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Bioactive borate glass coatings for titanium alloys

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Abstract Bioactive borate glass coatings have been developed for titanium and titanium alloys. Glasses from the Na_2O–CaO–B_2O_3 system, modified by additions of SiO_2, Al_2O_3, and P_2O_5, were characterized and compositions with thermal expansion matches to titanium were identified. Infrared and X-ray diffraction analyses indicate that a hydroxyapatite surface layer forms on the borate glasses after exposure to a simulated body fluid for 2 weeks at 37°C; similar layers form on 45S5 Bioglass® exposed to the same conditions. Assays with MC3T3-E1 pre-osteoblastic cells show the borate glasses exhibit in vitro biocompatibility similar to that of the 45S5 Bioglass®. An enameling technique was developed to form adherent borate glass coatings on Ti6Al4V alloy, with adhesive strengths of 36 ± 2 MPa on polished substrates. The results show these new borate glasses to be promising candidates for forming bioactive coatings on titanium substrates.

1 Introduction

Titanium (Ti) and Ti6Al4V alloy are commonly used for load-bearing implants because they possess good mechanical strength and excellent biocompatibility [1]. One drawback of these materials, however, is that they do not directly bond with bone [2]. To overcome this limitation, bioactive coatings of hydroxyapaptite (HAp) are often applied to Ti orthopedic implants to promote osteointegration and improve the stability of the implant/bone interface [3]. There is substantial clinical evidence that HAp coatings enhance the stability of a Ti implant compared with non-coated Ti implants, and also decrease the duration required for implant bonding with bone [4–7]. Most of these HAp coatings are applied to Ti by high temperature plasma-spray techniques [8–10].

Despite the enhanced osteointegration, there are problems associated with plasma-sprayed HAp coatings on Ti implants. Poor adherence of the coating is due, in part, to the difference in the thermal expansion coefficients of HAp (13.3×10^{-6}/°C) and Ti6Al4V (9.4×10^{-6}/°C) [11]. This mismatch commonly causes numerous microcracks in the coating during the quick cooling following plasma spraying [1]. Subsequent release of dislodged particles from the coating can trigger inflammation followed by osteolysis and implant failure [12, 13]. The high temperature of the plasma spray process (above the Ti6Al4V $\alpha \rightarrow \beta$ phase transition temperature) can also damage the Ti alloy and cause changes in the structure and chemical composition of HAp, compared to that which forms under in vivo conditions [14]. The structure and composition of the HAp that forms on bioactive 45S5 Bioglass® does promote osteointegration [15] and the use of Bioglass® coatings to improve the adherence of implant alloys to surrounding tissue has been proposed [16]. However, forming reliable coatings of 45S5 on Ti has proven difficult due to a significant thermal expansion mismatch and the formation of a weak silicide interfacial reaction layer [1].

Borate-based glasses are known to form strong hermetic seals to titanium [17]. This appears partly due to the

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formation of a thin layer of Ti-boride at the glass/titanium interface which apparently acts as a diffusion barrier against further interfacial redox reactions that could weaken bonding. In addition, the close thermal expansion match of borate glasses and Ti alloy contributes to strong adhesion. Borate glasses also convert to HAp when exposed to phosphate-containing solutions [18, 19] and show other signs of biocompatibility [20], and so are potential candidate materials for biocompatible coatings on titanium.

The present work was undertaken to develop a new family of borate-based glasses capable of adhering firmly to titanium and forming HAp layers when soaked in physiological fluids. Glass compositions tested were from the Na_2O–CaO–B_2O_3 system with silica (0–10 mol% SiO_2), alumina (0–4 mol% Al_2O_3) and P_2O_5 (0–4 mol%) added to meet design criteria. We report here two borate based glass compositions, designated B18 and H12, which have good adherence to titanium and also exhibit bioactivity. The thermal and chemical properties of these glasses are described, as are the characteristics of the glass films on titanium. The conversion of the borate glass to HAp in phosphate solution and simulated body fluids is described. Finally, initial evidence of the biocompatibility of these borate glasses is also described.

