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Developments of plasma-sprayed biomedical coatings

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Developments in the field of plasma-sprayed biomedical coatings are presented in this paper. Plasma-sprayed hydroxyapatite (HA)/Ti composite coatings were fabricated to enhance the bonding strength between coating and the Ti-6Al-4V substrate and the issue of bioactivity and biocompatibility were addressed. The Ti coating possesses high mechanical strength as well as excellent biocompatibility, but has no bioactivity. A NaOH solution was used to treat the Ti coating and bioactivity of Ti coating was achieved. A new biomedical coating, wollastonite coating, has been fabricated successfully *via* plasma spraying as well. A simulated body fluid (SBF) test gave the testimony of excellent bioactivity for the coating.

Key words: biomedical coating, plasma spray, HA, Ti, Wollastonite.

Introduction

Plasma spraying has been around for more than four decades and has been applied to deposit a wide range of metals, ceramics and even composite materials for many different applications [1]. Biomedical application of these coatings has become one of the most important fields. Plasma-sprayed biomedical coatings on Ti alloy substrates have been widely used as implant materials in orthopedics and dentistry because of their high level of biocompatibility as well as mechanical strength.

Despite the successful application of plasma-sprayed coatings in the biomedical field, there has still been a great interest among material scientists and orthopedists to develop these coatings to meet the increasing demands of patients. Although the HA coating possesses an excellent biological property, the bonding condition between the coating and the Ti-6Al-4V substrate should be improved [2]. In this work, plasma-sprayed HA/Ti composite coatings were fabricated to enhance the bonding strength. Take advantage of its high mechanical strength and good biocompatibility, Ti coating has been used as orthopedic and dental implant material [3, 4]. However, Ti coating doesn't possess bioactivity. While embedded in the body, a fibrous tissue isolating it from the surrounding bone is formed on its surface instead of forming a direct bond to living bone. To endow Ti coating bioactivity, NaOH solution was used to modify the coating. A new biomedical coating, namely wollastonite ($CaSiO_3$), was developed successfully and its biological property was examined as well.

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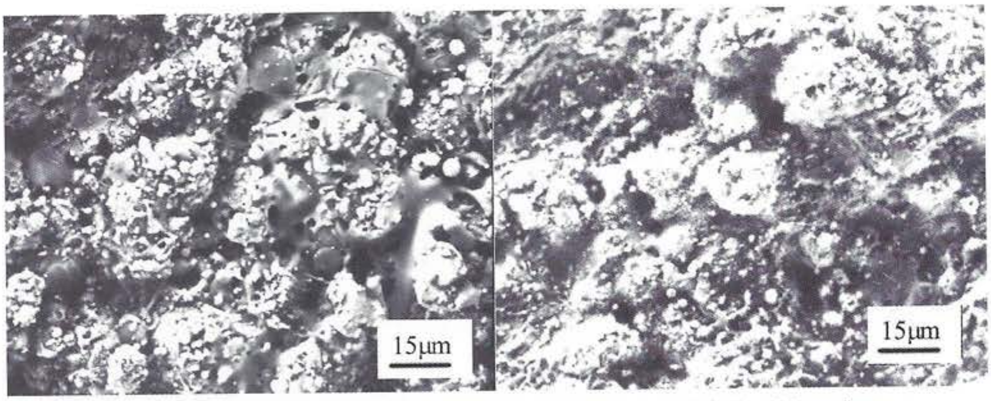
HA/Ti Composite Coating

In order to improve the bonding strength of plasma-sprayed HA coating, HA/Ti composite coatings on Ti-6Al-4V substrate were fabricated. Commercially available HA and Ti powders, with typical size ranges of 45-160 μm and 60-100 μm respectively, were mixed in a ball mill pulverizer for 5 hrs. Mixed powders were deposited onto Ti-6Al-4V substrates using a plasma spraying system (Sulzer Metco, Switzerland).

