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Compositional dependence of formation of an apatite layer on glass–ceramics in simulated physiological solution

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In simulated physiological solution, an apatite layer is formed on the surface of apatite-containing glass–ceramics having the ability to bond to living bone. In this study, the influence of composition in the system $CaO–P_2O_5–SiO_2–MgO$, Al_2O_3 on apatite layer formation is investigated. On $CaO–P_2O_5–SiO_2$ glass–ceramics, an apatite layer was formed rapidly in simulated physiological solution. However, a solution containing an excess of Mg^{2+} prevented apatite layer formation. On glass–ceramics containing MgO, the amount of apatite formed on the surface decreased. An apatite layer was not formed on glass–ceramics containing Al_2O_3. The prevention of apatite layer formation on glass–ceramics containing MgO is attributed to an increase of Mg^{2+} concentration in the solution. It is thought that glass–ceramics containing Al_2O_3 form an Al_2O_3-rich layer, and that this layer prevents the formation of an apatite layer.

1. Introduction

Recently, a new type of glass–ceramic in the system $MgO–CaO–P_2O_5–SiO_2$ was developed [1]. These glass–ceramics can form a tight chemical bonding with bone [2] and have a high strength. They contain oxyapatite ($Ca_{10}(PO_4)_6O$) and wollastonite ($CaO \cdot SiO_2$) (A–W glass–ceramics).

An apatite layer is formed on the glass–ceramics in simulated physiological solution. However, A–W glass–ceramics containing Al_2O_3 or TiO_2 in the composition (for example, 3.7 MgO–40.0 CaO–31.9 SiO_2–15.7 P_2O_5–4.0 Al_2O_3–4.7 TiO_2) do not form a chemical bond to living bone and an apatite layer is not formed on them in simulated physiological solution [3]. It is assumed that apatite layer formation is closely related to bonding ability of the glass–ceramics to living bone.

The effect of MgO in glass–ceramics on apatite formation has not been investigated before. In this work, the influence of composition in the system $CaO–P_2O_5–SiO_2–MgO$, Al_2O_3 on apatite layer formation was examined, and further a formation mechanism of an apatite layer on these glass–ceramics is proposed.

2. Experimental procedure

2.1. Sample preparation

A batch mixture of the composition (wt %) of 49.5 CaO–$(16.3 - x)P_2O_5$–$(34.2 + x)SiO_2$, or $(49.5 - x)$ CaO–16.3 P_2O_5–34.2 SiO_2–xMgO (or Al_2O_3) ($x = 0$ to 9.8) was melted in a platinum crucible at 1550° C for 1 h. The melt was quenched into water. This resultant glass was pulverized into powders of particle size below 30 μm. Compacts were prepared by pressing the glass powders with 5 wt % paraffin under a hydrostatic pressure of 100 MPa. The compacts were heated up to 1050° C at a rate of 3° C min^{-1} and held at the temperature for 2 h to sinter and crystallize.

2.2. Immersion into pseudo-extracellular fluid (immersion test)

The glass–ceramics were shaped into rectangular plates (15 mm × 10 mm × 2 mm) and the surfaces ground with 1200-grit alumina powder. The plates were immersed in simulated physiological solution which was a buffered solution (pH 7.4) consisting of tris-hydroxymethylaminomethane and hydrochloric acid. The chemical composition of this pseudo-extracellular fluid (PECF) is shown in Table I. After a few days the specimens were taken out of the PECF and their surfaces were analysed by X-ray diffraction (XRD).

2.3. Ion concentrations in PECF

To consider the formation mechanism of an apatite layer, the following experiment was carried out. The glass–ceramics shown in Table II were prepared by the method described in Section 2.1. These glass–ceramics (pulverized to 140 to 230 mesh) were immersed in PECF held at 37° C with shaking. The PECF

TABLE I Composition of PECF*

Cation	Amount ($\times 10^{-3}$ M)	Anion	Amount ($\times 10^{-3}$ M)
Na^+	142.0	Cl^-	148.8
K^+	5.0	HCO_3^-	4.2
Mg^{2+}	1.5	HPO_4^{2-}	1.0
Ca^{2+}	2.5		

*Including 0.05 M tris-hydroxymethylaminomethane and 0.045 M hydrochloric acid.