2 Experimental procedures

Molar compositions of the B18 and H12 borate-based glasses investigated in this study are listed in Table 1 along with 45S5 Bioglass® used as a control for comparisons. To prepare the glasses, reagent grade raw materials were batched in the proportions listed in the table, mixed extensively, and melted in platinum crucibles in air, first at 900–1,000°C for 30 min, and then at 1,200–1,250°C for 2 h to form a homogeneous melt. (The 45S5 compositions were melted at 1,450°C in platinum). The melts were poured into a metal mold and the resulting glass bars were annealed between 500 and 550°C for 6 h to remove residual stress. A low speed wafering saw was used to cut the annealed glasses into samples of various dimensions. The samples were ground in isopropanol to a final finish with 800 grit silicon carbide paper. The glass pieces were then ultrasonically cleaned for 15 min each in acetone and ethanol and stored in desiccators.

Table 1 Composition (mole %) of glasses evaluated in this study

Glass	CaO	Na_2O	B_2O_3	SiO_2	Al_2O_3	P_2O_5
B18	35.0	12.5	41.5	6.5	3.5	1.0
H12	40.0	8.0	40.0	7.5	2.0	2.5
45S5	26.9	24.3	–	46.3	–	2.5

Measurements of the coefficient of thermal expansion (CTE) and the dilatometric softening point (T_d) were performed with 25 mm × 10 mm diameter glass rods heated at a rate of 3°C/min in an Orton Dilatometer (Model 1600). The CTE was calculated between 100 and 500°C with an uncertainty of 3% and the estimated uncertainty for T_d is ±10°C. The glass transition temperature, T_g, and crystallization temperature, T_X, were measured using crushed glass particles (75–125 μm) heated at a rate of 10°C/min in air in a Perkin Elmer Differential Thermal Analyzer (Model DTA7). Estimated uncertainty for T_g and T_X is ±5°C.

The chemical durability of bulk glasses was evaluated from weight loss during soaking in deionized (DI) water. Samples (surface areas ~6cm^2) were suspended in 100 ml of DI water in Nalgene bottles maintained at 37°C for 1 day, 1 week, and 2 weeks. Duplicate measurements of weight loss were obtained at each interval and averaged to obtain the dissolution rate (DR).

Effects of soaking at 37°C in phosphate-containing media were tested with crushed glass particles (75–108 μm) soaked for one day in a 0.1 M solution of K_2HPO_4 at pH 7.3, and for 2 weeks in simulated body fluid (SBF) prepared as described by Kokubo and colleagues [21]. Sample amounts used were 110 mg glass/110 ml liquid. The soaked glass particles were collected by vacuum filtration and completely dried prior to analysis. Dried samples were tested for the presence of crystalline phases by powder X-ray diffraction (Scintag XDS 2000X) performed in step mode between 3° and 90° (2θ) with a step of 0.03° and a counting time of 1 s per step. These samples were also characterized by Fourier transform infrared (FTIR) spectroscopy, with a resolution of 2 cm^{-1} over a range of 400–4000cm^{-1} (Perkin Elmer Nicolet Magna-IR 750 FTIR Spectrometer), using the KBr pellet technique.

Ti6Al4V plates (15 mm × 15 mm × 1mm) were polished to 1200 grit and cleaned by soaking for 1 h in 5 mM NaOH for glass-coating experiments. H12 borate glass was pulverized to 3–10 μm particles by milling in an yttria-stabilized zirconia ball mill for 18 h. Finely pulverized H12 glass was placed in ethanol (0.125 mg glass/ml ethanol) and maintained in suspension with a sonic oscillator and 40 μl of the suspension (5 mg glass) was deposited on each Ti plate. The Ti/glass couples were then fired in an alumina muffle furnace for 15 min at 650°C under flowing argon. These sealing conditions are much different from those used to bond bioactive silicate glasses to titanium, where higher temperatures (~850°C) and short times (<5 min) are needed to get the requisite wetting while avoiding the formation of deleterious interfacial reaction products [22].

X-ray photoelectron spectroscopy (KRATOS analytical Axis 165) was used to examine interfacial reaction layers between Ti6Al4V alloy and borate glass (H12). A non-monochromatic Mg-anode operating at 225 W was used as the excitation source, and the spectra were collected using band pass energy of 80 eV. A dwell time of 500 s and acquisition time of 1100 s was used for collecting the spectra. Argon ion sputtering was used to remove adventitious carbon from the sample surfaces.