The morphologies of the plasma-sprayed HA/Ti composite coatings are shown in Fig. 1. The HA/Ti composite coating with Ti 20 wt% was characterized by a rough surface and some pores (Fig. 1a). The HA/Ti 60 wt% coating possessed a rougher surface and more pores along but with no distinct cracks, as can be seen from Fig. 1b. As a biomaterial, a rough surface and appropriate pores are considered to be beneficial to bonding with surrounding tissues *in vivo*.

The results of bonding strength evaluation according to ASTM C-633 are shown in Fig. 2. Figure 2 indicates that the mean bond strength is heightened from [illegible] MPa of the HA coating to 17.5 MPa and 23.5 MPa when reinforcing the coating with 20 and 60 wt% Ti respectively. The relatively poor adhesion of pure HA coating mainly arises from the mismatch of the thermal expansion coefficients between the Ti alloy substrate and HA coating [5]. The mismatch of the thermal expansion coefficients is reduced and most of the residual stress occurred during the plasma spray process is prevented by addition of Ti into the HA coating. Furthermore, the bonding strength of the Ti coating is very high. The average datum for the Ti coating on the Ti-6Al-4V substrate is 35.0 MPa. This is enough to prove that the addition of Ti into the HA coating can reinforce the adhesion of the coating to the substrate.

An SBF test was carried out to examine the bio-



(a) HA/Ti 20 wt% coating (b) HA/Ti 60 wt% coating

Fig. 1. Surface morphologies of HA/Ti composite coatings.

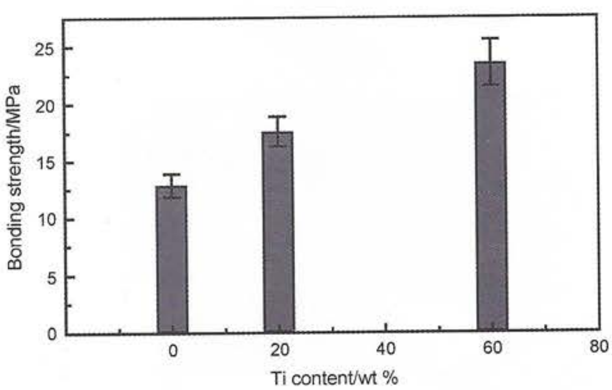


Fig. 2. Bonding strengths of HA coating and HA/Ti composite coatings.

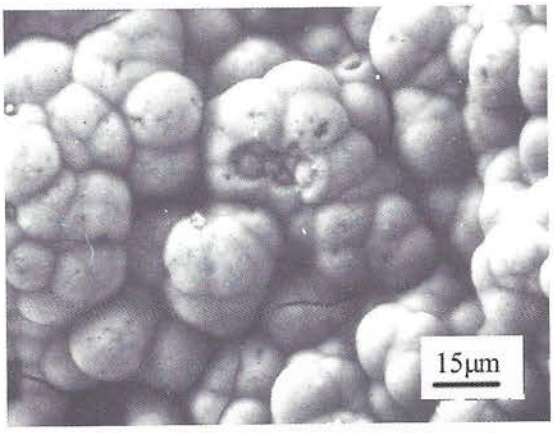


Fig. 3. Surface morphology of HA/Ti 60 wt% composite coating after being immersed in SBF for 7 days.

activity of the HA/Ti 60 wt% composite coating. The composition of the SBF has been tabulated elsewhere [2]. An SEM picture of the HA/Ti 60 wt% composite coating after being immersed in SBF is given in Fig. 3. Figure 3 shows that the coating surface is completely covered by a newly-formed dune-like layer after being immersed in SBF for 7 days. A fourier transform infrared (FT-IR) spectrum of the layer is shown in Fig. 4. In Fig. 4, the peaks appearing in 1000-1150 cm^{-1}

