

BIOACTIVE SILICIUM-CONTAINING COATINGS ON TITANIUM SUBSTRATE

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Abstract

Two borate-silicate glasses were developed. They were applied to titanium substrate by an enameling method. To increase adhesion strength of the glass coating to the substrate, a titanium silicide interlayer was applied. Solubility of the glasses was studied and low solubility of both glasses in either distilled water or in an isotonic solution was revealed. The rupture tensile strength of the coating/substrate composite system was in the range from 15 to 20 MPa, being dependent on the glass composition.

Keywords: titanium, bioactive coating, glass

INTRODUCTION

Titanium and its alloys are commonly used for load-bearing implants because they possess good mechanical strength and excellent biocompatibility [1]. A drawback of these materials is that they do not bond directly to the bone tissue. To overcome this limitation, bioactive inorganic coatings are often applied to Ti orthopedic implants to promote osteointegration and to improve the stability of the implant/bone interface [2]. Such implants combine the mechanical strength and fracture toughness of the metal with the ability of the coating to present a bioactive surface to the surrounding tissue [2]. One of the most widely used coating methods is the high-temperature plasma-spraying technique [3]. Despite the enhanced osteointegration, there are problems associated with plasma-sprayed bioactive coatings on Ti implants. The high temperature plasma spray process can cause changes in structure, crystallinity and phase composition of the coating material, poor adherence of the coating to substrate. Apart from this, to apply these techniques special high-value equipment is required [3]. Many other techniques have been explored to address these problems, including ion-beam deposition, chemical deposition, metallo-organic chemical vapour deposition, derivation from sol-gels, pulsed laser deposition, and electrophoresis [3, 4, 5]. An alternative of these methods can be the more available enameling technique [6, 7]. However, the ability of Ti to form poor adherent surface suboxide films turn the creation of Ti implants with ceramic or glass bioactive inorganic coating into a complex technological problem [6, 8]. The present work was aimed at the development of enameling method for coating on Ti substrate. A direct ceramic application on the Ti substrate is impossible because of the difference in the thermal expansion coefficients of hydroxyapatite and Ti or its alloys [9]. Therefore, we developed two borate-silicate based glass compositions, designated V and N, having the theoretical value of the thermal expansion coefficient close to Ti and possessing good adherence to the Ti substrate.

To prevent its oxidation, the Ti substrate was treated by metallic silicium resulting in titanium silicide formation.

EXPERIMENTAL

Ti₅Si₃ layer

For applying titanium silicide (Ti₅Si₃) layer, a commercially pure metallic silicium (Si) powder was used. Plates (15 mm x 15 mm x 2mm) of commercially pure Ti were polished followed by cleaning in alcohol, acetone, and after that, in distilled water. Si was applied on Ti plates' surface by mechanical method at room temperature. Then plates were heat-treated in air at 850°C. To study interactions in the system, a model experiment was performed. Pure Ti powder was mixed with Si powder in an equal volume ratio. The mixture was pressed into cylinders of 10 mm height and 5 mm diameter under a pressure of 100 MPa and sintered at different temperatures. Model samples were studied by powder X-ray diffraction (XRD, Shimadzu XRD – 6000 diffractometer).

Glass layer

Molar compositions of the N and V borate-silicated based glasses were as follows: 2% CaO – 7.75% Na₂O – 39.2% B₂O₃ – 7.25% SiO₂ – 1.9% Al₂O₃ – 2.45% P₂O₅ – 2.25% K₂O and 35.0% CaO – 12.5% Na₂O – 41.5% B₂O₃ – 6.5% SiO₂ – 3.5% Al₂O₃ – 1.0% P₂O₅ respectively. To prepare the glasses, reagent grade raw materials were batched in proportions, mixed extensively, and melted in alumina crucibles in an air atmosphere at 900 – 950°C to form a homogeneous melt. Then the glasses were milled in ethanol using a planetary-type mill and dried. Size of glass particles was less than 35 µm.

The thermal expansion coefficients were theoretically calculated by an additivity method for both glass compositions. The wetting angle was measured. For this purpose the glass discs (3 mm height, 5 mm diameter) were pressed, situated on Ti substrates with a Ti₅Si₃ layer and sintered at 750°C in air. The wetting angle was calculated according to formula:

$$\cos \theta = ((0.5 d)^2 - h^2) * ((0.5 d)^2 + h^2)^{-1} \quad (1)$$

where d is glass drop diameter, h is glass drop height.