Bonding strengths of the H12 glass coatings on the Ti6Al4V plates were determined using a pin-pull coating adherence test based on Mil Std 883. Nail-shaped, 2.6 mm diameter aluminum pins were bonded to the coating with a cyanoacrylate adhesive capable of withstanding a maximum stress of 70–97 MPa. The coated sample with pin attached was mounted in a Romulus adhesion testing machine and the force required to pull the pin loose was measured, with at least five replicate samples, and values averaged to obtain adhesion strength of the coatings.

Additional glass-coated titanium plates were soaked for up to 1 week in 0.1 M K_2HPO_4 solution (pH 7.3) at 37°C for further analyses. Some of the phosphate-soaked, glass-coated titanium plates were analyzed by thin film XRD using a Phillips X'Pert Thin Film Diffractometer (Model PW3040/60) operated in a continuous mode between 10° and 90° (2θ) and a 1 s counting time. Other phosphate-soaked glass-coated titanium plates were sectioned with a diamond wafering blade and polished to a sub-micron finish. The sectioned samples were then examined using analytical scanning electron microscopy (Hitachi 4700 SEM) with associated energy dispersive spectroscopic analysis (Phoenix EDAX system).

An initial evaluation of the biocompatibility of the H12 and B18 borate glasses was conducted in vitro with MC3T3-E1 mouse pre-osteoblastic cells obtained from American Type Culture Collection [23]. The cells were grown at 37°C in a 5% CO_2 atmosphere in α-MEM medium supplemented with 10% fetal calf serum, pencillin (100 U/ml), streptomycin sulfate (100 μg/ml), plus 25 mM HEPES (pH 7.3). Vigorously growing cells were seeded into 35 mm culture dishes at a density of 20,000 cells/cm^2 and incubated 2-h to permit cell attachment. Dry heat-sterilized glass samples ($\sim 1 \times 5 \times 10$ mm) were then placed in the dishes and affixed with ~5 μl of sterile silicone stopcock lubricant. After incubations of one and three days, digital images of cells at the glass interface were obtained with a phase contrast microscope fitted with a CCD camera. To assure repeat viewing of the same section of each glass interface, the x- and y-coordinates of the mechanical stage were recorded with the 35 mm dish secured in a special jig on the microscope stage. The morphology and relative density of cells at the interface of the borate and 45S5 glasses were compared to qualitatively assess biocompatibility.

3 Results and discussion

The thermal expansion characteristics of B18, H12, and 45S5 glasses are shown in Fig. 1 in comparison with Ti6Al4V alloy. Measurements of the CTE between 100 and 500°C yielded values of $9.7–10.1 \times 10^{-6}$/°C for the two borate glasses, values just slightly less than the 10.8×10^{-6}/°C CTE of Ti6Al4V. In contrast, the CTE of 45S5 glass measured between 100 and 500°C is 17.0×10^{-6}/°C. The close CTE matches of the borate glasses to the titanium alloy would dramatically reduce thermal stresses in a borate-glass coating, compared with a 45S5 coating.

Additional thermal properties of the two borate glasses, including softening temperature (T_d), glass transition temperatures (T_g), and crystallization temperatures (T_x), are presented in Table 2. The T_g of the borate glasses is in a range of 500–570°C with crystallization temperatures (T_x) an additional 190–240°C greater than T_g. The large difference between the T_X and T_g temperatures offers a wide temperature range for processing without the risk of significant crystallization. Also presented in Table 2 are the results of measurements of the chemical durability of test glasses soaked for 1 week in deionized water. The data show that the dissolution rate (DR) of the borate glasses is $1–2 \times 10^{-6}$ g/cm^2 min, approximately an order of magnitude faster than the 45S5 bioglass which has a dissolution rate of $\sim 2 \times 10^{-7}$ g/cm^2 min.

The X-ray diffraction patterns of samples of pulverized H12, B18, and 45S5 glass soaked in 0.1 M phosphate solution for 1 day, and in SBF for 2 weeks, are presented in Fig. 2a and b, respectively. Also shown is the XRD pattern reported for hydroxyapatite (JCPDS 72-1243). The distinctive peaks at 26 and 32° (2θ), are evidence that a crystalline hydroxyapatite (HAp) has formed on the surfaces of each glass under both conditions. XRD patterns