TABLE II Compositions of glass–ceramics

Component	Composition (wt %)			
	CPS	CPS-Mg	CPS-Al	CS
CaO	49.5	39.9	41.5	48.3
P_2O_5	16.3	16.3	16.3	–
SiO_2	34.2	34.2	34.2	51.7
MgO	–	9.6	–	–
Al_2O_3	–	–	8.0	–
Crystalline phases*	Ap, Wo	Ap, Di	Ap, Wo, An	Wo

*Ap = apatite, $Ca_{10}(PO_4)_6O$; Wo = wollastonite, $CaO \cdot SiO_2$; Di = diopside, $CaO \cdot MgO \cdot 2SiO_2$; An = anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$.

(5 ml) was pipetted out every few hours and the concentration of ions in the solution was analysed by atomic absorption.

3. Results and discussion

3.1. Effect of P_2O_5 content on apatite layer formation

Fig. 1 shows the result of immersion tests of glass–ceramics with the composition 49.5 CaO–(16.3 − x) P_2O_5–(34.2 + x)SiO_2 (x = 0 to 9.8). In spite of a large SiO_2 content (a small P_2O_5 content), an apatite layer is formed on the glass–ceramics. Glass–ceramic containing no P_2O_5 ("CS" glass–ceramic; Table II) was immersed in PECF. This glass–ceramic consists of wollastonite. After immersion for 10 days, an apatite layer was formed on "CS" glass–ceramic (Fig. 2). PO_4^{3-}, required in order to form an apatite layer, is supplied from the PECF. It is not necessary for glass–ceramics to contain apatite in order to form an apatite layer.

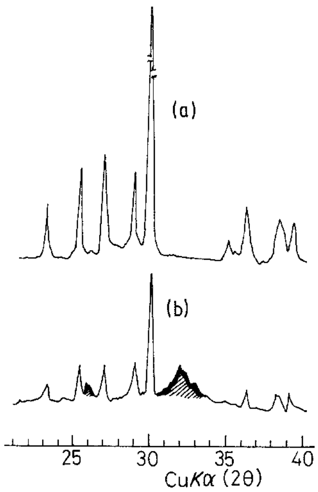

Figure 2 XRD patterns (a) before and (b) after immersion tests (for 10 days) of "CS" glass–ceramics (Table II). The shaded peaks are from apatite.

3.2. Effect of MgO content on apatite layer formation

Fig. 3 shows the effect of MgO content in glass–ceramics on the ability to form an apatite layer in PECF. The XRD peak height of apatite increases and the peak profile sharpens progressively as wollastonite decreases. The I_a/I_b value of apatite decreases with increasing MgO content in the glass–ceramic.

On glass–ceramics containing more than 8% MgO, no apatite forms in PECF. The XRD peak height of diopside ($CaO \cdot MgO \cdot 2SiO_2$) does not change. The ability for apatite layer formation decreases with increasing MgO content. Glass–ceramics containing no MgO are superior in their apatite-forming ability.

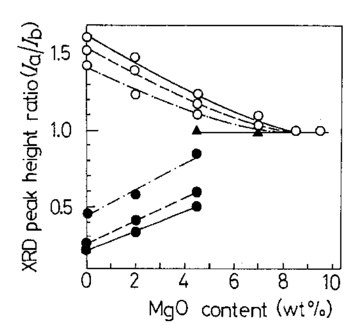

Figure 3 Effect of MgO content in glass–ceramics on apatite layer formation. (○) Apatite, (●) wollastonite, (▲) diopside; (– · –) after immersion for 10 days, (– – –) after immersion for 20 days, (——) after immersion for 30 days.

