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Apatite coating on ceramics, metals and polymers utilizing a biological process

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A novel method of apatite coating is presented. The main characteristics of the method are that the apatite layer obtained consists of bone-like apatite and can be coated on various substrates including ceramics, metals and organic polymers. Coating is carried out in a simulated body fluid, the ion concentrations, temperature and pH of which are adjusted to almost equal to those of human blood plasma, using a plate of CaO, SiO_2-based glass as a source of nucleating agent of apatite on the surfaces of substrates. The apatite layer obtained, formed in a similar environment to that in the body, is thus expected to show higher bone-bonding ability than that formed by conventional methods, and this method is applicable to various materials having different mechanical properties.

1. Introduction

Several methods of apatite coating such as plasma spray, flame spray, sputtering, doctor blade and electrolysis have been carried out aiming at the use for medical applications. All of these methods except electrolysis, however, need heat treatment in their coating processes, so the layers obtained consist of apatite that is different from bone apatite in composition, and in the number of defects of apatite crystals and/or in the crystallites size. On the other hand, an electrolysis method requires an electrical conductor as the material to be coated. The present method improves these disadvantages.

We have shown that glass-ceramic A-W forms a bond to living bone through a bone-like apatite layer, which is formed by a chemical reaction of Ca(II) and Si(IV) ions dissolved from A-W with P(V) ions in the surrounding body fluid. In that reaction dissolved Ca(II) ions might increase the degree of supersaturation of the surrounding body fluid with respect to apatite, which is already supersaturated even in the normal state [1], while dissolved Si(IV) ions might provide favourable sites for the nucleation of apatite on the surface of the glass-ceramic [2–5]. On the basis of these findings, we speculated that the same type of bone-like apatite layer could be formed on the surfaces of non-bioactive materials if they were placed in the vicinity of a glass plate able to dissolve the Ca(II) and Si(IV) ions in a simulated body fluid, the ion concentrations, pH and temperature of which are adjusted to almost equal those of the body fluid. If such an apatite layer can be coated on various kinds of ceramics, metals and organic polymers, various highly bioactive materials with different mechanical. properties might become available.

In this study the conditions for obtaining such an apatite layer on various substrates were investigated, with a brief consideration of the mechanism of the apatite layer formation.

2. Experimental

2.1. Glass G preparation

A parent glass of glass-ceramic A-W, termed glass G hereafter, was chosen as a Ca(II) and Si(IV) ion supplier in a simulated body fluid. It was previously confirmed that glass G dissolved an appreciable amount of Ca(II) and Si(IV) ions and a small amount of P(V) ions into a simulated body fluid [5]. Glass G was prepared by pouring a melt of nominal composition (in wt %) MgO 4.6, CaO 44.7, SiO_2, 34.0, P_2O_5 16.2 and CaF_2 0.5 on to a stainless steel plate, followed by pressing with another stainless steel plate for the thickness of the glass plate obtained to be about 2 mm. Just after being pressed, the glass plate obtained was held at 700° C for 2 h in the furnace for strains in the glass plate to be removed. After furnace-cooling, the glass plate was cut into rectangular pieces of 12 mm × 18 mm × 2 mm and their surfaces were polished with 3 to 4 μm diameter diamond paste.

TABLE I Ion concentrations of simulated body fluid (SBF)

	Ion concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142	5	2.5	1.5	148.8	4.2	1	0.5
Blood plasma	142	5	2.5	1.5	103.0	27.0	1	0.5

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TABLE II Substrates examined

Silica glass (SiO_2)
Slide glass ($Na_2O–CaO–SiO_2$)
Alumina ceramic (Al_2O_3 > 99.85, MgO 0.1 wt %)
Zirconia ceramic (ZrO_2 > 94.76, Y_2O_3 5.15 wt %)
SUS 316 stainless steel (Fe > 64.34, Cr 18, Ni 12, Mo 2.5 wt %)
Titanium (Ti > 99.8 wt %)
Ti-6Al-4V (Ti > 89.7, Al 6, V 4 wt %)
Platinum (Pt > 99.95 wt %)
Gold (Au > 99.99 wt %)
Polymethylmethacrylate ($[C_5H_8O_2]_n$)
Polyethylene ($[CH_2CH_2]_n$)

2.2. SBF preparation

An aqueous solution, the ion concentrations of which were adjusted to almost equal those of the human blood plasma as shown in Table I, was prepared by dissolving the reagents NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 in ion-exchanged and distilled water. To this solution, to have the buffering function known in the body fluid, was added the buffering agent 50 mM tris-(hydroxymethyl)aminomethane ($(CH_2OH)_3CNH_2$) and 45 mM hydrochloric acid (HCl) to maintain the pH at 7.25 at 36.5° C. This is the simulated body fluid (SBF) used in this study as a soaking solution.

