Fabrication and Characterization of Bioactive Glass Coatings on Co-Cr Implant Alloys

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Silicate glass coatings on Vitallium®, a Co-Cr alloy were prepared using a simple enameling technique. The composition of the glasses in the SiO_2-Na_2O-K_2O-MgO-CaO-P_2O_5 system has been tailored to match the thermal expansion of the alloys. The optimum glass composition and firing conditions (temperature and time) needed to fabricate homogeneous coatings with good adhesion to the alloy were determined. The final coating thickness ranged between 40 and 60 μm. Coatings fired under the optimum conditions do not delaminate during indentation tests of adhesion. Excellent adhesion to the alloy has been achieved through the formation of 150 nm thick interfacial layers (CrOx). The silicate glass can be successfully coated to Co-Cr alloy and formed hydroxyapatite on the glass surface when immersed in a simulated body fluid (SBF) for 30 days.

1. Introduction

Coated metal implants have been used in orthopedic surgery for many years because the underlying metal has excellent mechanical properties while the calcium phosphate (CP) coating facilitates bonding of implants to the surrounding bone. Ti and its alloys have had considerable advantages over other metals because of their inertness, which yields excellent biocompatibilty and non-sensitization of tissues. Due to its relatively poor wear resistance, Ti6Al4V alloy has been recognized as unsuitable for load bearing surface applications (hip heads and femoral knees) without a surface treatment. At present, failures are usually related to the quality and quantity of bone available for fixture placement.[1] However, a common prosthetic complication associated with implant therapy is screw fracture or loosening.[1–3] More generally, distortion of internal implant surfaces can allow rotation or loosening of implants. Problems would be alleviated if smaller implants could be constructed of stronger alloys such as Co-Cr. Little has been reported on coating Co-Cr for improved osseointegration. It is thus important that methods investigated for Ti and its alloys are extended to include Co-Cr-based alloys.

Coatings of hydroxyapatite (HA) fabricated by plasma spraying have been extensively investigated,[4–6] although there are several critical problems associated with the degradation of HA due to the elevated temperature required in the process, and lack of strength at the metal/HA interface.[7–9] An alternative method is to coat the implant with a bioactive glass (able to form HA *in vivo*) that could provide the desired interfacial attachment to the bone. In a previous work, glasses in the system SiO_2-Na_2O-K_2O-CaO-MgO-P_2O_5 were successfully used to fabricate bioactive coatings on Ti-based alloys using a conventional enameling technique.[10–12] The objective of this study is to produce the glass coatings on Co-Cr alloys (Vitallium®) that exhibit adherence and bioactivity. The coating glass is required to satisfy these properties, which do not crack, delaminate, crystallize excessively or otherwise react. The optimum glass composition and firing condition is presented in order to obtain excellent adherence and good bioactivity with desired solubility in body.

2. Experimental

Glasses in the SiO_2-Na_2O-K_2O-CaO-MgO-P_2O_5 (Table 1) were prepared by conventional melting method. The batch of composition, consisting of 0.10 kg of raw materials, was well mixed with a mortar and pestle. The silicate glasses were melted in Pt crucible at 1450°C for 1.0 hours in air. The melt was cast into a graphite mold to obtain glass plates (~50 mm × 50 mm × 5 mm) that were subsequently annealed at 500°C for 6 hours to relieve stresses. The thermal expansion coefficient (α), softening (T_s) and transformation (T_g) temperatures were measured in a calibrated dilatometer with an alumina holder and push rod, using glass bars 25 mm long. The coatings were prepared using a standard enameling technique. The glasses (particle size <20 μm) in ethanol were sequentially deposited on Co-Cr alloy plates (Vitallium®, 99.0% purity, 15 mm × 10 mm × 1 mm), which had been previously polished with diamond (1 μm particle size) and cleaned in acetone and ethanol. After the deposition, the samples were dried in air at 75°C for 24 hours to eliminate organics and fired in air to make the glass flow and adherence to the alloy. Firing temperatures ranged between 650 and 850°C and heating rate is constant at 40°C/min from 550°C to desirable temperature. The firing times varied between 0.5 and 30 min in air. After the required time, they were cool down to room temperature. The final coating thickness ranged between 40 and 60 μm. Identification of the crystal phases in the fired samples was performed using X-ray diffraction (XRD: CuKα, 40 kV, 30 mA). The cross section of coated samples were examined by scanning electron microscopy with associated energy dispersive spectroscopy analysis (SEM-EDS). In order to investigate the adherence of the interface between glass and alloy, vickers indentations

