Graded glass coatings for Co-Cr implant alloys

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A graded glass coating for Vitallium®, a Co-Cr alloy, has been prepared using a simple enameling technique. The composition of the glasses 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 25 and 60 μm. Coatings fired under optimum conditions do not delaminate during indentation tests of adhesion. Excellent adhesion to the alloy has been achieved through the formation of 100 nm thick interfacial chromium-oxide (CrOx) layers. The graded glass (consisting of BIG and 6P50 layers) can be successfully coated to a Co-Cr alloy, and forms hydroxyapatite (HA) on the coating surface when immersed in a simulated body fluid (SBF) for 30 days.
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1. Introduction

The development of glass coatings that enhance the adherence of metallic implants to the bone and that protect alloys from corrosion by body fluids has been extensively investigated. The fabrication of coatings for medical applications involves a compromise between adhesion, mechanical stability, and bioactivity, but coatings that satisfy all these requirements are extremely difficult to develop. Hydroxyapatite (HA) coatings fabricated by plasma spraying have been extensively investigated [1–3] to address these requirements, although there are several critical problems associated with HA degrading under the high temperatures involved in this process and a lack of strength at the metal/HA interface [4–6]. In a previous work, glasses in the SiO_2-Na_2O-K_2O-CaO-MgO-P_2O_5 system were successfully used to fabricate bioactive coatings on Ti-based alloys using a conventional enameling technique [7–9]. It is important that methods investigated for coating Ti and its alloys are extended to include Co-Cr-based alloys; however, little has been reported on glass coating Co-Cr for improved osseointegration.

The objective of this study is to produce graded glass coatings for Co-Cr alloys (Vitallium®) that exhibit adherence and bioactivity; in addition, the glass coatings must not crack, delaminate, crystallize excessively, or otherwise react. Optimum glass composition and firing conditions were used in order to obtain excellent adherence and good bioactivity with desired solubility in the body.

2. Experimental

Glasses in the SiO_2-Na_2O-K_2O-CaO-MgO-P_2O_5 system (Table I) were prepared by a conventional melting method. The composition batch, consisting of 0.10 kg of raw materials, was well mixed with a mortar and pestle. The silicate glasses were melted in a Pt crucible at 1450°C for 1 h in air. The melts were cast into a graphite mold to obtain glass plates ($\sim$50 × 50 × 5 mm) that were subsequently annealed at 500°C for 6 h to relieve stresses. The thermal expansion coefficient (α) and 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%

TABLE I Glass compositions and the thermal properties of the glasses (T_g and T_s are glass transition and softening temperatures, respectively)

	SiO_2	Na_2O	K_2O	MgO	Cao	P_2O_5	α^a $(10^{-6\circ}C^{-1})$	$T_g(^\circ C)$	$T_s(^\circ C)$
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	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	8.2	2.2	5.7	10.1	6.0	8.8	565	644

^{a}Measured between 200 and 400°C.

purity, $15 \times 10 \times 1$ 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 h to eliminate organics, and fired in air to make the glass flow and adhere to the alloy. Firing temperatures ranged between 650 and 850°C, and the heating rate was constant at 40°C/min, from 550°C to the desirable temperature. The firing times varied between 0.5 and 30 min in air. After the required time, the samples were cooled to room temperature. The final coating thickness ranged between 25 and 60 μm. Identification of the crystal phases in the fired samples was performed using X-ray diffraction (XRD) (Cu Kα, 40 kV, 30 mA). The cross section of coated samples was 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 were performed on the polished cross sections using loads ranging from 0.5 to 1.2 kg. The cross-sectional specimens were mechanically ground to 100 μm in thickness, and thinned by a focused ion beam (FIB) technique for scanning transmission electron microscopy with energy dispersive X-ray (STEM-EDX) analysis. The STEM-EDX analysis was performed using an FEI TECNAI F20 electron microscope operated at 200 kV. In the STEM-EDX analysis, the focused electron beam, about 1 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. The HA formation of selected samples was 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 up to 60 days. After soaking, the coatings were rinsed in distilled water, dried, and then analyzed by XRD and SEM-EDS.

