1.4%	19.1%	23.9%	19.6%	23.4%	11.2%	1.4%

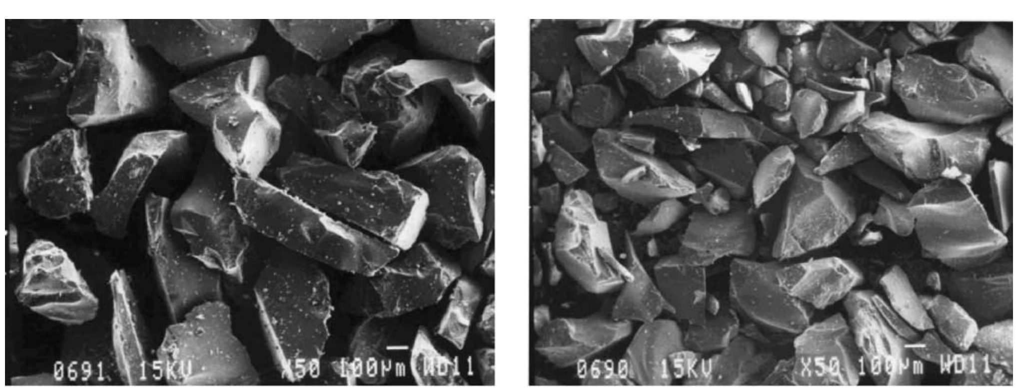

Fig. 1. Scanning electron microscopy images of bioglass powders after blade milling (600×).

observed at the thickness of 110 μm (Fig. 2). (b) Bio-glass–bond coating-substrate interface by back-scattered electron image; an approximate thickness of 20 μm bond coating and 80 μm bioglass coating layer were observed (Fig. 3). The presence of a reaction zone between substrate-glass and substrate-bond coating–glass coating interface was not detected (Figs. 3 and 4). However, this point needs further elucidation by employing more sensitive surface analytical technique. On the other hand little amount of porosity were observed for both type of coatings.

Surface roughness values of metal surface, bond coating and main coatings were determined by using surface roughness measurement unit perthometer. Average surface roughness values (R_a) of metal, bond coating layer, bioglass on bond coating and bioglass without bond coating were detected as 7.48±0.3, 9.05±0.3, 9.92±0.6 and 12.79±1.0 μm, respectively. The effect of surface roughness values on mechanical properties is mentioned in the discussion.

3.1. Mechanical characterization

Bonding strengths of the Ti substrate–bioglass and Ti substrate-bond coating–bioglass interfaces were tested using adhesion test ASTM C-633. All tests were carried out by using an Instron universal testing machine under ambient conditions with a cross head speed of 1 mm/min. Bisphenol A-Epichlorhidrinharze was used as glue. Adhesive and cohesive failures surface at the bioglass–titanium and bioglass-bond coating–titanium interfaces were evaluated by scanning electron microscopy. The bonding type of coating was determined by the measurement of the separation percents of coating on surface using milimetric paper.

Table 2
Wet chemical analysis of bioglass powders (wt.%)

Temperature (°C)	Na_2O	SiO_2	P_2O_5	CaO
1400	25.01	45.90	5.07	24.02
1450	25.13	45.42	5.40	24.04
1500	26.43	46.97	5.56	20.47

Table 3
Plasma spraying process parameters

Parameters	Standard setting
Injector nozzle diameter (mm)	1.5
Injector distance (mm)	6
Injector angle (degree)	90
Plasma spraying distance (mm)	75
Speed of rotation of substrate surface (m/s)	15.5–19.0
Speed of torch movement (m/s)	–
Current (A)	500
Voltage (V)	70
Primary gas	Argon
Primary flow	80 W
Flow rate (1/min)	15.5
Secondary gas	Nitrogen
Secondary flow	40 W
Flow rate (1/min)	12
Carrier gas	Argon
Flow rate (1/min)	4.5

Table 4
Bonding strengths of the coated samples according to ASTM C-633

Sample no.	Bonding strength (MPa)	
	Bioglass + bond coating	Bioglass
1	24.10	9.42
2	27.13	8.10
3	27.37	8.76
4	26.84	7.97
5	30.42	8.53
Average	27.18±2.24	8.56±0.57

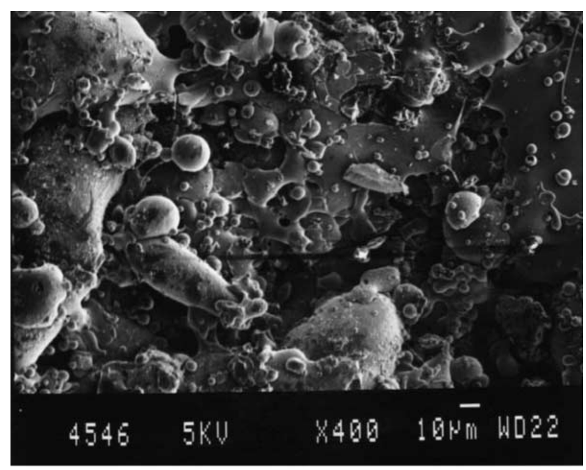

Fig. 2. Scanning electron microscopy image of bioglass–titanium coating surface.