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Table 1   Glass compositions (mass%) and its thermal properties of the glasses (T_g and T_s are glass transition and softening temperature, respectively).

	SiO_2	Na_2O	K_2O	MgO	CaO	P_2O_5	α^* $(10^{-6}°C^{-1})$	T_g (°C)	T_s (°C)
Bioglass®	45.0	24.5	—	—	24.5	6.0	15.1	511	557
6P44-a	44.2	23.6	6.5	7.1	12.6	6.0	15.6	449	503
6P44-b	44.2	17.0	4.6	10.2	18.0	6.0	13.0	516	560
6P44-c	44.2	10.3	2.8	13.3	23.4	6.0	11.3	527	599
6P50	49.8	15.5	4.2	8.9	15.6	6.0	12.2	522	560
6P53-a	52.7	17.0	4.6	7.1	12.6	6.0	12.9	530	565
6P53-b	52.7	10.3	2.8	10.2	18.0	6.0	11.5	531	608
6P55	54.5	12.0	4.0	8.5	15.0	6.0	11.0	548	602
6P57	56.5	11.0	3.0	8.5	15.0	6.0	10.8	557	609
6P61	61.1	10.3	2.8	7.2	12.6	6.0	10.2	564	624
6P64	64.1	9.8	2.7	6.3	11.1	6.0	9.1	565	622
6P68	67.7	8.3	2.2	5.7	10.1	6.0	8.8	565	644

*Measured between 200 and 400°C

were performed on the polished cross sections using loads ranging from 0.5 to 1.2 kg. The cross sectional specimens were mechanically ground up to 100 μm in thickness, and thinned by a focused ion beam (FIB) technique for STEM-EDX analysis. The STEM-EDX analysis was performed using an FEI TECNAI 20 electron microscope operated at 200 kV. In the STEM-EDX analysis, the focused electron beam about 4 nm in diameter was positioned across the glass/Co-Cr alloy interface and an X-ray spectrum was acquired for 1 sec at each position. HA formation of selected samples were investigated by in vitro tests in simulated body fluid (SBF: Kokubo solution). The samples were soaked in SBF at a temperature of 36.5°C for times up for 60 days. After soaking, the coatings were rinsed in distilled water, dried, and analyzed by XRD and SEM-EDS.

3.   Results and Discussion

Figure 1 shows the relationship between the coefficient of thermal expansion (α) and the softening point (T_s) of the glasses. As expected with increasing SiO_2 content and decreasing alkaline oxides, α decreases while T_s increases. The α of the Bioglass® developed by Hench[13,14] is close to that of the Co-Cr alloy and could be used to fabricate coatings without generating large thermal stresses. However, attempts to fabricate coatings with the original Bioglass® composition always failed because it crystallizes almost completely even at the lowest firing temperature (700°C), resulting in poor densification and lack of adhesion to the metal. The main crystalline phase is sodium calcium silicate (Na_2Ca_2-Si_3O_9).[12] Glasses 6P44-a, 6P44-b and 6P53-a have an adequate α to coat Co-Cr, but they have not been studied in this work due to their hygroscopic nature caused by their high alkaline content (over 20 mass%). The [OH^-] ions present on the surface of these glass powders promote their crystallization around the flow temperature (600–700°C). Therefore, this study investigates the fabrication of 6P50, 6P55, 6P57, and 6P61 coatings on Co-Cr and the evaluation of their in vitro behavior in SBF.