3. Results and discussion

Fig. 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 [10, 11] 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
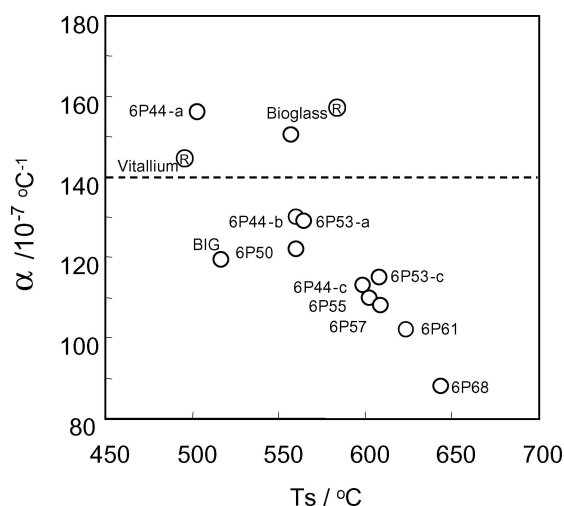

Figure 1 Relationship between the Thermal expansion coefficient (α) and the softnening point (T_s) of glasses.

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 ($Na_2Ca_2Si_3O_9$) [9]. 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 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.

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
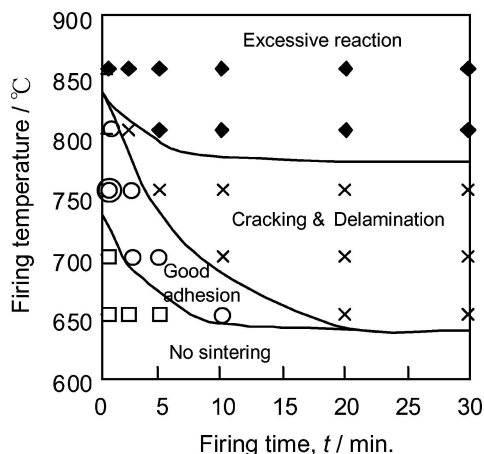
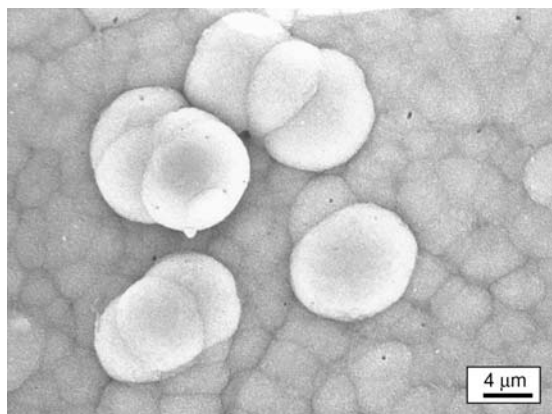*Figure 2* Effect of the firing time and temperature on the adhesion of 6P50 coatings.

Figure 3 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.

Figure 4 SEM micrograph and corresponding elemental line analysis of the cross section and a 6P50 coating fired at 750°C, 30 s after immersion in SBF for 30 days.

to their large difference in α between the 6P51 and the Co-Cr alloy (Fig. 1).

The apatite crystals precipitating on the surface of a 6P50 coating after 30 days in SBF are shown in Fig. 3. The crystals precipitate preferentially, with the *c*-axis perpendicular to the substrate, as has been observed in other silicate glass coatings and bulk bioactive glasses. The calibrated EDS analysis indicates that the apatite incorporates 1–5 wt% MgO in its structure. Cross-sectional analyses of 6P50 coatings soaked for 30 days in SBF show three separate regions (Fig. 4): (1) a layer of the remaining glass in contact with the metal; (2) a surface layer of precipitated apatite; and (3) 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 were visible. The *in vitro* response of the coatings depends strongly on their composition, their silica content in particular. 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 [8, 12, 13]. The mechanism of HA formation is similar to that described for
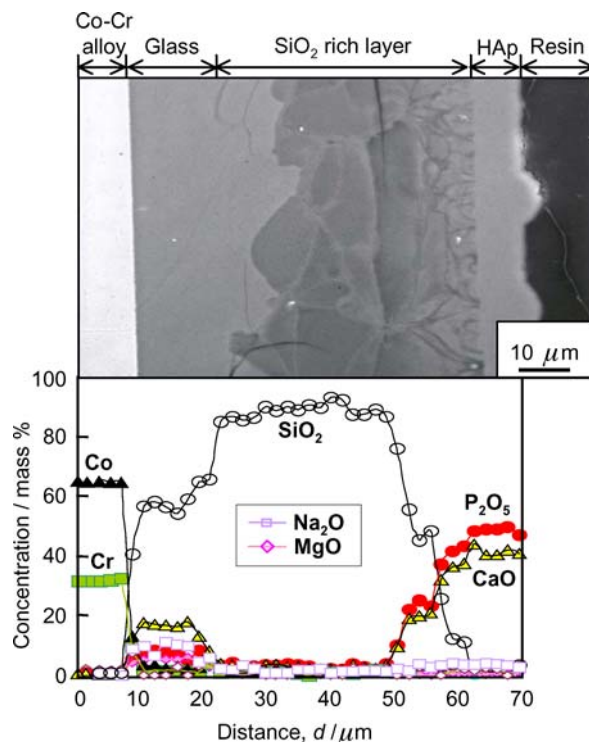
Bioglass by Hench [17]. The ionic exchange of H^+ or H_3O^+ from the SBF for soluble cations K^+, Na^+, and Ca^{2+} in the glasses leaves a silica-rich hydrogel layer on the glass prior to the formation of HA.