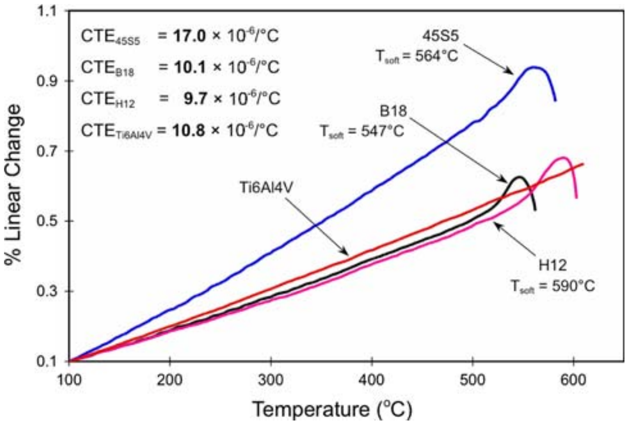

Fig. 1 Dilatometic curves for borate-based B18 and H12 glasses and silicate-based 45S5 Bioglass® compared with that from Ti6Al4V

Table 2 Physical properties of glasses evaluated in this study

Glass ID	CTE (PPM/°C)	T_d (°C)	T_g (°C)	T_x (°C)	Log DR (g/cm^2 min)
B18	10.1 ± 0.3	547 ± 10	510 ± 5	700 ± 5; 750 ± 5	−5.75 ± 0.2
H12	9.7 ± 0.3	590 ± 10	565 ± 5	755 ± 5; 780 ± 5	−5.83 ± 0.2
45S5	17.0 ± 0.5	564 ± 10	520 ± 5	700 ± 5	−6.69 ± 0.3

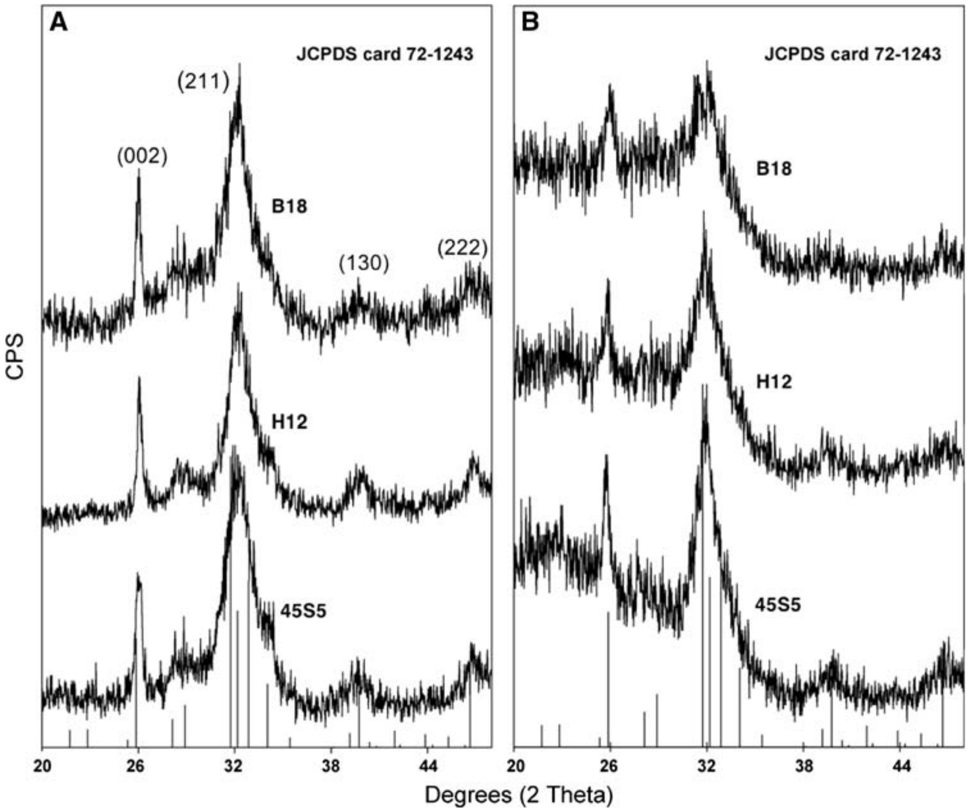

Fig. 2 XRD analyses of test glasses soaked at 37°C in: (**a**) 0.1 M K_2HPO_4, pH 7.3, for 1 day; and (**b**) SBF for 2 weeks

collected from the unreacted glass powders (not shown) revealed no crystalline phases.

