REACTIVITY OF HYDROXYAPATITE, \( \alpha \)-TRICALCium PHOSPHATE AND TETRACalciUM PHOSPHATE WITH ALUMINO-BOROSILICATE GLASS

SEIJI BAN\(^1\), SHIGEO MARUNO\(^2\), NORIHIRO ARIMOTO\(^1\), JUNKO HAYASHIZAKI\(^1\), and JIRO HASEGAWA\(^1\)

\(^1\) Department of Dental Material Science, School of Dentistry
Aichi-Gakuin University,
Kusumoto-cho, Chikusa-ku, Nagoya, 464, Japan

\(^2\) Department of Electric and Computer Engineering
Nagoya Institute of Technology
Gokiso-cho, Showa-ku, Nagoya, 466, Japan

Abstract
The present study was undertaken to evaluate the reactivity of hydroxyapatite (HA), \( \delta \)-tricalcium phosphate (\( \delta \)-TCP) and tetracalcium phosphate (TTCP) with an alumino-borosilicate glass during the firing process to make their composite. These three kinds of calcium phosphates and the glass powders were mixed so that the weight ratios of the calcium phosphate to the glass became 50:50, respectively, to prepare HA-glass, \( \delta \)-TCP-glass, and TTCP-glass mixtures. The characterization results of differential scanning calorimetry, X-ray diffractometry, and Fourier transform infrared spectroscopy suggest that HA particles slightly react on their surfaces with the glass above 840\( ^\circ \)C, \( \delta \)-TCP reacts with the glass around 700\( ^\circ \)C and transforms to \( \beta \)-TCP, and TTCP transforms to HA around 380\( ^\circ \)C and reacts with the glass around 750\( ^\circ \)C.

INTRODUCTION

Our previous studies\(^1\)-\(^4\) demonstrated that hydroxyapatite [Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\), referred to HA] containing glass coated titanium (HA-G-Ti) composite showed excellent biocompatibility and apposition to bone. The glass was an alumino-borosilicate glass having the suitable properties to constitute the composite; adhesiveness with substrate pure titanium or titanium alloy as substrate, biochemical stability for body fluid, and little reactivity with HA at firing temperature from 800 to 950\( ^\circ \)C. It is known that \( \alpha \)-tricalcium phosphate [\( \alpha \)-Ca\(_3\)(PO\(_4\))\(_2\), referred to \( \alpha \)-TCP] and tetracalcium phosphate [Ca\(_4\)(PO\(_4\))\(_2\)O, referred to TTCP] are more soluble calcium phosphates.\(^5\) Then, it is necessary to evaluate whether the composite consisting of \( \alpha \)-TCP or TTCP indicate the more bioactive behavior than the HA-G-Ti composite. The present study was undertaken to evaluate reactivity of the glass with HA, \( \alpha \)-TCP and TTCP during firing process and discuss the possibility of production of their composite.
MATERIALS AND METHODS

The glass composition used in the present work was 67.7% SiO₂, 10.4% B₂O₃, 5.2% Al₂O₃, 8.3% Na₂O, 4.2% K₂O, 2.1% Li₂O, 1.05% ZrO₂ and 1.05% TiO₂ by weight. HA powder was synthesized by a wet method using H₃PO₄ and Ca(OH)₂ aqueous solutions. The precipitate was finally fired at 1200°C for 6 hr, for preparing crystalline HA. α-TCP was prepared by firing of the mixture of CaCO₃ and CaHPO₄·2H₂O (molar ratio of 1:2) at 1400°C for 16 hr. TTCP was prepared by firing of equimolar of CaCO₃ and CaHPO₄·2H₂O at 1500°C for 16 hr.