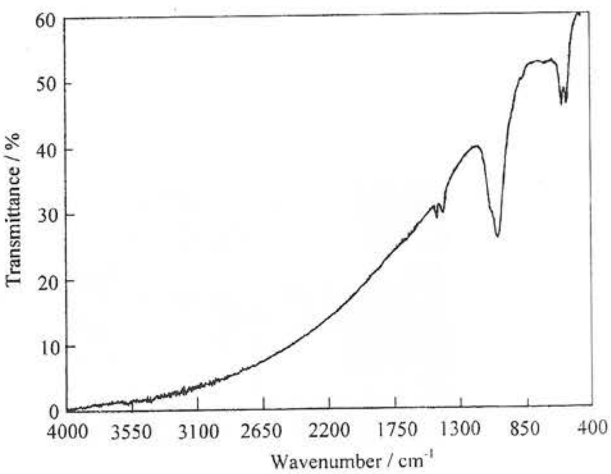


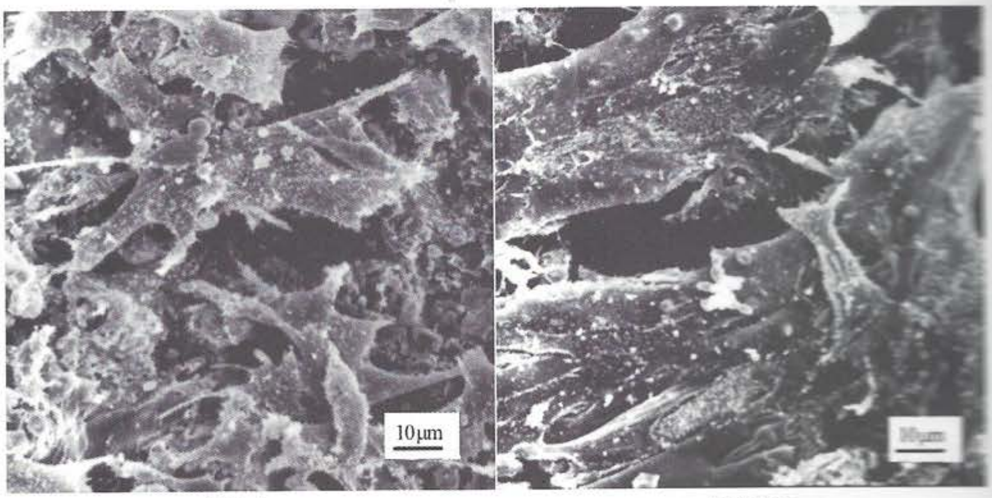
Fig. 4. FT-IR spectrum of HA/Ti 60 wt% composite coating after being immersed in SBF for 7 days.

and 550-650 cm^{-1} are attributed to the vibration of P-O in the PO_4 group and the peaks of 1450-1500 cm^{-1} belong to the vibration of C-O in the CO_3 group. This indicates that the newly-formed layer on the coating surface in the SBF is carbonate-containing apatite. The formation of carbonate-containing apatite is considered to be one of the characteristics of bioactivity for biomaterials [6, 7]. It is evident that the addition of Ti in HA coating doesn't affect the bioactivity significantly.

Osteoblasts isolated from neonatal rat calvaria were cultured on the HA/Ti 60 wt% composite coating. The appearance of osteoblasts examined by SEM is shown in Fig. 5. Osteoblasts grow very well and tightly attach to the coating surface after being cultured for 4 days (Fig. 5a). After 7 days, osteoblasts completely spread on the coating surface forming a continuous layer in which individual cells are indistinguishable. The osteoblasts cultures prove good cytocompatibility of the coating.

