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Mechanism of apatite formation on wollastonite coatings in simulated body fluids

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Abstract

The formation mechanism of apatite on the surface of wollastonite coating was examined. Plasma-sprayed wollastonite coatings were soaked in a lactic acid solution (pH = 2.4) to result in the dissolution of calcium from the coating to form silanol (≡Si–OH) on the surface. Some calcium-drained samples were soaked in a trimethanol aminomethane solution (pH = 10) for 24 h to create a negatively charged surface with the functional group (≡Si–O$^-$). These samples before and after treatment in a trimethanol aminomethane solution were immersed in simulated body fluids (SBF) to investigate the precipitation of apatite on the coating surface. The results indicate that the increase of calcium in the SBF solution is not the critical factor affecting the precipitation of apatite on the surface of the wollastonite coating and the apatite can only form on a negatively charged surface with the functional group (≡Si–O$^-$). The mechanism of apatite formation on the wollastonite coating is proposed. After the wollastonite coatings are immersed into the SBF, calcium ions initially exchange with H$^+$ leading to the formation of silanol (≡Si–OH) on the surface of the layer and increase in the pH value at the coating–SBF interface. Consequently, a negatively charged surface with the functional group (≡Si–O$^-$) forms on the surface. Due to the negatively charged surface, Ca^{2+} ions in the SBF solution are attracted to the interface between the coating and solution, thereby increasing the ionic activity of the apatite at the interface to the extent that apatite precipitates on the coating surface.

Keywords: Wollastonite coating; Mechanism; Apatite; Simulated body fluids

1. Introduction

Since the 1990s, wollastonite ($CaSiO_3$) ceramics have been studied as artificial materials for artificial bones and dental roots because wollastonite exhibits good bioactivity and biocompatibility. Some investigators have reported that wollastonite and pseudowollastonite ceramics are bioactive and observed that the formation of apatite on $CaSiO_3$ ceramics is faster than that on other bioglass and glass-ceramics in simulated body fluids (SBF) [1–4]. In our previous work, wollastonite was deposited onto Ti–6Al–4V substrate by plasma spraying and then immersed into the SBF solution to investigate its bioactivity and bone-like apatite was formed on the surface of the soaked plasma-sprayed wollastonite coatings [5–7]. Other studies have indicated that the essential condition for a bone implant to bond to a living bone is the formation of a bone-like apatite layer on its surface [8–10]. Hence, it is important to determine the mechanism of apatite formation on the surface of wollastonite coatings.

It has been reported that most bioactive glasses and glass-ceramics form a carbonate-containing hydroxyapatite layer similar to apatite on the bone surface in the body and bond to the living bone via this apatite layer [11,12]. The mechanism of apatite formation on CaO–SiO_2-based bioactive glasses has been discussed. Ohtsuki et al. have shown that calcium ions dissolved from CaO in the SiO_2-based glasses increase the degree of supersaturation of the surrounding body fluid with respect to the apatite, and the hydrated silica formed on their

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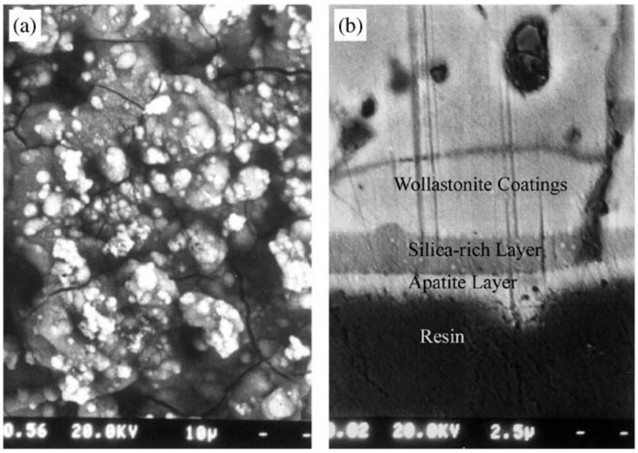

Fig. 1. SEM micrographs of the: (a) surface; and (b) cross-section of the wollastonite coating soaked in SBF solution for 2 days.

surface provides specific favorable sites for apatite nucleation [13]. Li et al. have applied a ‘charged surface’ theory to explain the reaction of bioactive glass in simulated physiological solution and it is believed that precipitation of apatite on the surface of the bioactive glass soaked in SBF is due to the formation of an electric double layer in the glass-solution system [14]. Takadama et al. investigated the mechanism of biomineralization of apatite on a sodium silicate glass using TEM-EDX and also proposed that the formation of apatite on the surface of sodium silicate glass was mainly attributed to the charge surface [15]. Therefore, the formation of charge surface on the bioceramics and bioglasses is thought to be very important to the precipitation of apatite.