FTIR spectra of pristine B18, H12, and 45S5 glass samples and after a one-day soak in 0.1 M K_2HPO_4 solution are shown in Fig. 3a. The FTIR spectra of the unreacted glasses are dominated by peaks due BO_3 and BO_4 vibrational modes [24] in the borate glasses, and by peaks assigned to the Si–O vibration modes [25] in the silicate glass, respectively. The spectra of the samples soaked in 0.1 M K_2HPO_4 solution exhibit well-defined PO_4^{3-} (bending) peaks at around 600 cm^{-1} and peaks around 1,023 cm^{-1} that are the characteristic signatures of PO_4^{3-} stretching modes of HAp. In addition, the small peaks present at 1,415, 1,480, and 1,630 cm^{-1} are indicative of a carbonated apatite layer [26, 27]. FTIR analyses of test glasses soaked in SBF for 2 weeks yielded similar spectral features, including the split peak at around 600 cm^{-1} plus the carbonated apatite peaks at 1,415, 1,480, and 1,630 cm^{-1} (Fig. 3b). These results show that the borate glasses transform to hydroxyapatite when in contact with phosphate solutions and SBF and provide further evidence that the B18 and H12 borate-based glasses are bioactive.

Borate glasses generally react faster in aqueous solutions than do silicate glasses with similar soda and calcia contents and hydroxyapatite forms on the surfaces of both types of glasses in the presence of phosphate species in solution, likely by similar precipitation reactions [19].

Representative phase contrast micrographs of the MC3T3-E1 cells at the interface of the test glasses after 1 and 3 days of culture are shown in Fig. 4. These micrographs show a similar morphology for MC3T3-E1 cells at the interface of H12 and B18 borate glasses compared with those at the interface of the 45S5 control glass. The micrographs also show essentially the same extent of increase in cell density at the interface of the three different glass samples. It is noteworthy that increased cell density is seen uninterrupted up to the interface of each sample.

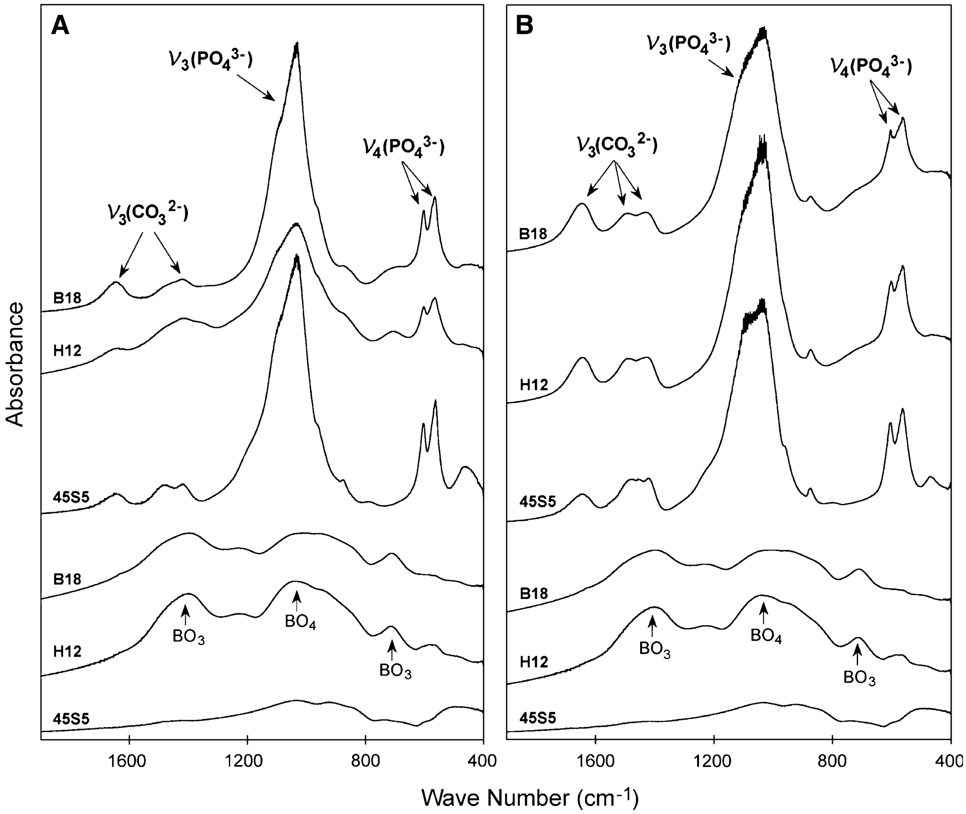

Fig. 3 FTIR analyses of test glasses soaked at 37°C in: (**a**) 0.1M K_2HPO_4, pH 7.3, for 1 day; and (**b**) SBF solution for 2 weeks. The bottom three spectra were obtained for samples of unreacted glass