The effect of firing time and temperature on the coatings manufactured with glass 6P50 is illustrated in Fig. 2. Four regions can be distinguished. Below a critical time and
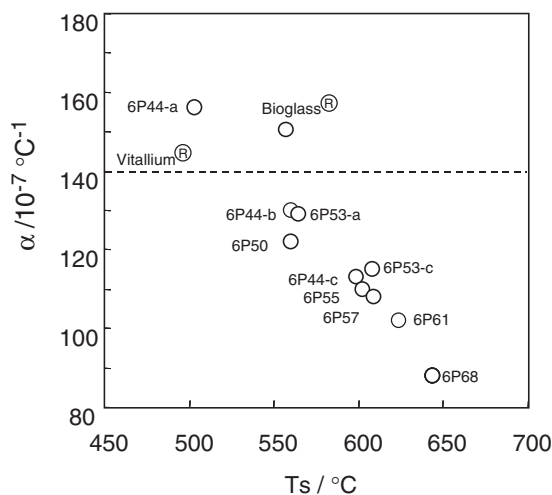

Fig. 1   Relationship between the Thermal expansion coefficient (α) and the softnening point (T_s) of glasses.
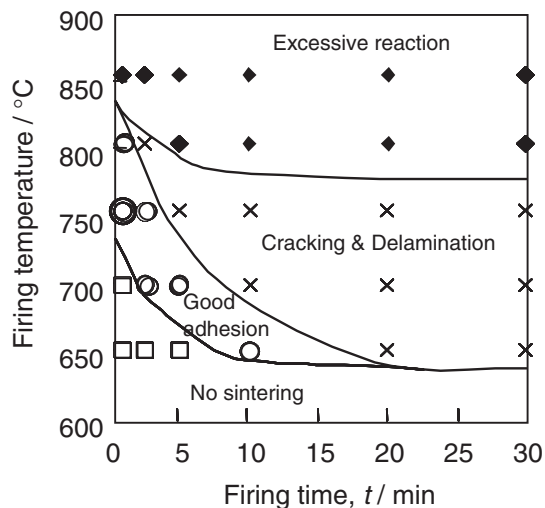

Fig. 2   Effect of the firing time and temperature on the adhesion of 6P50 coatings.
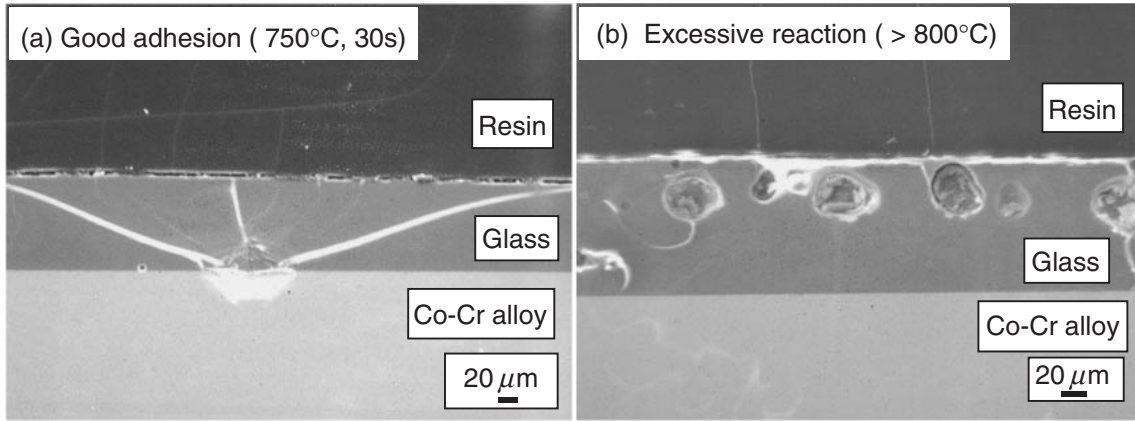
Fig. 3 Cross sections of 6P50 coatings fired in air (a)good adhesion (750°C, 30 s) and (b)excessive reaction (800°C, 5 min.).