2.3. Immersion into SBF

The substrates examined in this study were commercial fused silica glass, slide glass, sintered alumina ceramic, sintered yttria-stabilized zirconia ceramic, SUS316 stainless steel, commercially pure titanium, Ti–6Al–4V alloy, platinum metal, gold metal, polymethylmethacrylate and polyethylene, the compositions of which are given in Table II. These were cut into rectangular pieces of 10 mm × 15 mm × 2 mm or 10 mm × 15 mm × 0.1 mm and polished with 3 to 4 μm diameter diamond paste. These were faced to glass G plates through alumina spacers for the distance between the substrate and glass G plate to be kept constant at 0.5 mm, and were bound with a nylon line. These substrate–glass G sets were immersed in 30 ml SBF at 36.5° C with polystyrene bottles as shown in Fig. 1. After 7 days of immersion the sets were removed from the bottles, separated from each other, washed gently with ion-exchanged and distilled water, and dried at room temperature.

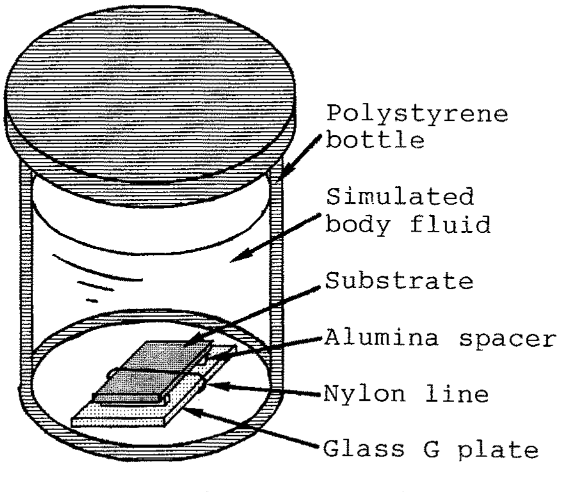

Figure 1 Arrangement of immersion of the substrate with glass G plate in the SBF.

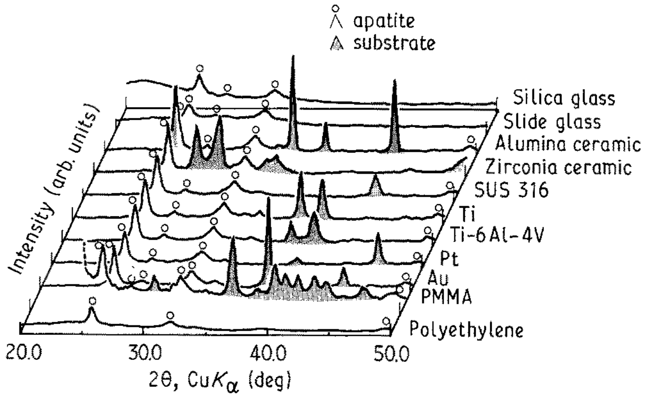

Figure 2 Thin-film XRD patterns of the surfaces of various substrates having faced glass G in SBF for 7 days.

2.4. Re-immersion into 1.5 SBF

Some of the alumina substrates, after immersion in SBF, were re-immersed in 1.5 SBF, the ion concentrations of which were those of SBF multiplied by 1.5, maintaining the relative ratios among each ion, at 36.5° C. After 7 days of re-immersion the substrates were removed from the bottles, washed gently with ion-exchanged and distilled water, and dried at room temperature. The alumina substrates, which were previously finished with a #600 diamond abrasive plate instead of 3 to 4 μm diameter diamond paste, were used in this experiment to fix a thicker apatite layer more tightly on the substrates.