The composition of wollastonite is similar to that of CaO–SiO_2-based bioactive glasses and glass-ceramics, and so the mechanism of apatite formation on wollastonite coatings may be similar. Calcium dissolved from the wollastonite coating is believed to increase the ionic activity of the apatite in the SBF leading to the formation of apatite on the coating surface [5]. The schematic of the apatite formation on the coating surface is illustrated in Fig. 1. In the work reported here, the roles of calcium and silica-rich layer in forming the apatite on the surface of wollastonite coatings are investigated and a mechanism is proposed. The formation and importance of the charge surface of wollastonite coating are also discussed in detail in this work.

2. Experimental

Commercial wollastonite ($CaSiO_3$) powders with a typical size between 10 and 60 μm were deposited onto Ti–6Al–4V substrates of size 10 mm × 10 mm × 2 mm using an atmospheric plasma spray (APS) system (Sulzer Metco, Switzerland) and modified spraying parameters. After ultrasonically cleaned in acetone and rinsed in deionized water, the specimens coated with wollastonite were soaked in a lactic acid solution (pH = 2.4) for 1, 3 and 7 days. These samples are denoted WL1, WL3 and WL7, respectively. Some WL3 specimens were rinsed in deionized water and soaked in a trimethanol aminomethane solution (pH = 10) for 24 h and they are designated as WL3T. Afterwards, the as-sprayed coating, WL3 and WL3T were soaked in the SBF solution whose ion concentrations are nearly equal to those of the human body blood plasma [16] for 4 days. In this work, after the WL3 and WL3T samples were taken out from lactic acid and the trimethanol aminomethane solution, they were rinsed using deionized water and then immediately soaked in the SBF solution but were not air-dried. The SBF solution was buffered at a pH of 7.4 with trimethyl aminomethane and HCl. In addition, the coatings after treatment by lactic acid for 3 days were soaked in the SBF solution with $2[Ca^{2+}]$ (the concentration of calcium is 5 mM and those of the other ions are equal to that of SBF solution) to evaluate the role of calcium in the SBF.

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) analysis were used to observe the morphologies and determine the composition of the coatings before and after immersion. The surface of the samples was sputter-coated with gold prior to the morphology observation or with carbon for elemental analysis. The elemental profiles were acquired by Auger electron spectroscopy (AES).

3. Results

The surface morphology and EDS spectra of the wollastonite coatings before and after immersion in the lactic acid solution (pH = 2.4) for 1, 3 and 7 days are depicted in Fig. 2. The rough surface morphology of the as-sprayed wollastonite coating indicates that the coating is formed by melted particles (Fig. 2a) and it is suitable as biomaterials. After immersion in the lactic acid solution for 1 day, the coating surface undergoes an obvious change. A thin layer characterized by micro-cracks manifests on the coating surface (Fig. 2b). With increasing immersion time, the calcium in the coating gradually dissolves into lactic acid solution (Figs. 2c and d) and eventually most of the calcium dissolves from the coating into lactic acid solution. A silica-rich layer forms on the surface of the wollastonite coating after immersion in the lactic acid solution.

Our previous work indicates that apatite forms on the surface of the wollastonite coating after immersion in SBF for 1 day. Fig. 3 depicts the top view and EDS spectrum of WL3 after immersion in SBF for 4 days. Only silicon and oxygen can be detected using EDS but no calcium or phosphorous can be found. This indicates