temperature, the glass does not sinter. Then, at higher temperatures, the glass flows and forms a dense layer. A time and temperature region exists where the coatings are dense, exhibit good adhesion, and do not delaminate under indentation tests. In indentations performed at the glass/metal interface on polished cross sections of these coatings, cracks do not propagate along the interface, but rather tend to be driven into the glass (Fig. 3(a)). At higher time and temperature, excessive reaction between the glass and the metal produced coatings that delaminate during indentation tests. Firing temperatures $\geq 800°C$ and firing times ≥ 5 min resulted in the formation of gas bubbles at the glass/metal interface and the coatings were porous with poor adhesion to the substrate (Fig. 3(b)).

Higher silica glasses, 6P57 and 6P55 have a narrower range of optimum firing conditions when compared with 6P50. They resulted in transparent, dense, adherent coatings only when they were fired at 800°C for 30 s. The 6P61 coatings cracked after cooling due to their large difference in α between the 6P51 and the Co-Cr alloy (Fig. 1).

Small amount of crystalline $0.6Na_2O \cdot 2.4CaO \cdot P_2O_5$ was detected in the 6P50 coatings at 750°C for 30 s (Fig. 4). For firing times over 2 min, sodium calcium phosphate and sodium calcium silicate ($Na_2O \cdot 2CaO \cdot 3SiO_2$) appear and grow. These crystalline phases are also found to grow at temperatures higher than 750°C. Although the softening point of 6P50 is similar to that of the Bioglass®, its crystallization is slower due to its lower alkaline content. The crystallization behavior of 6P57 and 6P61 had already been described in a previous paper.[12] Coatings fired between 800 and 840°C showed crystalline phases of $0.6Na_2O \cdot 2.4CaO \cdot P_2O_5$ and $Na_2O \cdot 3CaO \cdot 2SiO_2$. At 840°C, diopside crystals [$CaMg(SiO_3)$] also grow. The crystallization behavior of 6P55 is similar to that of 6P57. The only crystalline phase observed in the 6P61 coatings fired over 800°C was sodium calcium phosphate ($0.6Na_2O \cdot 2.4CaO \cdot P_2O_5$).

Figure 5 shows a bright-field STEM-EDX line profiles along the cross section of the glass coating on Co-Cr alloys fired at 750°C for 30sec. An interfacial CrOx layer, 150 nm thick, is mainly observed. From the thermodynamic point of view, chromium is the most reactive element in the alloy. Several reactions have been proposed to occur between Cr containing alloys and silicate glasses during enameling.[15]
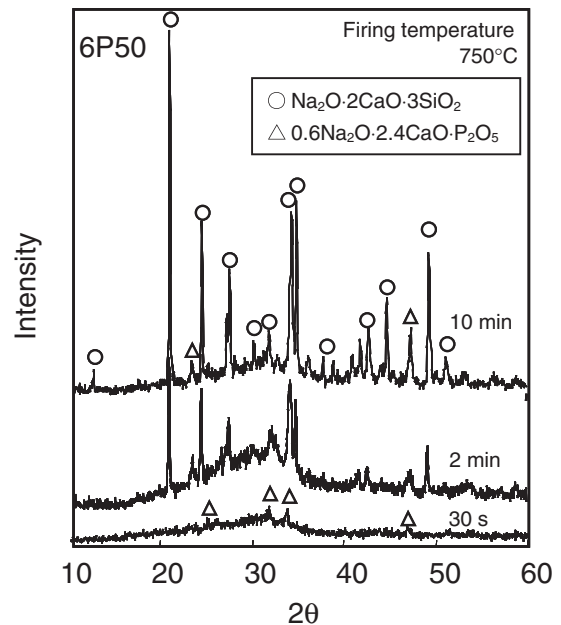

Fig. 4 Effect of the firing time and temperature on the crystallization of 6P50 coatings.