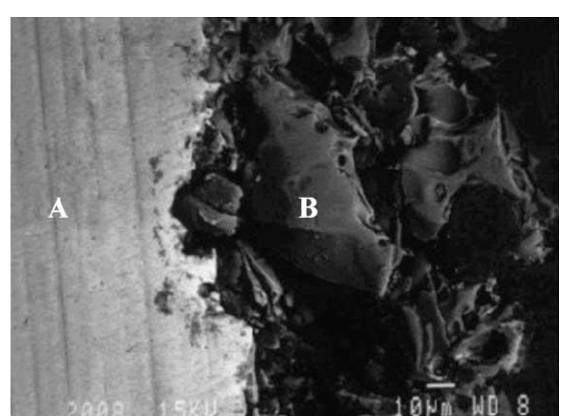

Fig. 3. Scanning electron microscopy image of substrate (A) substrate; (B) bioglass coating interface (600×).

The bonding strength values of the samples with respect to direct coating on titanium and bond coating application are listed in Table 4. Statistical method, Kwikstat 4-Texasoft-1995 software was used and an independent group of a non-parametric cross comparison Mann–Whitney U test was applied. Statistical data showed that Z statistic for the Mann–Whitney U test was -3.576 and corresponding P-value equals 0.000 ($P<0.05$). Thus the differences are statistically significant.

4. Discussion

The results of this study revealed that hydroxyapatite-coating plasma spray parameters of Fazans (Table 3) were also suitable for bioglass coatings [10]. Microstructure of coating surface indicated the typical morphology of plasma sprayed samples (Fig. 2); composed of molten glassy coating, unmelted glass particles and small amount of porosity.

It is known that in plasma spray process, bond-coating layers are used under the main coating so that the coating has better mechanical properties. The bond coatings are always thinner than the main coatings (20 μm in this study, Fig. 3) and they fit into the grooves of the substrate metal by flowing during plasma spraying process. The main coating powder fits on leveled bond coat result in a good wetting between two layers. Finally it leads to better mechanical properties. The experimental results gained were in close agreement with this claim. Bioglass coating on a metal surface with the average surface roughness of 7.48 ± 0.3 μm and on bond coating layer with average roughness value of 9.05 ± 0.3 μm resulted in the average surface roughness values of 12.79 ± 1.0 and 9.92 ± 0.6 μm for direct coating on titanium substrate and coating on bond coat layer, respectively. Lower average surface roughness of bond coating layer containing samples compared to direct coatings is the indication of good wettening between two coating layer. It is also an expectation that smooth surface helps in increasing of cell differentiation [13].

In the literature, true bonding strength of plasma sprayed coatings is a manifestation of mixed cohesive (lamellar layer themselves) and adhesive (coating to substrate) strength. Therefore as the adhesive test ASTM C633 was employed, the results of bonding strength in situ were suggested to be governed by a number of factors; thickness of ceramic coating, the microstructure influencing the inter-lamellar cohesive strength of the coating, surface condition (roughness and cleanliness of the metal surface), glue type and coating characteristics. The bonding type of bioglass–titanium coating was determined as approximately 98.82% adhesive and 1.18% cohesive character, whereas bond coat containing samples showed 7.04% adhesive and 92.96% cohesive character. Microstructural characterization results by scanning electron microscopy were all in close agreement with the statistical results. Cohesive and adhesive failure of the coating were determined depending on the coating type. It was observed that failure occurred in the form of delamination on the main coating for bond coating samples (Fig. 5), whereas bioglass–titanium coatings showed failure between the glass–substrate interfaces with micro cracks (Fig. 6).

