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# *Bioactive Calcium Borosilicate Glasses for Enameling Titanium*

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The thermal expansion coefficient of some bioactive glasses in the system $CaO$-$SiO_2$-$B_2O_3$ were adjusted to be similar to that of titanium by controlling the composition. A glass of composition $45CaO{\cdot}30SiO_2{\cdot}25B_2O_3$ was selected among those as the enameling glass. A slurry was prepared by mixing the glass powder and ethanol to be developed on titanium and heated at 740°C for 30 min. Thus treated specimen was soaked in a simulated body fluid (Kokubo solution). FT-IR reflection and thin film X-ray diffraction analyses indicated apatite formation on the glass coating layer within 12 h of soaking in the fluid. Thus titanium could be provided with bioactivity due to the enameling.

## 1. INTRODUCTION

Titanium is clinically used as one of the bone substitutes and bone repairing materials [1]. However, it is encapsulated by a fibrous tissue when embedded in the body and cannot directly bond to living bone while bioactive materials form an apatite layer instead to show direct bonding. Thus such bone-titanium bonds have been attempted by bioactive ceramics coating [2-5]. Ordinary methods such as plasma spray of hydroxyapatite are disadvantageous concerning the adhesive strength between the coating layer and Ti substrates: The coating layer peels off from substrate during surgery and implantation processes as well as in long term implantation. The glass coating technique in porcelain enamel is considered one of the methods to derive strong bonds with substrates. Several glasses in the system $CaO$-$SiO_2$-$B_2O_3$ were already confirmed bioactive [6] hence they were used for coating titanium substrates in this experiment so that the titanium substrates should be bioactive, that is, have bone-bonding ability. The bioactivity was confirmed by examining the apatite layer formed on the glass-coated Ti.

## 2. METHODS AND MATERIALS

### 2.1 Glass preparation and enameling of Ti

Glasses in the system $CaO$-$SiO_2$-$B_2O_3$ were prepared from reagent grade $SiO_2$, $CaCO_3$, and $B_2O_3$. The appropriate amounts of the starting materials were mixed and melted with a Pt crucible placed in an electric furnace at 1100 - 1600°C for an hour. The melts were poured onto a steel plate and immediately pressed with another one. The quenched glasses were subsequently annealed at 530 - 630°C for 30 min. The annealed glasses were pulverized and were sieved to the range 45 to 150 $\mu$m in diameter. Their glass transition temperature (Tg) and crystallization

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temperature ($T_x$) were determined by differential thermal analysis (DTA). Thermal expansion coefficient (α) and softening temperature ($T_f$) were obtained from thermal expansion measurements for the rod type glass samples (5 mm in diameter and 20 mm in length). A heating rate of 10°C/min was used for both thermal analyses.

Pieces of titanium specimens of 10 x 10 x 1 mm in size were cut from a sheet of commercially available pure titanium. They were polished on both surfaces with emery papers of #2000 grain size and washed with distilled water in an ultrasonic cleaner for 5 min. They were then treated with a 7 wt% $H_2SO_4$ aqueous solution at 60°C for an hour and then washed with distilled water in the ultrasonic cleaner for 5 min. Subsequently the titanium substrates were dried in air before they served enameling. A selected glass of a composition $45CaO{\bullet}30SiO_2{\bullet}25B_2O_3$ was annealed at 650°C (120°C lower than Tg). It was pulverized with a ball mill and the particles passing a 45μm-sieve were used for coating.

Coating slurries were prepared by mixing about 10 g glass powder and 5 ml ethanol in the ball mill for 30 min. The cleaned titanium substrates were dip-coated with the glass slurry. The specimens were then heat-treated in an oven in the heating schedule, shown in Fig. 1: the temperature was raised to about 60°C at a heating rate of 2°C/min and maintained at the temperature for an hour to dry the coated layer. The temperature was subsequently raised to the temperatures ranging from 680 to 780°C at a rate of 5°C/min and maintained at the temperatures for 30 min. With turning off the power the glass coated-titanium specimens were cooled spontaneously to the room temperature.

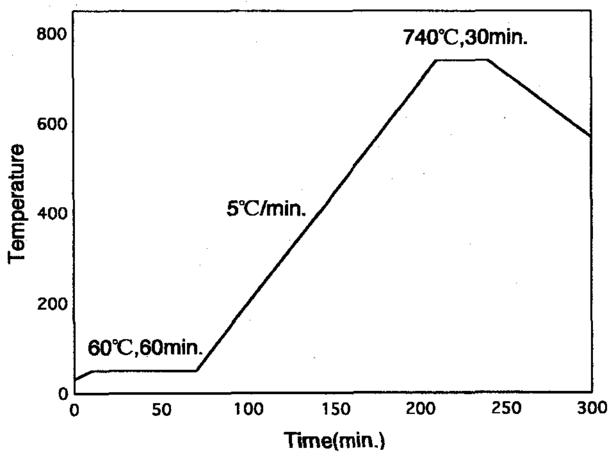


Fig. 1. Heating schedule for enameling of Ti.