The valence state of chromium depends on the experimental conditions such as temperature and oxygen partial pressure. Reactions (1) and (2) may occur at the interface for a short firing time(750°C for 30 s) and contribute to the formation of the bubbles observed in the samples fired in the high temperature region above 800°C

$$Cr + 3/2Na_2O = 1/2Cr_2O_3 + 3Na(g) \uparrow \qquad (1)$$

$$Cr + 1/2SiO_2 = CrO + 1/2Si \qquad (2)$$
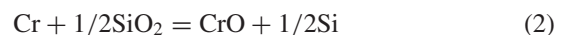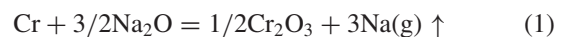
If firing temperature and time increases, the thickness of the interfacial chromium oxide layer (CrOx) increases. As a result the coating exhibit poor adhesion to the alloy and delaminates easily. The 6P50 glass coating on Co-Cr alloy was successfully fabricated that yield transparent, dense coatings, which do not crack during cooling or delaminate upon indentation. Excellent adhesion showed narrow range of temperature, 750°C for short time, 30 s.
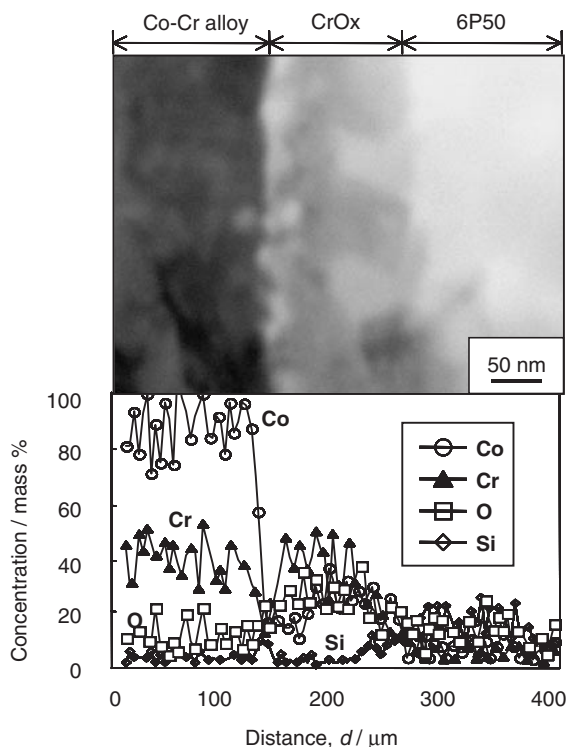
Fig. 5 Bright-field STEM image and EDX line profile across the 6P50 glass/Co-Cr alloy interface after firing at 750°C for 30 s.
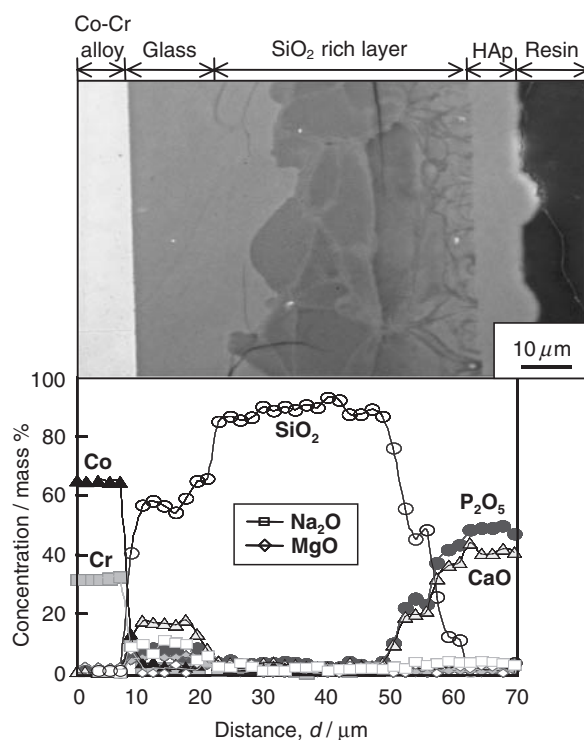