The 6P50 glass has a more open network structure, which enables a faster proton-alkali ion exchange with the solution, resulting in faster glass corrosion and precipitation of apatite. However, the coatings are not very resistant to corrosion and can crack during *in vitro* testing for longtime durability, reaching the alloy and initiating delamination. Thus, one motivation for a graded design is to develop coatings with optimum adhesion that will combine a bioactive surface and long-term stability by using a bio-inert glass (BIG) composition in contact with the alloy. Coatings with silica content higher than 60 wt% did not form apatite and were more resistant to corrosion. As expected with increasing SiO_2 content, T_s increases. The increasing firing temperature, results in larger crystallization of the 6P50 glass, delaying the precipitation of apatite. The BIG composition ($50SiO_2$-$14Na_2O$-$5K_2O$-$2MgO$-$20TiO_2$-$5B_2O_3$-$1ZrO_2$-$3AlF_3$) we developed did not change even after soaking in SBF for three months. The α and T_s of the BIG composition have values of 120×10^{-7} °C^{-1} and 520°C, respectively (Fig. 1). The basic enameling technique developed in this work was modified to prepare graded coatings.

Two layers of glasses with different compositions (BIG and 6P50) were deposited on the Co-Cr alloy and then fired at 750°C for 2 min to provide optimum adhesion for the glass in contact with the alloy. The electron probe microanalysis (EPMA) along the cross sections of the two-layer coatings reveals a graded variation in the concentration of glass components that corresponds to the composition of the different deposited glass
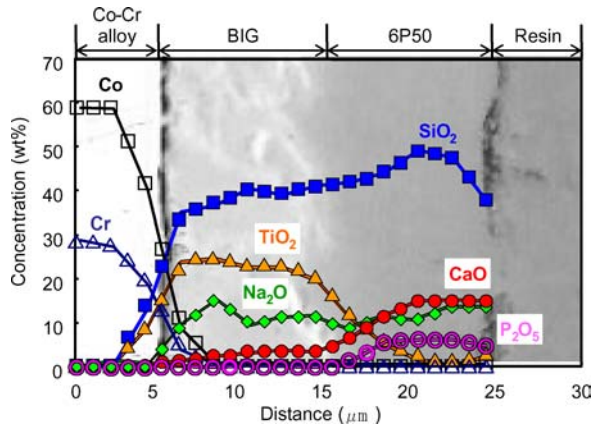
Figure 5 SEM micrograph and corresponding elemental line analysis of the cross section and a graded (BIG/6P50) coating fired at 750°C, 2 min.
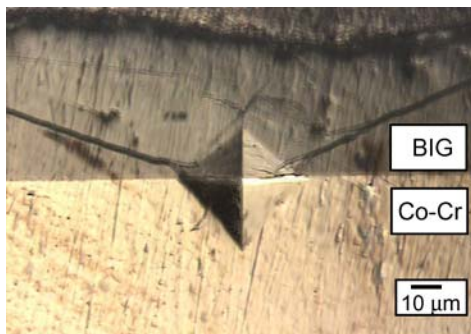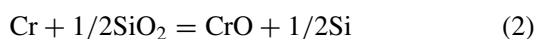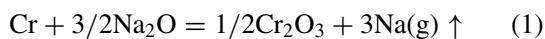

Figure 6 Cross sections of graded (BIG/6P50) coatings fired at 750°C, 2 min (good adhesion).

Figure 7 A bright-field STEM image and EDX line profile across the BIG/Co-Cr alloy interface after firing at 750°C for 2 min.