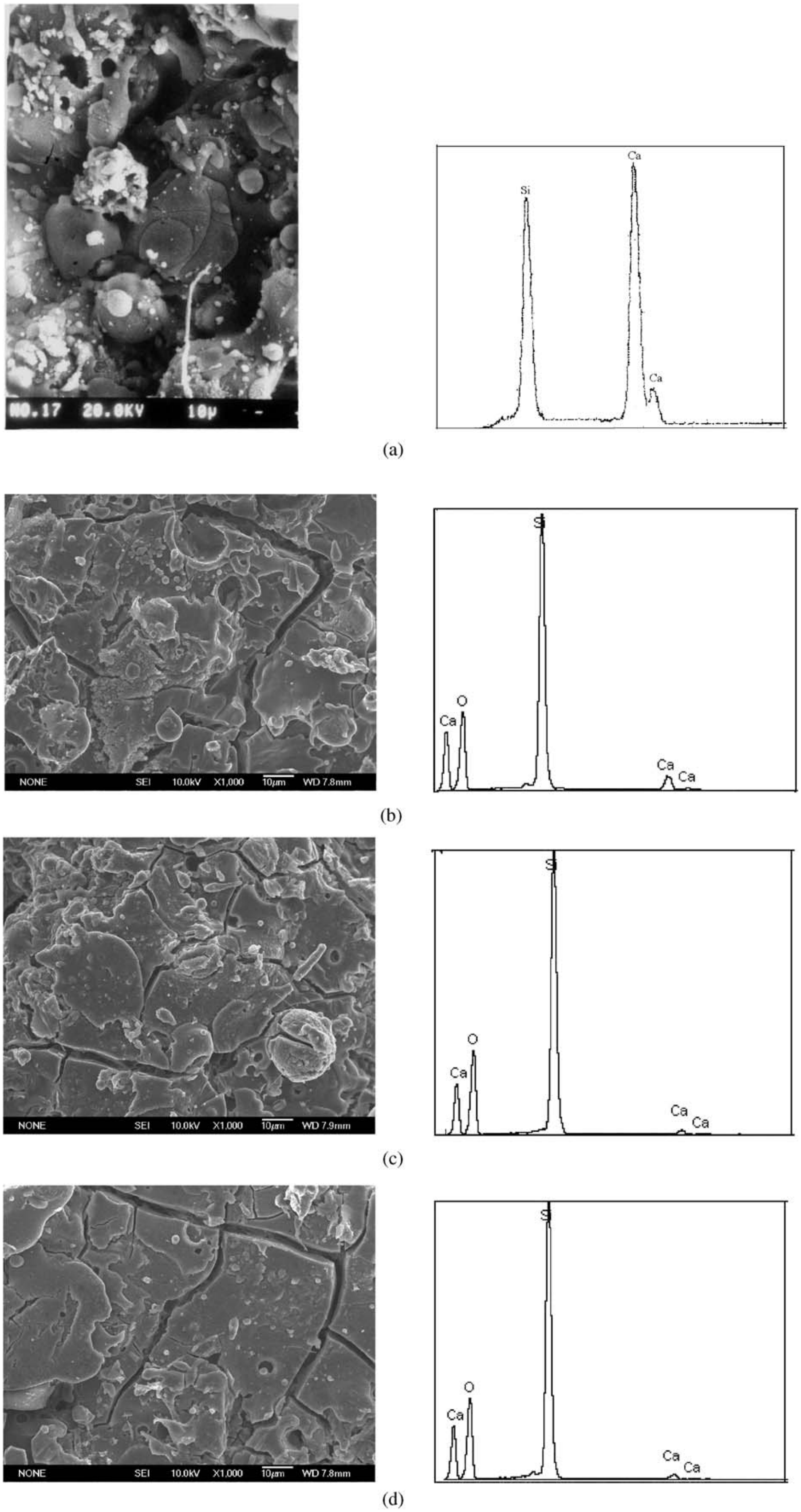

Fig. 2. Top view and EDS spectra of the: (a) as-prayed wollastonite coatings; (b) after immersion in lactic acid solution for 1 day; (c) 3 days; and (d) 7 days.

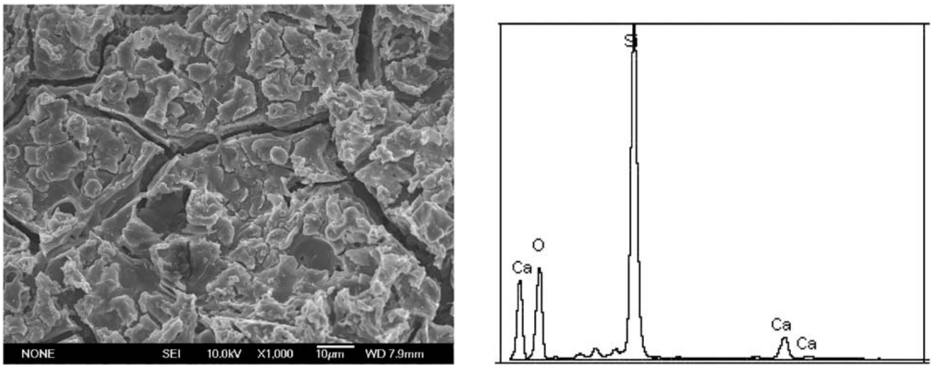

Fig. 3. Top view and EDS spectrum of WL3 after immersion in SBF for 4 days.