ASTM C-633 testing results regarding to bonding strength of the coated samples are given in Table 4. Results indicate that bond coating layer containing samples have average bonding strength of 27.18 ± 2.24 MPa, whereas directly bioglass (45S5) coated samples have average bonding strength of 8.56 ± 0.57 MPa which is only one third of the strength of the bond coated samples. Application of bond coating has a

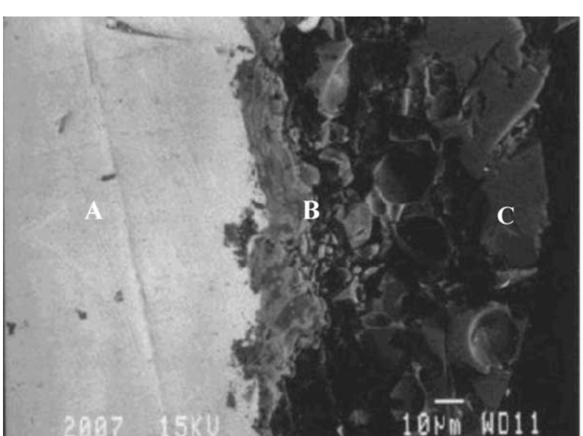

Fig. 4. Scanning electron microscopy images substrate (A) substrate; (B) bond coating; (C) bioglass interface (600×).

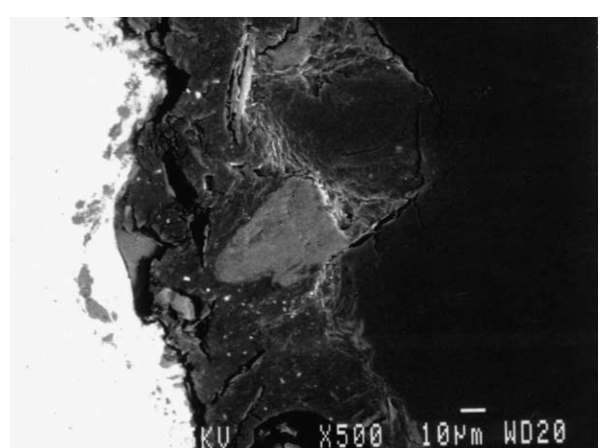

Fig. 5. Scanning electron microscopy image of failure cross-section for bioglass-bond coating–titanium coating (bonding strength: 30.42 MPa).

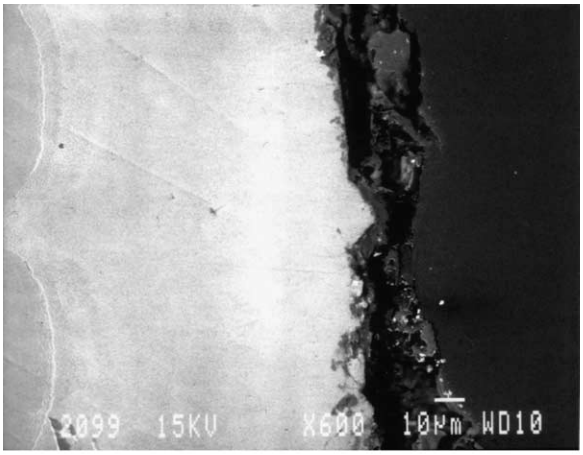

Fig. 6. Scanning electron microscopy image of failure cross section for bioglass on titanium (bonding strength: 7.97 MPa).

positive effect on mechanical performance of coatings, but it seems that even with improved values, bioglass coatings still show lower bonding strength than hydroxyapatite coatings [4,5]. The reason of low mechanical properties can be attributed to thermal expansion mismatch between the coating and the metal substrate which is 18×10^{-6} °C^{-1} for 45S5 up to 450 °C and 8.7×10^{-6} °C^{-1} for titanium up to 500 °C [2]. During plasma spraying the coefficient of thermal expansion mismatch between the coating and the metal substrate, coupled with the fast cooling rate of the coating material, gave rise to residual tensile stress in coating at the coating–substrate interface. This effect can result in cracking or delamination of coating from the substrate. Although relatively lower bonding strength of glass coatings over hydroxyapatite coatings seems as a disadvantage, superior properties of bioglasses such as bioactivity and preserving of amorphous structure at high temperature is a great advantage that are expected to result in better performance and long-term stability.

5. Conclusion

It is possible to coat bioglass on titanium substrate by utilizing present conditions which are being used for hydroxyapatite coating procedure. Application of Amdry 6250 (60 wt.% Al_2O_3 40 wt.% TiO_2) as bond coat in the plasma spraying of (45S5) bioglass on titanium substrate has increased the bonding strength about three times. Adhesive bonding characteristic observed at the bioglass–metal interface turned into a cohesive bonding characteristic by the application of a bond coat layer.

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