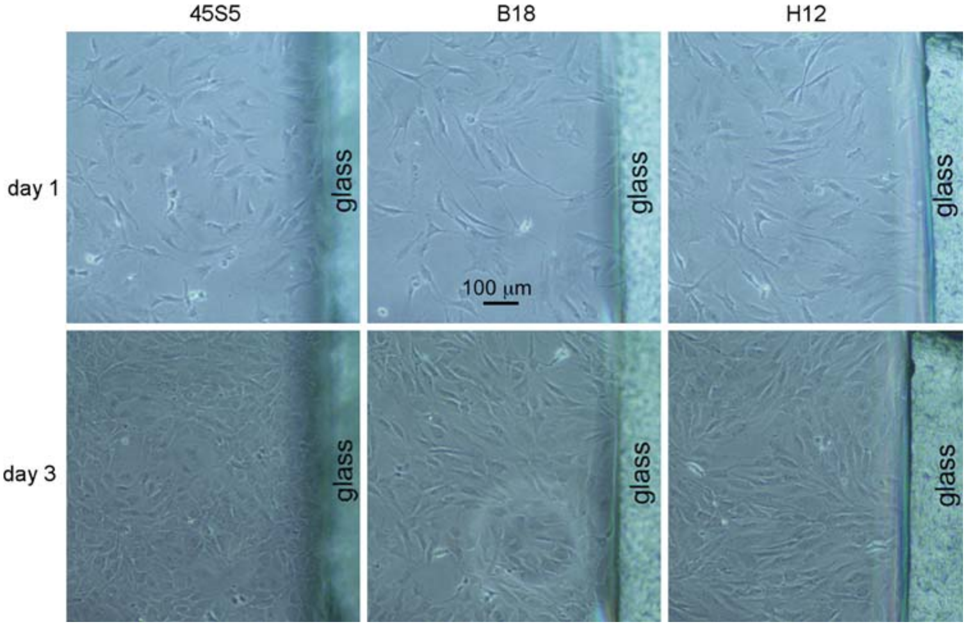

Fig. 4 Phase contrast images of MC3T3-E1 cell densities at the glass interface of H12 and B18 borate and 45S5 control glass after 1 and 3 days of culture

While qualitative in nature, this assay of cell density at the glass interface provides evidence that the H12 and B18 borate glass compositions are biocompatible under in vitro conditions. Repeated tests revealed that the MC3T3-E1 cells grew to a slightly, but consistently greater, density with the H12 glass, compared to the B18 glass. For this reason, the H12 glass was preferred for subsequent enameling studies. Additional results showing that osteoblastic cells seeded on borate glasses are able to proliferate and undergo differentiation have been presented elsewhere [20].

The scanning electron microscope image in Fig. 5a is a cross-sectional view of a H12 glass coating on a sand-blasted Ti6Al4V plate after soaking in 0.1 M K_2HPO_4 for