2.5. Thin-film X-ray, FT-IR analyses and SEM observation

After immersion and/or re-immersion the surfaces of the substrates were subjected to thin-film X-ray diffraction (XRD), Fourier-transformed infrared (FT-IR) reflection spectroscopy and scanning electron microscopic (SEM) observation. The θ-angle of the X-ray was fixed at 1° and the reflection angle of

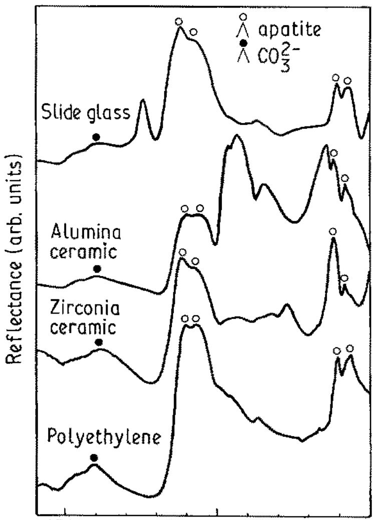

Figure 3 FT-IR reflection spectra of the surfaces of various substrates having faced glass G in SBF for 7 days.

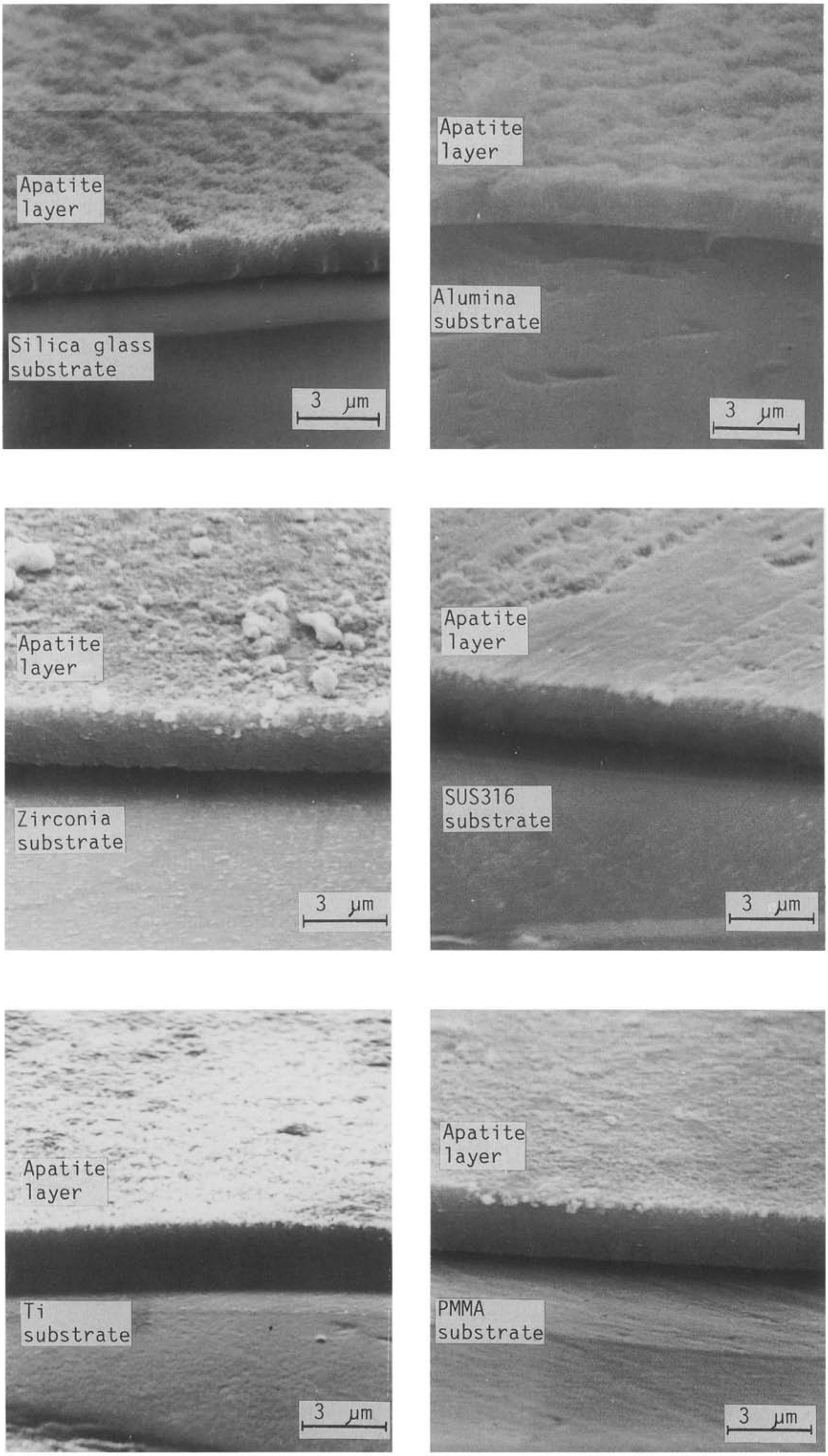

Figure 4 SEM photographs of apatite layers formed on various substrates.