The glass solubility was studied in distilled water and in physiological solution (0,9% NaCl) at 37°C. Glasses were soaked for 45 days in liquids. The measurements were detected by ionometer Expert-001 with using Ca²⁺-selective electrode Elit-041.

Glass was applied on Ti substrate over the first layer using an organic solvent-based suspension by dip method. Then the coating was fired at 700 – 750°C. The coatings were then examined by scanning electron microscopy (LEO 1420). The mechanical tests on the substrate-coating rupture were performed using a tensile testing machine INSTRON 5581. The glass coating was applied between two Ti cylinders (20 mm height, 10 mm diameter) over Ti₅Si₃ layers.

RESULTS AND DISCUSSION

Ti₅Si₃ layer

The XRD pattern (Fig.1) of Ti-Si model samples showed that the interaction between components started at a temperature above 800°C (line 4) resulting in the formation of Ti₅Si₃ and of Si disappearing. At temperatures below 800°C Ti and Si do not interact (lines 1 – 3).

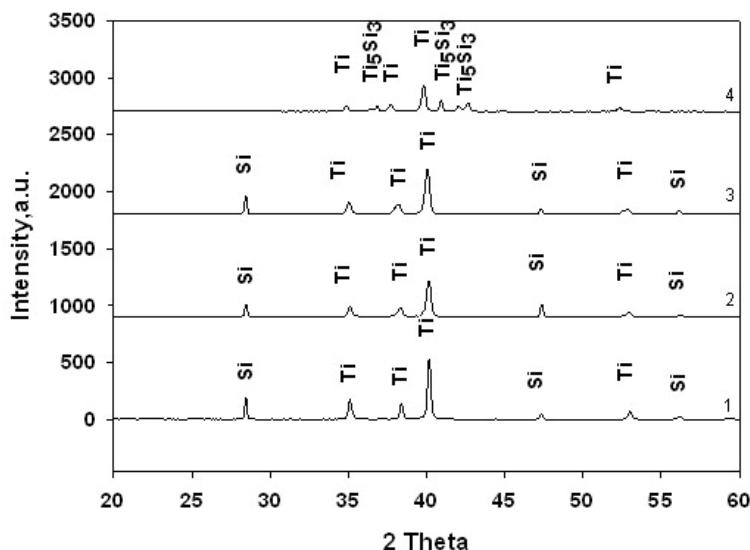


Fig.1. XRD diagrams of Ti and Si mixed powders: line 1 – mechanical mix of Ti + Si without heat-treatment; line 2 - Ti + Si mix at 650°C; line 3 - Ti + Si mix at 700°C; line 4 - Ti + Si mix at 800°C.

According to this finding, the first layer on the Ti substrate was fired at 850°C, forming an interlayer of firm adherence to Ti substrate, the thickness of this layer being of about 3 – 4 μm (Fig.2).

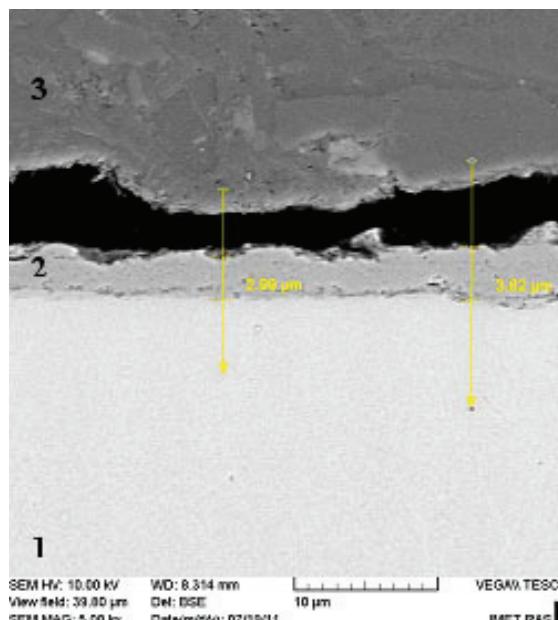


Fig.2. SEM micrograph of Ti_5Si_3 coating on Ti substrate (1 – Ti substrate; 2 – layer of Ti_5Si_3 ; 3 – glue).