Fig. 7 SEM micrograph and corresponding elemental line analysis of the cross section and of a 6P50 coating fired at 750°C, 30 s after immersion in SBF for 30 days.
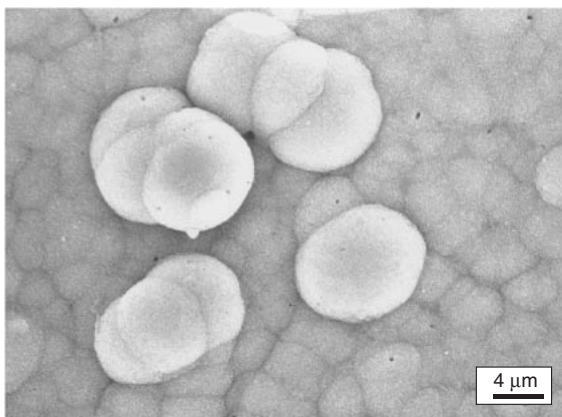

Fig. 6 SEM micrograph of the apatite crystals formed on the surface of a 6P50 coating fired at 750°C, 30 s after immersion in SBF for 30 days.

The apatite crystals precipitating on the surface of a 6P50 coating after 30 days in SBF are shown in Fig. 6. The crystals precipitate preferentially with the c-axis oriented perpendicular to the substrate as has been also observed in other silicate glass coatings and bulk bioactive glasses. The calibrated EDS analysis indicates that the apatite incorporates 1–5 mass% MgO in its structure. Cross sectional analyses of the 6P50 coatings soaked for 30 days in SBF show three separate regions (Fig. 7): a layer of the remaining glass in contact with the metal; a surface layer of precipitated apatite and a Si-rich layer between them. The thickness of the apatite layer is ~1 μm after 2 weeks in SBF and grows to ~8 μm after 30 days. The apatite layer is porous and does not protect the

coating from corrosion in SBF. Consequently after 60 days in SBF, the 6P50 glass was almost completely dissolved and only the silica rich layer and the precipitated apatite are visible. The *in vitro* response of the coatings depends strongly on their composition, in particular on their silica content. The observed behavior is similar to that reported for bulk glasses in the SiO_2-Na_2O-CaO-P_2O_5 system (which includes Bioglass®), and other related compositions and for silicate glass coatings on Ti and Ti6Al4V.[11,16,17] The mechanism of HA formation is similar to that described for Bioglass by Hench.[17] The ionic exchange of H^+ or H_3O^+ from the SBF for soluble cations K^+, Na^+, Ca^{2+} in the glasses leaves a silica-rich hydrogel layer on the glass prior to the formation of HA.

Glasses with lower SiO_2 content have a more open network structure, which enables a faster proton-alkali ions exchange with the solution, resulting in faster glass corrosion and precipitation of apatite. The critical silica content was around 60 mass%. A layer of apatite grows *in vitro* on the surface of the coatings with lower silica content whereas coatings with higher silica content are more resistant to corrosion and do not form apatite. Increasing firing times results in larger crystallization that changes the composition of the remaining glass and increases its resistance to corrosion, delaying the precipitation of apatite. The results of the *in vitro* tests show that, due to their fast corrosion in SBF, glasses with low silica content degrade fast during the in vitro testing and do not provide coatings with long-term stability. The results obtained with single layer coatings can be used as guidelines for the design and fabrication of multi-layer graded coatings.

4. Conclusions

6P50 glass coating with 50 mass% silica on Co-Cr alloy was successfully fabricated that yield transparent, dense coatings, which do not crack during cooling or delaminate upon indentation. Excellent adhesion showed narrow range of temperature, 750°C for short time, 30 s. In the 6P50 glass coatings on Co-Cr alloy adhesion is achieved through the formation of a CrOx layer (150 nm thickness) at the glass-metal interface. The bioactive glass 6P50 can be successfully coated to Co-Cr alloy and formed hydroxyapatite on the glass surface when immersed in a simulated body fluid (SBF) for 30 days.

Acknowledgements

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