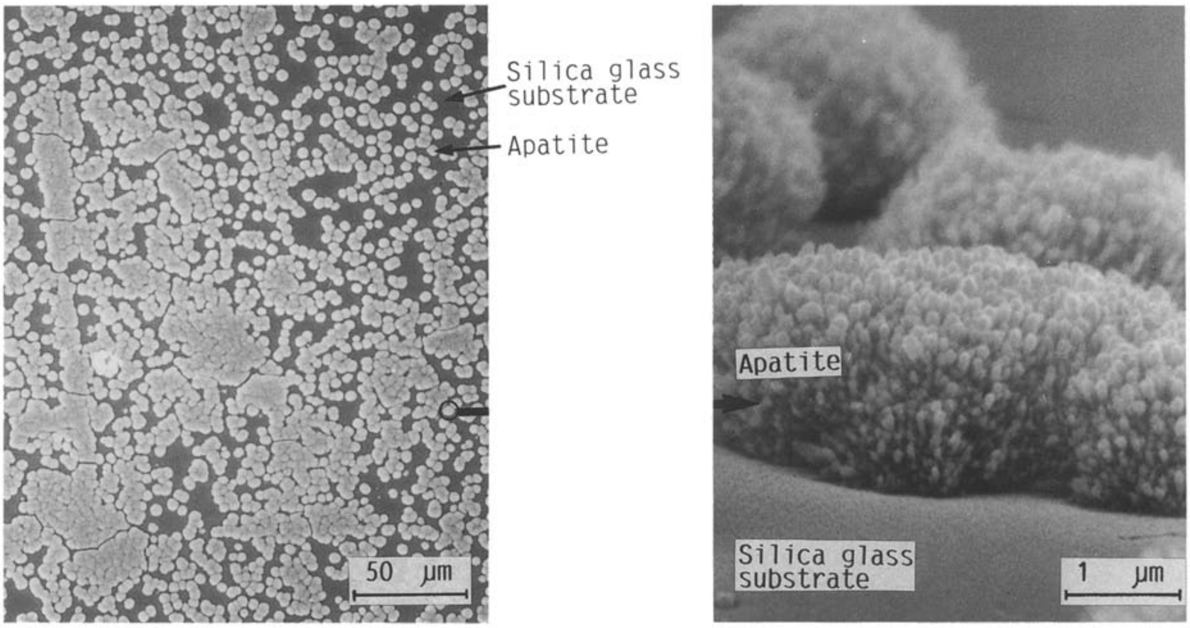

Figure 5 SEM photographs of apatite growing on the silica glass substrate at an early stage of layer formation. (a) Top view and (b) side view.

the FT-IR was chosen as 75° so that only close to the surface of the specimen could be analysed.

3. Results and discussion

3.1. Apatite formation on various substrates

Fig. 2 shows thin-film XRD patterns of the surfaces of various substrates having faced glass G in SBF for 7 days. It can be seen from Fig. 2 that all of the substrates examined are covered with apatite layers. The very large broadening of the 2 1 1, 1 1 2 and 3 0 0 reflections at 32 to 34°, and the relatively high intensity and sharpness of the 0 0 2 reflection at 26° show that very thin fibrous apatite crystallites elongated along the *c*-axis or apatite crystallites having many defects in the $(h\,k\,0)$ plane are oriented perpendicularly to the substrate.

Fig. 3 shows the FT-IR reflection spectra of the same surfaces of the slide glass, alumina ceramic, zirconia ceramic and polyethylene as in Fig. 2. It can be also seen from Fig. 3 that all of the substrates examined were covered with apatite layers. A broad reflection peak observed at $1400\,\mathrm{cm}^{-1}$, which is ascribed to CO_3^{2-} ion, shows that the apatite obtained is carbonate-containing hydroxyapatite. The crystal structural and compositional characteristics seen from Figs 2 and 3 are of the same nature as that seen in natural bone. The apatite layer obtained can hence be called the "bone-like" apatite layer.