Glass layer

Varying the composition, the melting temperature of glass over the range 700 – 750°C and thermal expansion coefficients ($\alpha = (13.78 - 14.53) \cdot 10^{-6}$) is close to the Ti thermal expansion coefficient ($\alpha = (9 - 12) \cdot 10^{-6}$) in the temperature range of 20 - 700°C.

Scanning electron microscopy observations revealed that the glass coatings are homogenous possessing firm adherence to Ti substrate. The coating thickness is changed from 20 – 120 μm in dependence on the coating route. Interaction between Ti_5Si_3 interlayer and glass coating is different for different glasses. In the case of N glass the interlayer-glass interface is diffused, for V glass this boundary is clearer (Fig.3a, b). More intense interlayer-N glass interaction results in the formation of an intermediate transition layer. At the same time, apparently the interaction between interlayer and V glass is less active, without noticeable formation of the intermediate layer. Figure 3b shows three areas with clear sharply defined boundaries. In Figure 3a one can see between the interlayer and N glass an area consisting of one more layer with very firm adherence to adjacent areas. Thus, firmer adhesion between Ti-substrate and N glass coating can be supposed. This hypothesis was confirmed by studying the wetting angle and rupture mechanical tests. For both glasses the wetting angle is less 10°, indicating good wettability, and excellent adhesion can be supposed. The rupture tensile strength on N glass coating is 22 MPa, whereas for V glass this value is 15 MPa. Enhanced adhesion strength of the samples with silicide interlayer is due to the prevention of titanium suboxides forming.

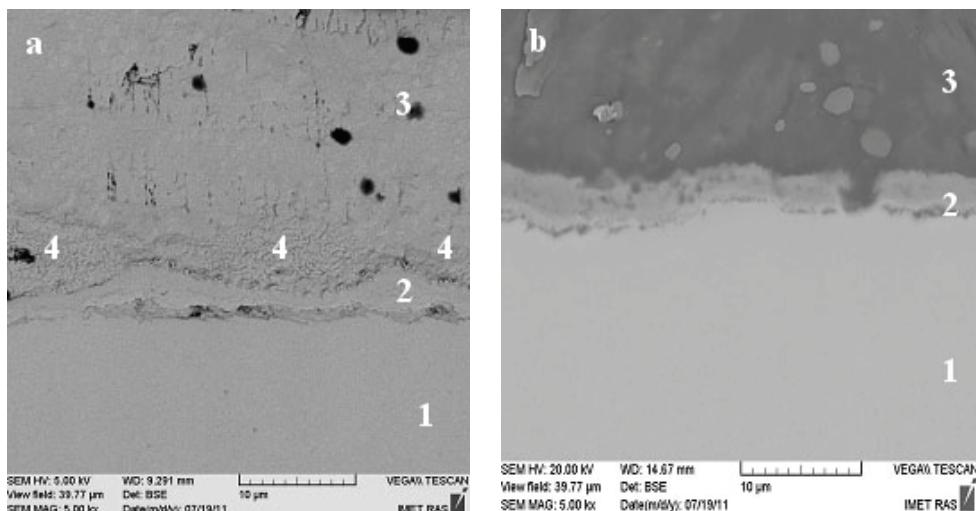


Fig.3. SEM micrograph of V (a) and N (b) glass coating on Ti substrate (1 – Ti substrate; 2 – interlayer of Ti_5Si_3 ; 3 – glass coating; 4 - intermediate transition layer between the interlayer of Ti_5Si_3 and glass coating).

The V glass solubility changes from 0.47 to 0.67 mmol/l (Fig.4), and the N glass solubility changes from 0.47 to 0.66 mmol/l (Fig.5) over 45 days. An insignificant solubility increase of both glasses results from the gradual saturation of solutions with Ca^{2+} ions. Solubilities in distilled water and in physiological solution were close to each other. Thus, the glass coatings on Ti possess low solubility both in neutral (distilled water, pH 7.0) and in weak acid (isotonic solution 0.9% NaCl, pH 5.6 – 5.8) medium at physiological temperature, which is important for the reliability of implants.