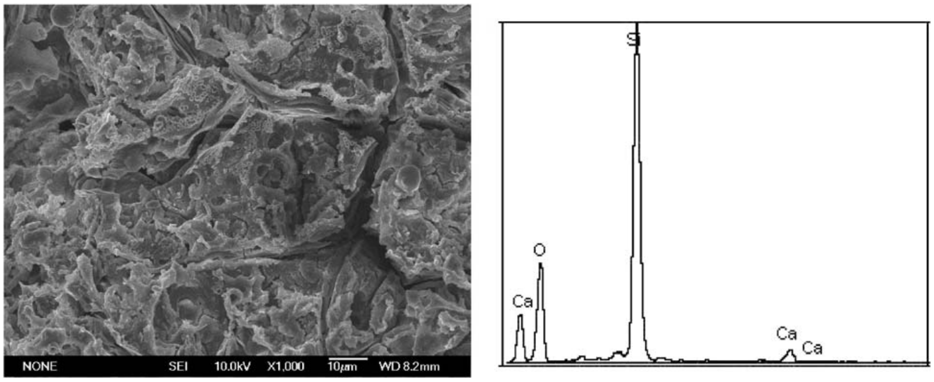

Fig. 4. SEM photograph and EDS spectrum of the surface of WL3 after immersion in a 2[Ca^{2+}] SBF solution for 4 days.

that apatite cannot precipitate on the silica-rich surface of the WL3.

The ionic activity product (IP) of the apatite in the SBF solution has been considered to be key to the formation of apatite on the surface of the substrate. The increase in the calcium ion concentration and pH of the SBF solution can result in the increase in the IP of the apatite and is beneficial to the precipitation of apatite on the surface of the substrate [5]. In this work, the WL3 was soaked in the 2[Ca^{2+}] SBF solution to investigate the contribution of calcium to the formation of apatite. The SEM photograph and EDS spectrum of the surface of WL3 after immersion in the 2[Ca^{2+}] SBF solution for 4 days are displayed in Fig. 4. No apatite formation can be observed on the silica-rich surface of WL3, and so it can be inferred that the increase of the calcium concentration in the SBF solution is not the critical factor affecting precipitation of apatite on the surface of the wollastonite coating.

The SEM micrograph and EDS spectrum of WL3T after immersion in SBF for 4 days are depicted in Fig. 5. The surface of the wollastonite coating is completely covered by the ball-like particles. Micro-cracks resembling a tortoise shell appear on the newly formed layer. Under higher magnification, the apatite layer exhibits very small crystallites (Fig. 5a). The EDS spectrum indicates that the granules are composed of mainly calcium and phosphorus (Fig. 5b). The Na, Mg and Cl in the EDS spectrum originate from the SBF. Quantitative analysis yields a Ca to P ratio of around 1.6 that is nearly the composition of apatite. There is obvious difference between the surface with apatite and without apatite. The surface without apatite shows a silica-rich layer as shown in Fig. 5c.

4. Discussion

The composition of the wollastonite coating is similar to that of calcium silicate glass. Therefore, the reaction mechanism of the wollastonite coating in an aqueous solution can in principle be explained similar to that of alkali-silicate and alkali-lime silicate glasses [14]. When the wollastonite coating is immersed in the lactic acid solution, ion exchange occurs between the surface layer of the coatings and the solution as a result of the different chemical potentials of the ions. Coupled with the dissolution of calcium ions from the coating surface into the solution and the penetration of protons from the lactic acid solution into the coating surface, silanol