Figure 8 SEM micrograph and corresponding elemental line analysis of the cross section of a graded (BIG/6P50) coating fired at 750°C, 2 min after immersion in SBF for 30 days.

layers (Fig. 5). In indentations performed at the glass/metal interface, on polished cross sections of these coatings, cracks do not propagate along the interface but tend to be driven into the glass (Fig. 6).

Fig. 7 shows a STEM-EDX line profile along the cross section of the two-layer glass coating on a Co-Cr alloy fired at 750°C for 30 sec. An interfacial CrOx layer, 100 nm thick, is mainly observed. From a 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 [14]. The valence state of chromium depends on 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 may contribute to the formation of the bubbles observed in the samples fired in the high-temperature region above 800°C.

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

$$Cr + 1/2SiO_2 = CrO + 1/2Si \quad (2)$$

If firing temperature and time increases, the thickness of the interfacial CrOx layer increases. As a result, the coating exhibits poor adhesion to the alloy and delaminates easily. The graded glass coating on the Co-Cr alloy was successfully fabricated to yield transparent, dense coatings, which do not crack during cooling or delaminate upon indentation.
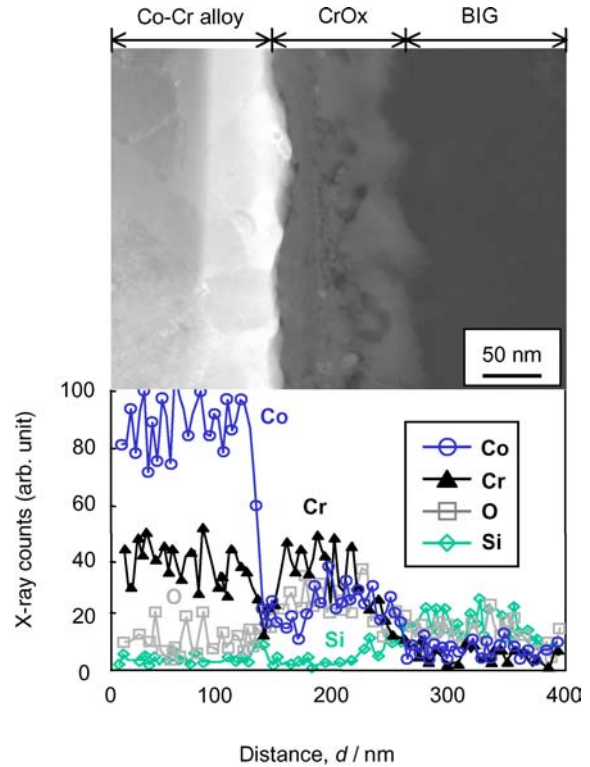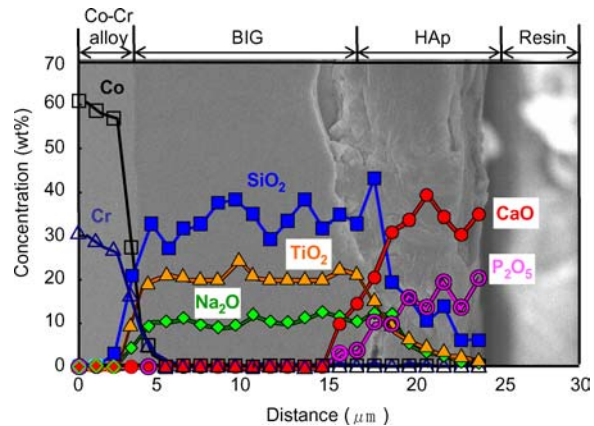
Fig. 8 shows a BIG/6P50 two-layer coating on a Co-Cr alloy after 30 days in SBF. A layer of HA precipitated on the coating surface whereas the BIG layer in contact with the alloy remained unaltered, providing good adhesion and protection of the alloy from the body fluid.

4. Conclusions

A new family of silicate-based glasses with compositions tailored to match the thermal expansion coefficient of a Co-Cr alloy has been developed to coat metallic implants, using a simple enameling technique. To better adjust the properties of the coating (in particular, to enhance bioactivity and increase longtime chemical stability) a two-layer approach has been used to fabricate graded glass coatings. A graded glass coating

consisting of a corrosion-resistant glass composition (BIG) layer, which protects the alloy from body fluids, and a 6P50 glass surface layer was successfully fabricated. Adhesion of this graded glass coating to a Co-Cr alloy is achieved through the formation of a CrOx layer (100 nm thickness) at the glass-metal interface. The coating forms HA on its surface when immersed in a simulated body fluid (SBF) for 30 days.

Acknowledgments

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