## 2.2 Bioactivity of the glass-coated titanium

Thus obtained glass-coated titanium specimens were soaked in 10 ml of Kokubo solution at 36.5°C, which had inorganic species similar in concentration to those of the human blood plasma [7] as shown in Table 1. The solution was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\bullet}3H_2O$, $MgCl_2{\bullet}6H_2O$, $CaCl_2$ and $Na_2SO_4$ in distilled water as described in the literature [8,9]. It was buffered at 7.25 in pH with 50 mM trishydroxymethyl-aminomethane ($(CH_2OH)_3CNH_2$) and 45 mM HCl. After the soaking for various periods the specimens were removed from the solution, and gently washed with distilled water.

Surface of the specimens before and after being soaked in the Kokubo solutions was examined due to thin-film X-ray diffraction and Fourier transform infrared (FT-IR) reflection spectroscopy. Fracture surface of them was observed using a scanning electron microscope (SEM) attached with an energy dispersive X-ray(EDX) microanalyser.

Table 1 Concentrations of inorganic ions in simulated body fluid (SBF) and the human blood plasma.

| | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $HPO_4^{2-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|
| SBF | 142.0 | 5.0 | 2.5 | 1.5 | 147.8 | 4.2 | 1.0 | 0.5 |
| Blood plasma | 142.0 | 5.0 | 2.5 | 1.5 | 103.0 | 27.0 | 1.0 | 0.5 |

buffered with 50mM$(CH_2OH)_3CNH_2$ and 45mM HCl

## 3. RESULTS AND DISCUSSION

### 3.1 Glass for enameling

Matching in thermal expansivity between the coating glass and the substrate is one of the essential factors for successful enameling. Another is the softening temperature of the coating glass: the glass should soften well below the temperatures that cause some harmful effects on the substrates like reduction in mechanical strength due to phase transformation. Titanium experiences an α–β phase transformation (hcp to bcc) at 885°C accompanied by strength reduction. Fig. 2 indicates the thermal expansion coefficient (α) of the borosilicate glasses with each content of CaO plotted as a function of $B_2O_3$ content (mol %) where that of α-Ti (8.6 ppm/K) is also indicated. It increases with increasing CaO content while it depends only a little on the $B_2O_3$ content hence on the ratio $SiO_2/B_2O_3$. The glasses containing 45 mol% CaO are mostly similar to titanium in the coefficient, among which a glass of composition $45CaO{\bullet}30SiO_2{\bullet}25B_2O_3$ matches best with titanium in thermal expansivity. Fig. 3 shows the characteristic temperatures of the glasses for the present system, indicating that the present glasses may soften well below the temperature of phase transformation. Moreover $45CaO{\bullet}30SiO_2{\bullet}25B_2O_3$ glass has been shown bioactive since it deposits apatite within 7 days when soaked in the Kokubo solution [6]. Thus it was taken for the glass of enameling Ti.

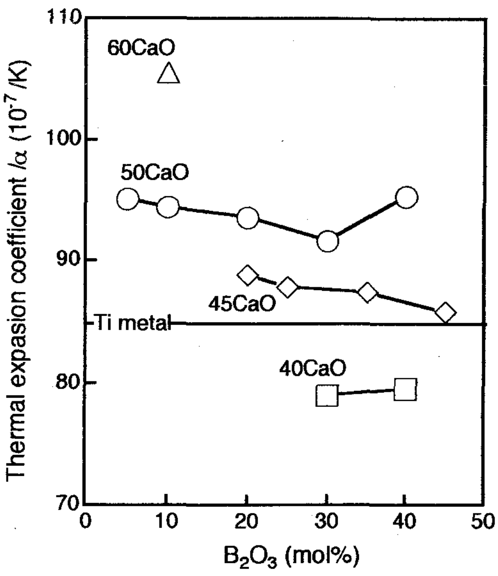


Fig. 2. Thermal expansion coefficient for the borosilicate glasses plotted as a function of the $B_2O_3$ content.

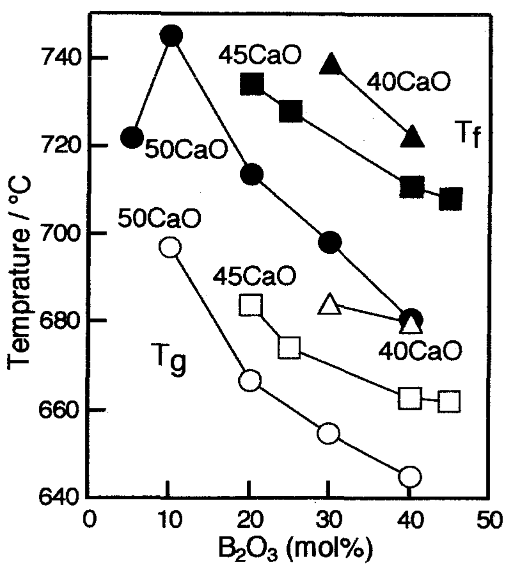


Fig. 3. Characteristic temperatures of glass for the present system.