After pulverization, the three kinds of calcium phosphates and the glass powders were mixed so that the weight ratios of the calcium phosphate to the glass became 50:50 , respectively, to prepare HA-glass, α-TCP-glass and TTCP-glass mixtures. Thermal behavior of these mixtures from room temperature to 950°C were analyzed by differential scanning calorimetry (DSC) at 10°C/min. Furthermore, the mixtures, heated from room temperature to some adequate temperatures at 50°C/min and maintained for 2 min using an electric furnace in air, were characterized by X-ray diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

Figure 1 shows DSC curves for the glass, HA, α-TCP and TTCP. The glass showed the glass transition temperature around 504°C. HA and α-TCP showed no exothermic and endothermic peaks in their DSC curves. TTCP showed a sharp exothermic peak around 373°C due to the decomposition. It is known that TTCP decomposes to hydroxyapatite and CaO around 400°C.6

Figure 2 shows DSC curves for the three kinds of mixtures. The DSC curve of the HA-glass mixture showed an endothermic step around 505°C due to the glass transition. Although this curve was basically similar to that of the pure glass, the endothermic step around 660°C was not observed. The DSC curve of the α-TCP-glass mixture showed an endothermic step at 510°C due to the glass transition and a broad exothermic peak around 704°C that was not observed in each curve of the pure glass and α-TCP. The DSC curve of the TTCP-glass mixture showed a sharp exothermic peak around 388°C due to the decomposition of TTCP, an absorption step around 512°C due to the glass transition and a broad exothermic peak around 751°C.

Figure 3 shows FTIR spectra of the HA-glass mixtures after firing at 700, 800, 840, 870 and 900°C for 2 min. The absorption band around 630 cm⁻¹ decreased with firing temperature. This band are assigned to OH liberation mode.7 Decreases in
intensity of OH band in HA suggest the formation of oxyapatite due to partial dehydration. On the other hands, there was no remarkable change in their XRD patterns with different firing temperatures and all the diffraction peaks could be ascribed.

FIGURE 1 DSC curves of the glass, HA, α-TCP and TTCP.

FIGURE 2 DSC curves of the mixtures of the glass and HA, α-TCP, and TTCP.

FIGURE 3 FTIR spectra of the HA-glass mixtures fired at 700, 800, 840, 870, and 900°C for 2 min.

FIGURE 4 XRD patterns of the α-TCP-glass mixtures fired at 400, 600, 800, and 900°C for 2 min.
to hydroxyapatite. It seems to be resulted from that there is no remarkable differences in the XRD patterns between hydroxyapatite and oxyapatite.

Figure 4 shows XRD patterns of the $\alpha$-TCP-glass mixture after firing at 400, 600, 800 and 900°C for 2 min. Diffraction peaks due to $\alpha$-TCP were only observed in the patterns at 400°C and 600°C, whereas strong diffraction peaks due to $\beta$-TCP and weak peaks due to HA and $\alpha$-TCP were observed at 800°C and 900°C. It suggests that the broad exothermic peak around 700°C in the DSC curve of the $\alpha$-TCP-glass mixture mainly depended upon the transformation of $\alpha$-TCP to $\beta$-TCP. Monma et al.\textsuperscript{8} reported that the $\alpha \rightarrow \beta$ transformation was so late that no DTA exothermic peak was observed. The present study also showed that no exothermic peaks were observed in the DSC curve of pure $\alpha$-TCP. However, the broad exothermic peak of the $\alpha \rightarrow \beta$ transformation was clearly observed around 700°C in that of the $\alpha$-TCP-glass mixture. It seems that the contact and reaction with the softened glass above the glass transition temperature promoted the $\alpha \rightarrow \beta$ transformation of TCP.

In the XRD patterns of the TTCP-glass mixture after firing at 200, 400, 600 and 800°C for 2 min, the diffraction peaks due to TTCP were only observed at 200°C and 400°C, whereas the peaks due to HA were only observed at 600°C and 800°C. It is concluded that the broad exothermic peak around 751°C was due to the reaction of the glass matrix with HA and CaO decomposed from TTCP around 388°C.

ACKNOWLEDGMENT

The authors wish to express appreciation to the Ministry of Education, Science, and Culture of Japan for support through Grant-in-Aid for General Scientific Research.

REFERENCES

6 H. Monma et al., Gypsum and Lime, 202, 151 (1986).