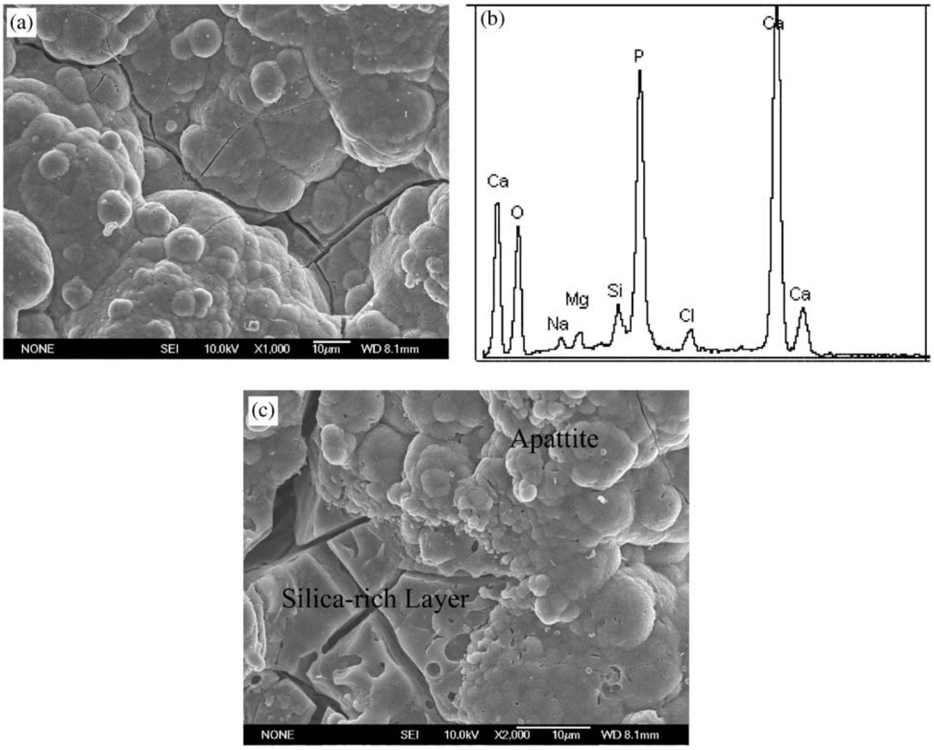

Fig. 5. Top view and EDS spectrum of WL3T after immersion in SBF for 4 days.

(≡Si–OH) is produced in the surface layer:

$$\equiv \mathrm{Si-O-Ca-O-Si} \equiv +2\mathrm{H}^+ = 2 \equiv \mathrm{Si-OH} + \mathrm{Ca}^{2+} \quad (1)$$

After immersion into the lactic acid solution and trimethanol aminomethane solution (pH = 10), the following reaction takes place on the surface of the coating:

$$\equiv \mathrm{Si-OH} + \mathrm{OH}^- = \equiv \mathrm{Si-O}^- + \mathrm{H_2O}. \quad (2)$$

A negatively charged surface with the functional group (≡Si–O$^-$) is created.

The surface charge of a substrate plays an important role in the reaction of the substrate in an aqueous solution. A negatively charged surface attracts cations from the solution to decrease the total energy of the system, thus leading to an increase of cations at the interface. This region, consisting of a charged surface and an equal but opposite charge in the solution, is called an electric double layer in which compounds may form on the coating surface under suitable conditions. Therefore, when the coating is treated by lactic acid and trimethanol aminomethane, for instance, WL3T, and immersed in SBF solution, Ca^{2+} in the SBF solution is initially attracted to the interface between the coating and solution. It is reasonable that the IP of the apatite at the interface is higher than that in the bulk solution. When the IP of the apatite at the interface is high enough, apatite precipitates on the coating surface. As soon as the apatite nucleates on the surface of the coating, spontaneous growth occurs and calcium and phosphate ions are consumed from the surrounding body fluid.

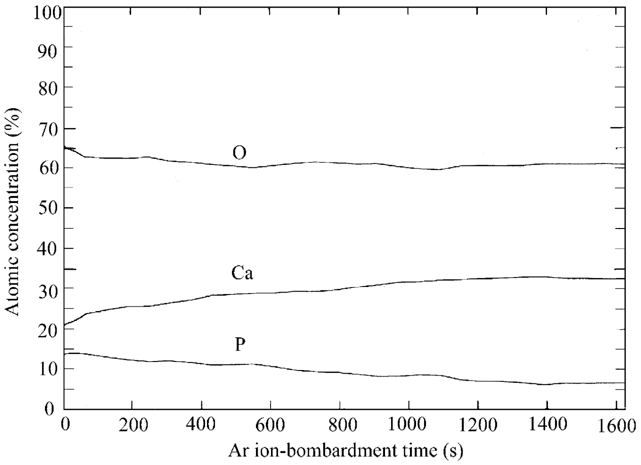

Fig. 6. Auger depth profile acquired of the wollastonite coatings soaked in SBF 12 h.