Figs 4 and 5 show the changes of ion concentration in PECF in which the glass–ceramics were immersed. They were "CPS" and "CPS-Mg" glass–ceramics (Table II), respectively. The increase of Si^{4+} concentration is due to dissolution of the glass–ceramics. The decrease of PO_4^{3-} concentration is due to adsorption to the surface of the glass–ceramics. On "CPS" glass–ceramics, the Ca^{2+} concentration increases with increasing immersion time. On the other hand, on

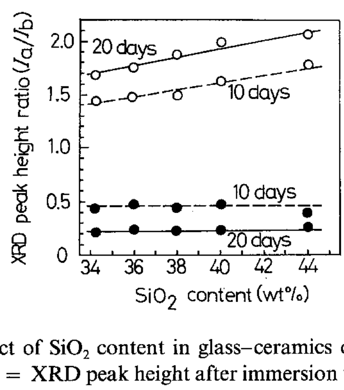

Figure 1 Effect of SiO_2 content in glass–ceramics on apatite layer formation. I_a = XRD peak height after immersion test, I_b = XRD peak height before immersion test; (○) apatite, (●) wollastonite. "10 days" = after immersion for 10 days, "20 days" = after immersion for 20 days.

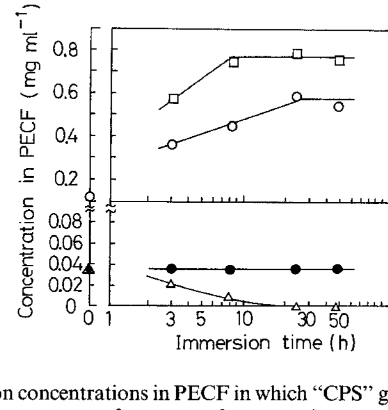

Figure 4 Ion concentrations in PECF in which "CPS" glass–ceramics were immersed; (○) Ca^{2+}, (●) Mg^{2+}, (□) Si^{4+}, (△) PO_4^{3-}.

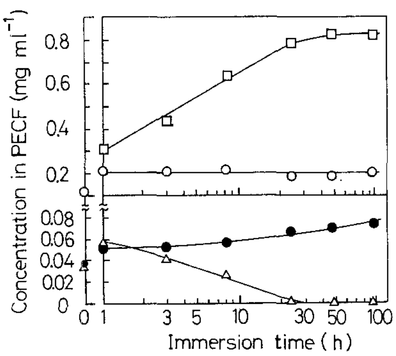

Figure 5 Ion concentrations in PECF in which "CPS-Mg" glass–ceramics were immersed; (○) Ca^{2+}, (●) Mg^{2+}, (□) Si^{4+}, (△) PO_4^{3-}.

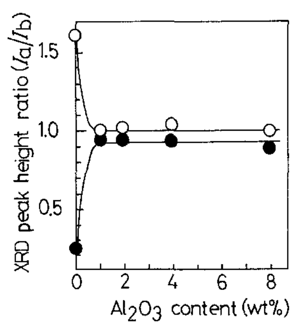

Figure 7 Effect of Al_2O_3 content in glass–ceramics on apatite layer formation (after immersion for 30 days). (○) Apatite, (●) wollastonite.

"CPS-Mg" glass–ceramics the Ca^{2+} concentration does not change and the Mg^{2+} concentration increases.

Two kinds of modified pseudo-extracellar fluid containing excess Mg^{2+} (4.5×10^{-3} and 15.0×10^{-3} mol l^{-1}) were prepared. "CPS" glass–ceramics were immersed in these solutions. Fig. 6 shows the relation of Mg^{2+} concentration and ability of apatite layer formation. The ability of apatite layer formation decreases with increasing Mg^{2+} concentration. Bosky and Posner [4] have reported that, on formation of hydroxyapatite in aqueous solution, the induction period of the transformation (time before crystals are first observed) increased with increasing Mg^{2+} concentration in amorphous calcium phosphate.