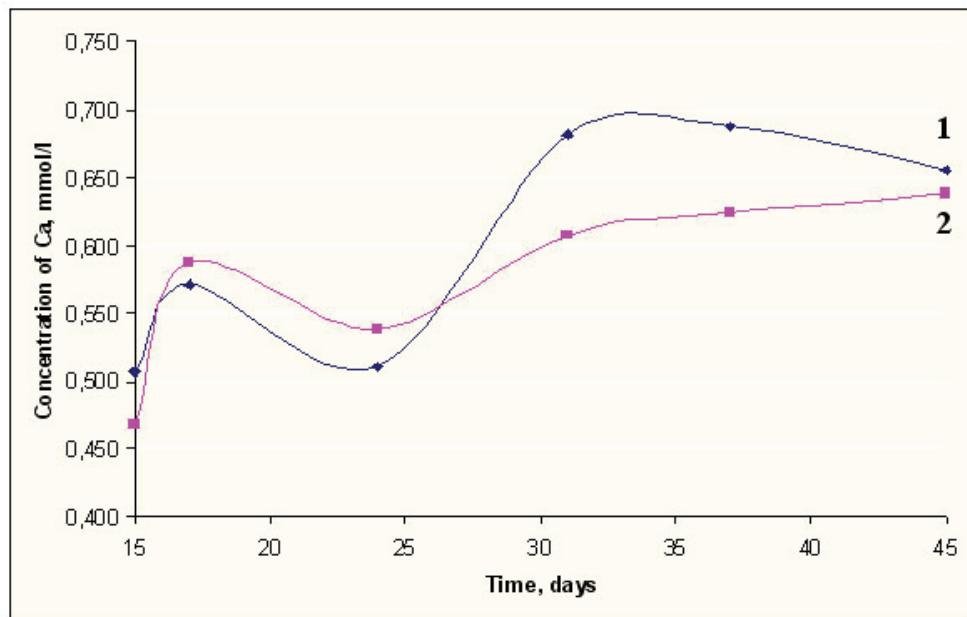


Fig.4. Solubility diagram of V glass in distilled water (line 1) and in physiological solution (line 2).

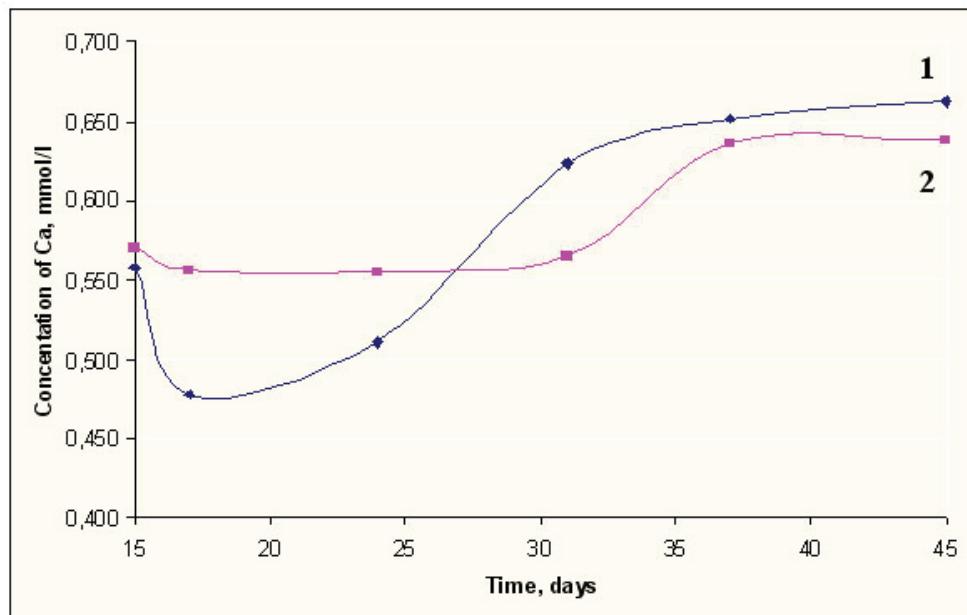


Fig.5. Solubility diagram of N glass in distilled water (line 1) and in physiological solution (line 2).

CONCLUSIONS

Two glasses of thermal expansion coefficients close to that of Ti, of low melting temperature and good wettability, were developed. These glasses possess low solubility both in distilled water and in an isotonic solution (0.9% NaCl) at physiological temperature. To bond these glasses, an intermediate titanium silicide layer was applied to the Ti substrate surface. It was revealed that the interaction between metallic Ti and Si started at a temperature above 800°C resulting in Ti_5Si_3 formation. Rupture tensile strength of the coating/substrate composite was in the range from 15 to 22 MPa.

Acknowledgements

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