Fig. 4 shows SEM photographs of the same surfaces of the silica glass, alumina ceramic, zirconia ceramic, pure titanium, SUS 316 stainless steel and polymethylmethacrylate as Fig. 2. It can be seen from Fig. 4 that apatite crystals take a form of continuous and homogeneous layer about 1 µm thick on all of these substrates.

Figs 5a and b show SEM photographs of the surface of silica glass substrate at an early stage of apatite formation. Fig. 5a is a top view and Fig. 5b is a side view taken at an angle of 30°, enlarging a part of Fig. 5a. It can be seen from Fig. 5b that very thin fibrous apatite crystals are growing radially from some points on the surface. It is apparent that at an early stage of apatite formation the same phenomena must occur on all of the substrates examined in this study. Figs 5a and b lead us to the following coating mechanism; first, silicate ions dissolved from the glass G plate are adsorbed on the substrate; secondly, apatite nucleation occurs from on the adsorbed silicate ions; thirdly, apatite nuclei grow directly on the substrate by a reaction with SBF, which is supersaturated to apatite [1]. If this speculation is true, it can be thought that bone-like apatite layers are coated on all of the substrates that are stable in SBF, i.e. dissolve no inhibitors of apatite nucleation in SBF.

3.2. Conditions for the layer formation

Fig. 6 shows thin-film XRD patterns of the surfaces of alumina substrates immersed in SBF with various substrate–glass G distances. It can be seen from Fig. 6 that a distance of 0.5 mm gave the strongest X-ray intensities of apatite relative to those of the alumina

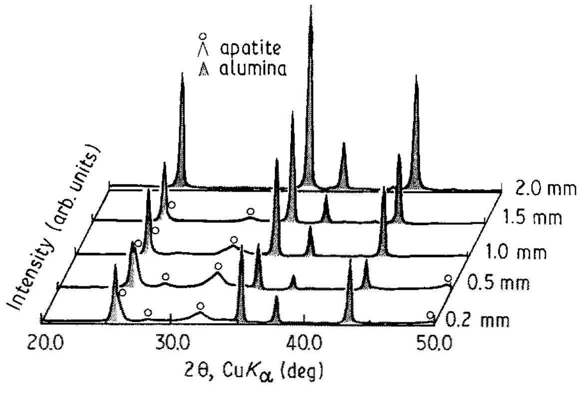

Figure 6 Thin-film XRD patterns of the surfaces of alumina substrates having faced glass G in SBF for 7 days with various glass G–substrate distances.

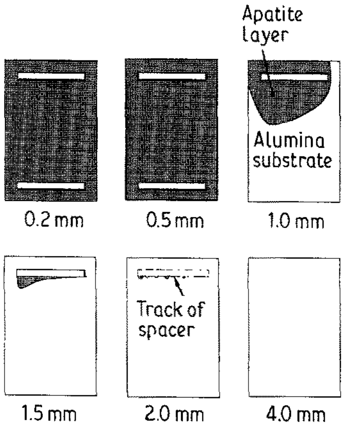

Figure 7 Apatite-formed area on alumina substrates as a function of glass G–substrate distance.

substrate, and apatite intensities decrease as the distance changes from 0.5 mm.

Fig. 7 is a schematic representation of the apatite-formed area on the alumina surfaces as a function of the substrate–glass G distance. It can be seen that the apatite layer covers the whole surface of the substrate only when the distance is $\leqslant 0.5$ mm. In Fig. 6, the intensities of apatite formed at different distances of 0.2 and 0.5 mm, both of which cover the whole surfaces of the substrates, show that the thickness of the layer made at 0.5 mm is greater than that at 0.2 mm. The relationship between the layer formation and substrate–glass G distance can be summarized from Figs 6 and 7 as that in the range 0.2 to 0.5 mm apatite covers the whole surface and the thickness increases with increasing distance; in the range 0.5 to 1.5 mm the coverage ratio decreases abruptly; and in the range 2 to 4 mm little apatite formation occurs. The result shows that the apatite layer formation depends strongly on the ion concentration in the vicinity of the surface of the substrates, where the degree of supersaturation of SBF to apatite increases with increasing Ca(II) and P(V) ions dissolved from glass G and the amount of Si(IV) ions adsorbed on the substrate, which act as a nucleating agent, also increases. The layer can accordingly be formed more easily as the substrate locates closer to glass G. Conversely, it may seem from Fig. 6 that in the range 0.2 to 0.5 mm the layer inclines to be easily formed with increasing distance because the thickness increases with increasing distance. This result contains, however, two steps of the apatite layer formation mentioned above: the apatite nucleation and the apatite crystal growth. The former controls the coverage ratio and the latter affects the thickness. Once nucleation occurs, the glass is not needed because it interferes with ion flows in the solution and apatite formed on glass G itself consumes Ca(II) and P(V) ions, thereby lowering the degree of supersaturation near the surface of the substrate.