3.2 Appearance of the enameled titanium

Figure 4 shows thin-film X-ray diffraction patterns of the glass-coated titanium specimens heat-treated at the temperature ranging from 740 to 780°C. Some crystalline diffraction lines appeared though the heating temperatures was below the crystallizing temperature due to DTA but exceeded the glass transition temperature of the enameling glass. They were assigned to those of for $CaSiO_3$ (wollastonite, JCPDS 42-550) and unidentified crystal(s). Appearance of the specimens were: When heat-treated at 680°C the glass was not softened enough to bond strongly to titanium, and heat-treating at 720-730°C covered the substrate with the partly softened glass. The substrate was well coated by the glass when heat-treated at 740°C. Since the softening temperature of the glass is 728°C from the thermal expansion curve partial crystallization may take place in the glass layer. Fig. 5 shows an SEM photograph and the EDX line analysis for the glass-titanium interface region. No cracks were seen in the glass layer, indicating good thermal expansivity matching between the substrate and partially crystallized glass layer. However, pores of 5-10$\mu$m in diameter remained in the layer probably because the crystallization retarded the viscous flow of the glass to be sintered to a dense layer. The EDX line profile of Ti indicated that the titanium diffusion during the heat-treatment at 740°C was almost negligible: This can be accounted for as lower temperature and shorter heating not only depressed titanium oxidation but greater viscosity of the glass minimize Ti diffusion from the substrate surface into the glass coating layer.

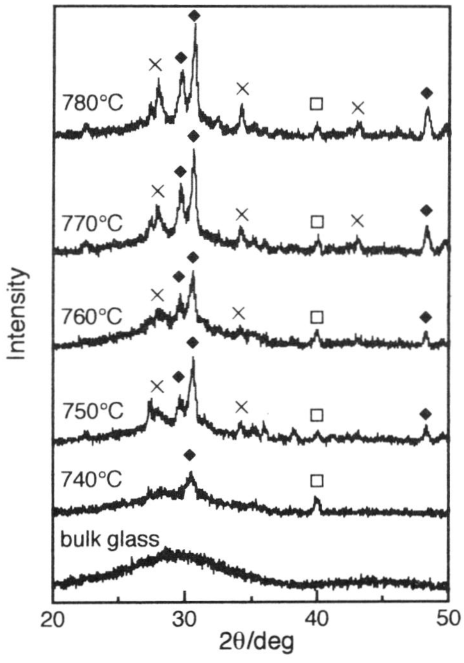


Fig. 4. Thin-film X-ray diffraction patterns of the bulk glass and glass-coated titanium substrate heat-treated at the temperatures ranging from 740 to 780°C.

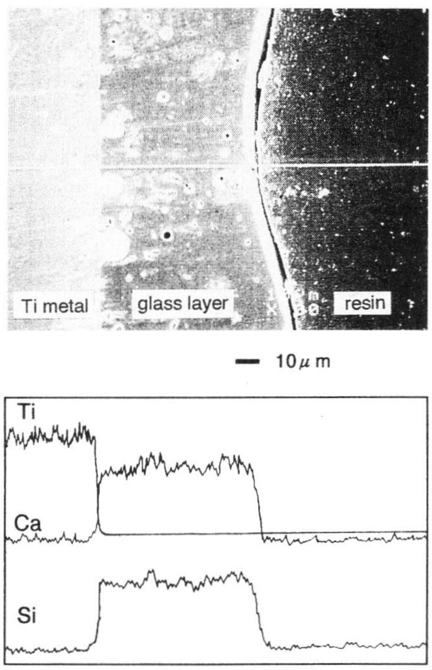


Fig. 5. The SEM-EDX analysis of the interface between the glass and titanium metal substrate.

### 3.3 Bioactivity of titanium coated with $45CaO \cdot 30SiO_2 \cdot 25B_2O_3$ glass

Figures 6 (a) and (b) show FT-IR reflection spectra of the bulk glass (a) and the glass-coated surface of the titanium specimen (b) before and after the soaking in the Kokubo solution for various periods, respectively. The peaks denoted with O indicates that some phosphate salts are adsorbed within 12 hours on the surfaces of both bulk glass and coated glass. Thus they naturally gave very similar IR profiles except earlier (within 6 h) deposition of phosphates for the coated glass. This can be attributed to the presence of $CaSiO_3$ in the enamel layer which has great apatite inducing ability as confirmed in A-W glass ceramics [9]. Fig. 7 shows the thin-film X-ray diffraction patterns of the enamel layer before and after the soaking in the Kokubo solution. Within 6 h soaking the diffractions of apatite (JCPDS 9-432) appeared to grow at the expense of $CaSiO_3$. Both FT-IR reflection spectra and X-ray diffraction patterns shows that apatite is formed on the surfaces of the glass coating layer within 12 h and it grows with the soaking period. Thus it has been confirmed that titanium is provided with bioactivity due to the glass coating layer.