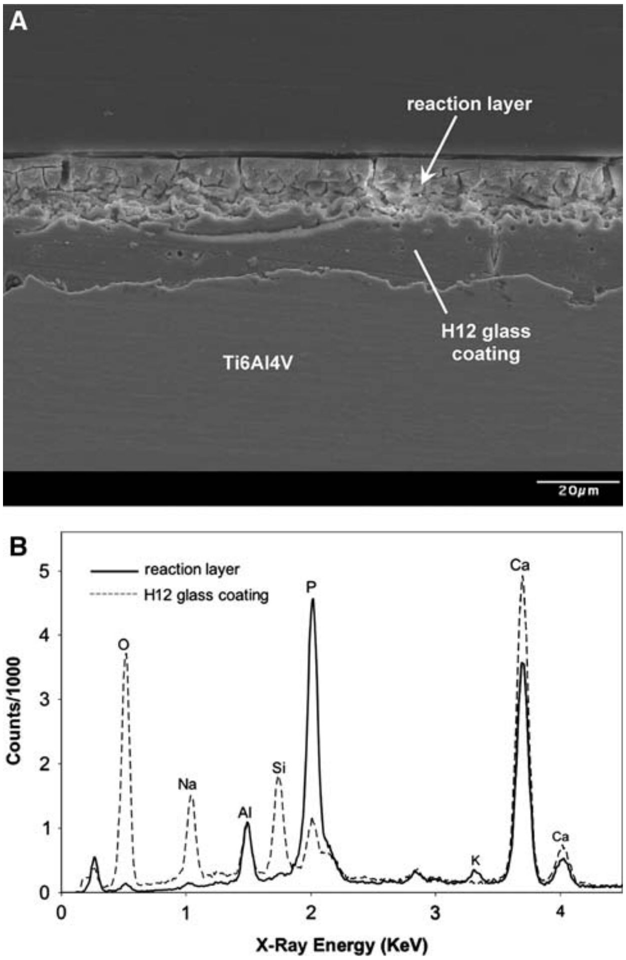

Fig. 5 Scanning electron micrograph (**a**) of the polished interface of H12 glass/Ti6Al4V alloy after soaking in 0.1 M K_2HPO_4, pH 7.3 solution for 3 days at 37°C; (**b**) EDS spectra obtained for the reaction layer near the site indicated by the white arrow on the SEM image and the underlying unreacted H12 glass layer

three days at pH 7.3 and 37°C. An important feature evident in this image is the uniform filling of the pitted surface of the sandblasted Ti6Al4V plate by the H12 glass coating. Clearly, the glass has flowed and is well-adhered as a result of the 650°C/15 min firing conditions. A second prominent feature visible in this image is the ∼20 µm thick reaction layer on the top surface of the H12 glass coating formed during the soaking in phosphate solution. This reaction layer forms a continuous interface with the underlying residual glass. (Much of the cracking seen in the reaction layer is likely an outcome of dehydration during SEM sample preparation.) Figure 5b shows an EDS spectrum collected from the reaction layer. These results indicate that a calcium phosphate rich layer has formed on the glass coating surface. EDS analyses of this sample, and others prepared in a similar manner, yielded Ca/P molar ratios that range from 1.2 to 1.9 for the reacted layers, compared to the Ca/P molar ratio of 7.7 for the original glass coating. Stoichiometric hydroxyapatite has a Ca/P = 1.67. Similar results were obtained after longer (4 weeks) exposures of coated-substrates to SBF. The formation of the calcium phosphate surface layer further attests to the bioactive nature of the borate glass coatings on the Ti6Al4V alloy.

Measurements of the adhesion (tensile) strengths of the H12 glass coatings on Ti6Al4V alloy are summarized in Table 3. A mean value of 36 ± 2 MPa was obtained for the adhesion strength of H12 glass on smooth (roughness ∼0.19 ± 0.1 µm) Ti6Al4V, whereas a mean value of 41 ± 8 MPa was obtained for H12 glass coatings on sand-blasted (roughness ∼5.6 ± 2.4 µm, as determined by profilometry) Ti6Al4V. In general, failure occurred at the glass/titanium interface, although some residual glass could be found still adhered to the titanium. Attempts were made to coat 45S5 Bioglass® on Ti6Al4V by the same enameling technique used for borate glass sealing. However, the 45S5 coatings were very fragile and delaminated from the Ti6Al4V plates before the samples could be mounted in the instrument for the adhesion strength measurement. An adhesion strength value for plasma-sprayed 45S5 bioglass coatings on Ti6Al4V alloy has been previously reported [28] and is included for comparison in Table 3. The latter value is for a 45S5 coating on substrates with a surface roughness of 7.48 ± 0.3 µm. From these data, it is evident that the adhesion strength of the borate glass coating on smooth titanium alloy substrates is almost four-fold greater than the adhesion strength reported for 45S5 bioglass on rough titanium alloy substrates. These results indicate that borate glass adheres to titanium to a much greater extent than does the silicate glass. The strength of the borate glass coatings on Ti6Al4V alloy is equivalent to the ASTM recommended strength of plasma sprayed hydroxyapatite coatings on Ti6Al4V alloy is 35 MPa [29].