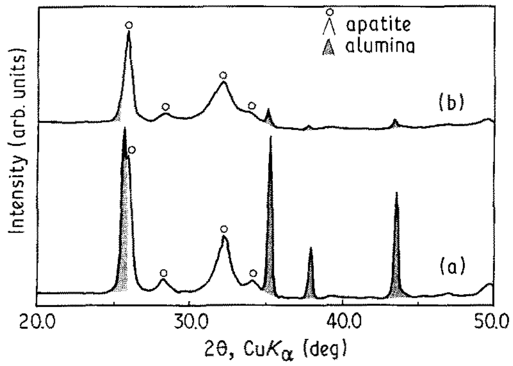

Figure 8 Thin-film XRD patterns of the surfaces of alumina substrates: (a) immersed in SBF and (b) re-immersed in 1.5 SBF.

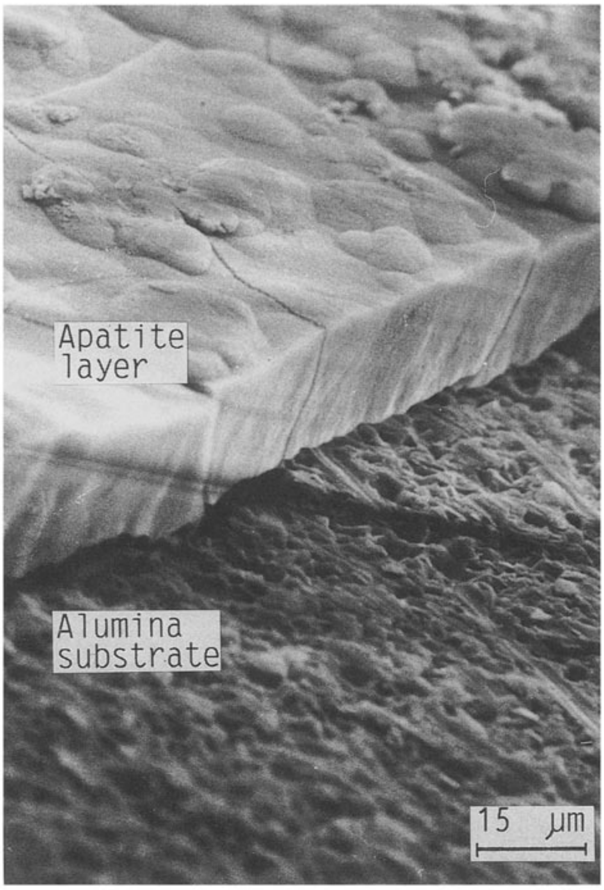

Figure 9 SEM photograph of an apatite layer formed on an alumina substrate re-immersed in 1.5 SBF.

3.3. Layer thickening

Fig. 8 shows thin-film XRD patterns of the surfaces of alumina substrates before and after re-immersion in 1.5 SBF following immersion in SBF by the use of glass G. It can be seen from Fig. 8 that re-immersion increases the apatite X-ray intensities while having no effect on the crystal phase of the layer.

Fig. 9 shows an SEM photograph of the same specimen used in Fig. 8b. It can be seen from Fig. 9 that the thickness of the layer increases up to about 15 μm. The 1.5 SBF solution, having ion concentrations 1.5 times as large as those of SBF, accordingly increases the degree of supersaturation to apatite. In such a solution apatite can grow spontaneously, even without glass G, on the substrate which has apatite seeds.

4. Conclusions

This study showed that a continuous and homogeneous bone-like apatite about 1 μm thick could be coated on all of the substrates examined, including glasses, sintered ceramics, metals and organic polymers, by the use of both the glass and aqueous solution, and that the thickness could be increased up to about 15 μm with successive immersion in 1.5 SBF. This novel method, carried out in an environment similar to that in the body, is therefore expected to enable a bone-like apatite layer to be produced which shows higher bioactivity than those coated by other methods such as plasma or flame spraying of hydroxyapatite. This novel method might give various kinds of highly bioactive materials with different mechanical properties, since the apatite layer can be formed even on organic materials as well as on inorganic and metallic materials.

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