According to these results, it is supposed that Mg^{2+} interferes with apatite layer formation on glass–ceramics.

When the glass–ceramics were immersed in PECF, three phenomena appear to occur: (a) dissolution of ions (Ca^{2+}, PO_4^{3-}, Si^{4+}) from glass–ceramics, (b) adsorption of PO_4^{3-} on glass–ceramics, and (c) formation of an apatite layer.

3.3. Effect of Al_2O_3 content on apatite layer formation

Fig. 7 shows the results of immersion tests of glass–ceramics containing Al_2O_3. An apatite layer was not formed by addition of 1% Al_2O_3. According to this result, the component Al_2O_3 has a remarkable ability to prevent apatite layer formation.

Fig. 8 shows the changes of ion concentration in PECF when "CPS-Al" glass–ceramics (Table II) were immersed. Each change of ion concentration (Ca^{2+}, Si^{4+}, Mg^{2+}, PO_4^{3-}) in Fig. 8 is similar to that in Fig. 4. Al^{3+} was not detected in the PECF. The reason why an apatite layer is not formed on glass–ceramics containing Al_2O_3 is thought to be as follows. The solubility of Al^{3+} is very small, and Al^{3+} does not exist in PECF (pH 7.4). As other ions dissolve into PECF, Al_2O_3 is condensed to form an Al_2O_3-rich layer. This layer interferes with the formation of an apatite layer. As noted, the prevention mechanism of apatite formation on glass–ceramics containing Al_2O_3 is different from the mechanism for those containing MgO.

4. Conclusions

The influence of the components P_2O_5, MgO and Al_2O_3 in A–W glass–ceramics on apatite layer formation in PECF was investigated.

1. It is not necessary for glass–ceramics to contain P_2O_5 in order to form an apatite layer.

2. In glass–ceramics containing MgO, the ability of apatite layer formation decreases with increasing MgO content. The prevention of apatite layer formation on glass–ceramics containing MgO is attributed to an increase of Mg^{2+} concentration in the PECF.

3. Apatite layer formation is interfered with by slightly adding Al_2O_3 into the composition of glass–ceramics. It is thought that Al_2O_3 is condensed on the surface of the glass–ceramics, and that this layer prevents the formation of an apatite layer.

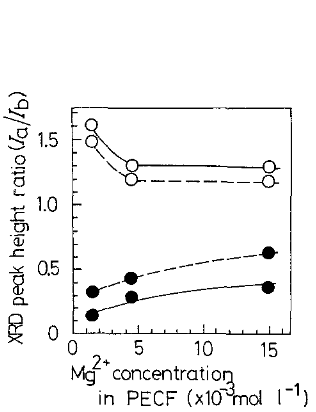

Figure 6 Effect of Mg^{2+} concentration in PECF on apatite layer formation. (○) Apatite, (●) wollastonite; (——) after immersion for 10 days, (– – –) after immersion for 20 days.

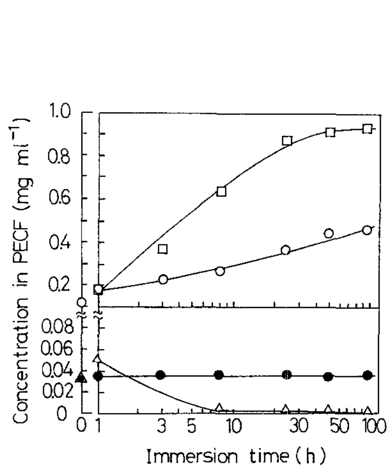

Figure 8 Ion concentrations in PECF in which "CPS-Al" glass–ceramics were immersed: (○) Ca^{2+}, (●) Mg^{2+}, (□) Si^{4+}, (△) PO_4^{3-}.

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