The mechanism of apatite formation on the surface of the wollastonite coating in the SBF can be interpreted as follows. When the as-sprayed wollastonite coating is immersed in the SBF, calcium ions in the coating first exchange with H^+ in the solution leading to the formation of silanol (≡Si–OH) in the surface layer, a pH increase, and finally the production of a negatively

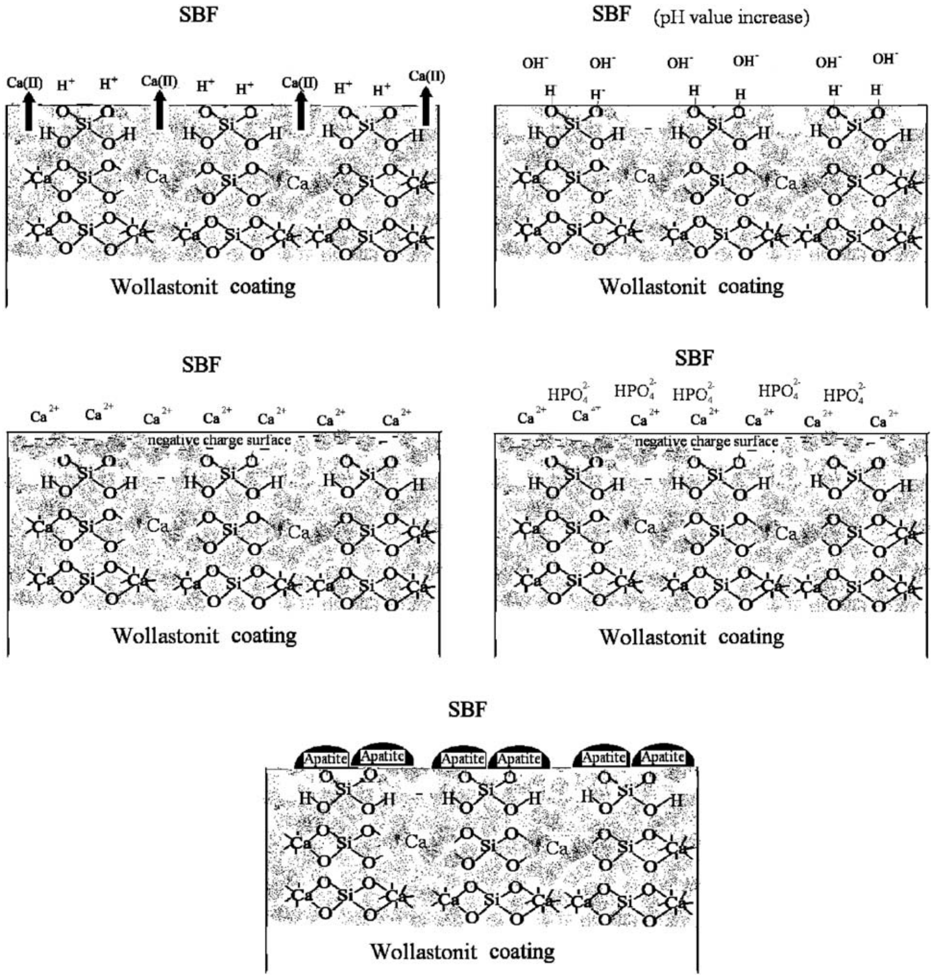

Fig. 7. Schematic diagram of the mechanism of apatite formation on the wollastonite coating in SBF (formation sequence is from (1) to (5)).

charged surface with the functional group (≡Si–O$^-$). The Ca ions in the SBF solution are initially attracted to the interface between the coating and solution. The Auger depth profile acquired from the surface of the wollastonite coatings soaked in SBF for 12 h is displayed in Fig. 6. The phosphorus concentration diminishes but that of calcium increases with depth. It indicates that calcium accumulation on the silica-rich layer takes place prior to that of phosphorus. Subsequently, the IP of the apatite at the interface is high enough such that apatite precipitates on the coating surface. The mechanism of apatite formation on the wollastonite coating in SBF is schematically illustrated in Fig. 7.

5. Conclusion

Apatite is formed on the surface of plasma sprayed wollastonite coatings soaked in simulated body fluid (SBF) solution. The apatite can only form on a negatively charged surface with a functional group (≡Si–O$^-$). The increase of the calcium concentration in the SBF solution is not the critical factor affecting the precipitation of apatite on the surface of the wollastonite coating. The mechanism of apatite formation can be envisaged as follows. When the wollastonite coating is immersed in the SBF, calcium ions in the wollastonite coating exchange with H$^+$ in the SBF solution leading to the formation of silanol (≡Si–OH) in the surface layer, an increase in the pH value at the coating–SBF, and eventually the production of a negatively charged surface with the functional group (≡Si–O$^-$). The Ca ions in the SBF solution are first attracted to the interface between coating and solution and consequently, the ionic activity product of the apatite in the interface is high enough to precipitate apatite on the coating surface.

Acknowledgements

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