Table 3 Adhesion strengths of glass coatings on Ti6Al4V

Coating ID	Surface roughness of Ti6Al4V (µm)	Coating technique and treatment	Coating type	Adhesion strength (MPa)
H12/Ti6Al4V	0.19 ± 0.1	Enameling, 650°C, 15 min, Argon	Glassy	36.0 ± 2.0 ($n = 5$)
H12/Ti6Al4V	5.6 ± 2.4	Enameling, 650°C, 15 min, Argon	Glassy	40.6 ± 7.8 ($n = 7$)
45S5/Ti6Al4V[a]	7.48 ± 0.3	Plasma spraying	–	8.6 ± 0.6

[a] Ti6Al4V substrate sandblasted (source: Goller [28])

Following the pin pull adhesion test, XPS analysis was performed on both the 'as sealed' glassy region of the H12/Ti coating and on the region where the pin had been pulled free during the pin pull test. The B1s spectra from the fractured H12 borate glass-titanium seal are shown in Fig. 6. (Region 'A' is from the interface where the coating was removed during the pin-pull test, and region 'B' is from the glass coating itself.) The lower energy B1s peak (~188 eV) from the interfacial region (Fig. 6a) is identified as a boride and the higher energy B1s peak evident in the spectrum from the 'as sealed' glass (Fig. 6b) is associated with 'borate' species [30]. These results indicate the presence of an interfacial boride layer similar to the interfacial boride layer reported for Sr-aluminoborate glass bonding to titanium [17, 31]. Maximum glass/metal adherence, as described by Pask [32], requires interfacial chemical bonding with a continuous 'electronic structure' across the interface, a condition met when the metal substrate and the glass are saturated with an oxide of the metal. This condition is likely met by a reaction that produces the interfacial boride; e.g. [17, 31],

$$5\mathrm{Ti} + 2\mathrm{B}_2\mathrm{O}_{3\,(\mathrm{glass})} \rightarrow 2\mathrm{TiB}_2 + \mathrm{TiO}_{2\,(\mathrm{glass})}$$

The adherence between this boride layer and the H12 borate glass seems to be greater than the respective adherence between 45S5 silicate glass and an interfacial silicide. This is consistent with previous studies of glass adhesion to titanium, where it was reported that the interfacial boride layer that forms at the lower sealing temperatures is likely to be thinner when compared to the interfacial silicide layer formed at the greater sealing temperatures required for silicate glass/Ti6Al4V seals [31, 33]. In addition, the better CTE-match of the borate glasses to the Ti-substrates will produce better-adhered coatings than will 45S5.

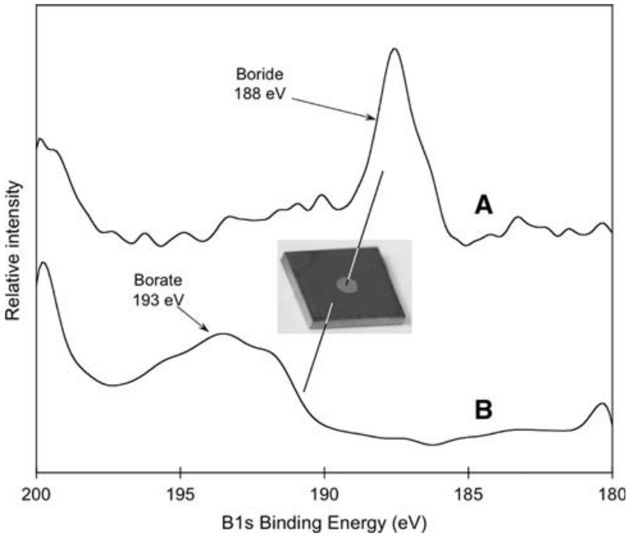

Fig. 6 B1s spectra of H12 borate glass/Ti seal (a) at the fracture interface; (b) in the glassy region of the coating. Inset photo image shows location of areas from which B1s spectra were obtained

4 Conclusions

Modified calcium-borate based glasses were developed with requisite thermal properties to form well-adhered coatings to titanium alloys. The glasses convert to bio-active hydroxyapatite coatings when exposed to simulated body fluid. An enameling technique was developed to form adherent glass coatings on smooth Ti6Al4V alloy, with adhesive strengths of 36 ± 2 MPa (H12 borate based glass coating on polished Ti6Al4V alloy substrates). These new glasses exhibit biocompatibility similar to that of the well-known bioactive glass 45S5. The combination of robust coatings and bioactivity make these new borate glasses excellent candidates for forming bio-active films on titanium alloy.

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