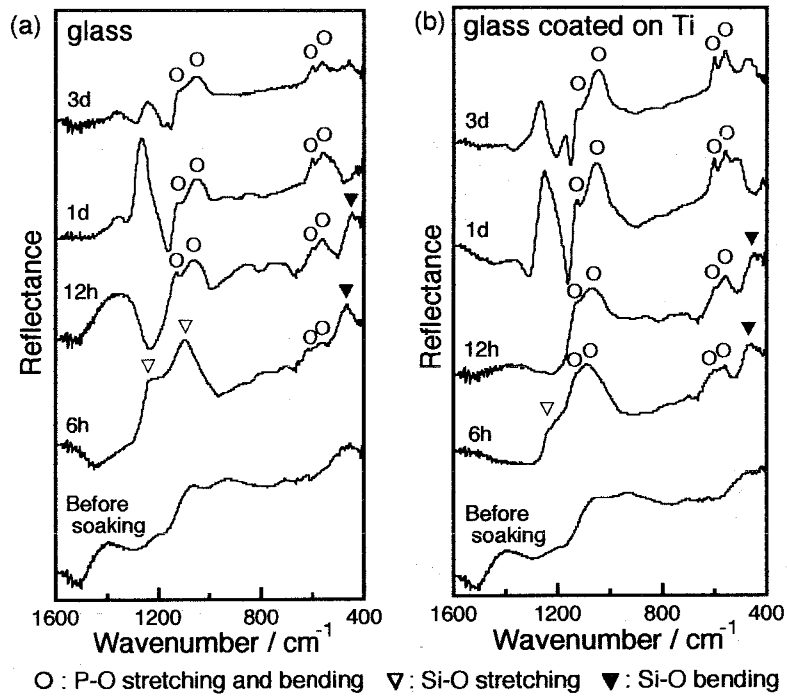


Fig. 6. FT-IR reflection spectra of the surfaces of bulk glass(a) and the glass coating layer on Ti metal substrate(b) before and after the soaking in the Kokubo solution for various periods.

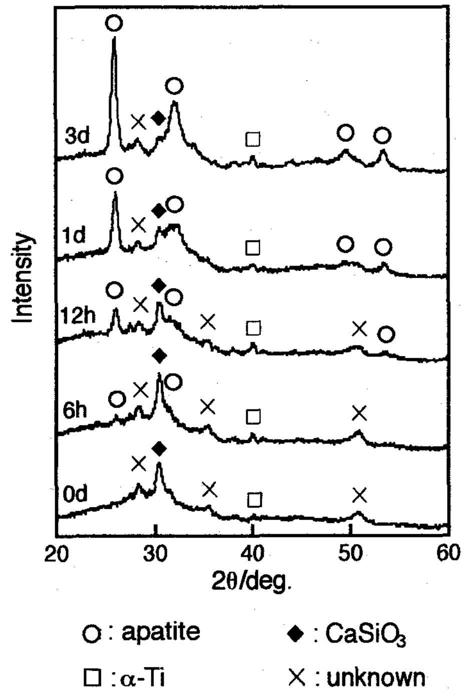


Fig. 7. Thin-film X-ray diffraction patterns of the glass coating layer on titanium before and after the soaking in the Kokubo solution for various periods. Apatite deposited in only 6h soaking.

## 4. CONCLUSIONS

The thermal expansion coefficient and characteristic temperatures of the glasses in the system $CaO$-$SiO_2$-$B_2O_3$ were measured as a function of composition. Thermal expansivity of some glasses could be adjusted to be similar to that of titanium: A series of glasses containing 45 mol% CaO not only had the thermal expansion coefficient closest to that of titanium but softening temperatures well below the α-β transformation temperature of titanium. A glass of composition $45CaO{\bullet}30SiO_2{\bullet}25B_2O_3$ was selected among those as the enameling glass. A slurry was prepared by mixing the glass powder and ethanol to be developed on titanium and heated at 740°C for 30 min. Thus treated specimens were soaked in a simulated body fluid (Kokubo solution). FT-IR reflection and thin film X-ray diffraction analyses indicated apatite formation on the glass coating layer within 12 h of soaking in the fluid. Thus titanium could be provided with bioactivity due to the enameling.

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