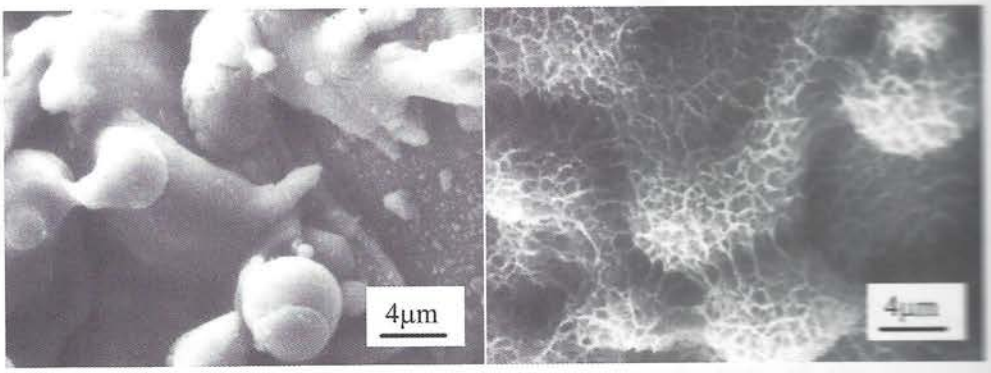
Bioactive Ti Coating

The Ti coating was deposited via vacuum plasma



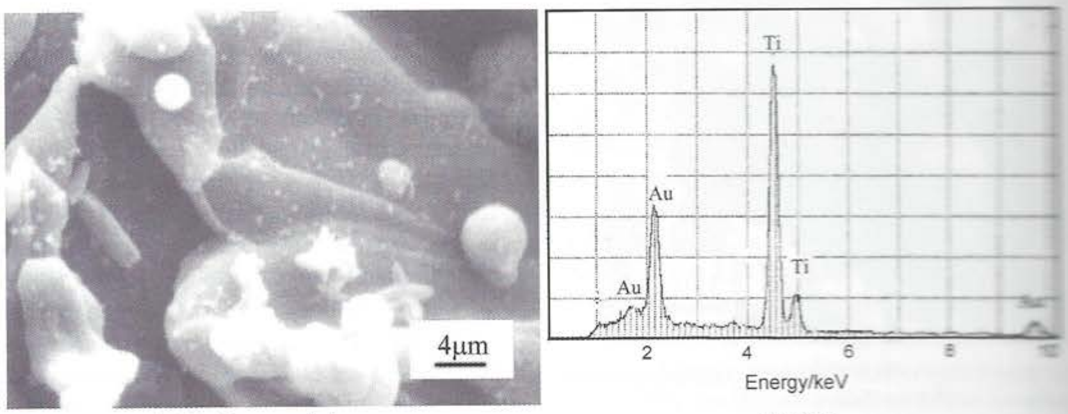
(a) 4 days (b) 7 days

Fig. 5. Morphologies of Osteoblasts cultured on HA/Ti 60 wt% composite coating.



(a) as-sprayed (b) NaOH-treated

Fig. 6. Surface morphologies of as-sprayed and NaOH-treated Ti coatings.

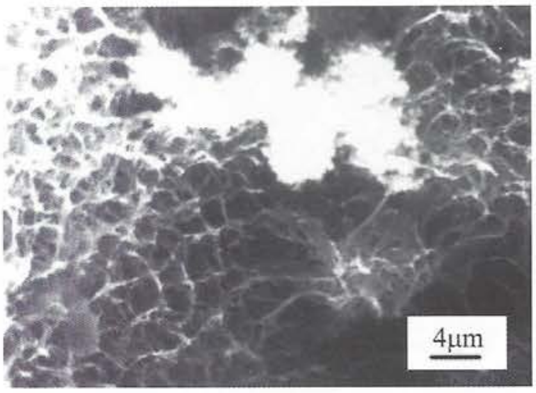


(a) Surface morphology (b) EDS

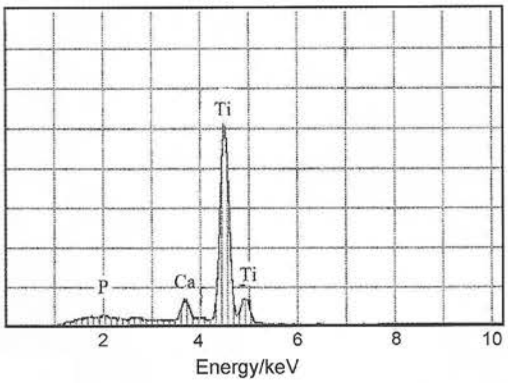
Fig. 7. Surface morphology and EDS of as-sprayed Ti coating after immersed in SBF for 14 days.

spraying using Ti powder of 60-100 μm. Surface modification of the Ti coating was performed in 5.0 M NaOH solution at 40-60°C for 24 h. The bioactivity of the as-sprayed and NaOH-modified Ti coatings were evaluated by an SBF test.

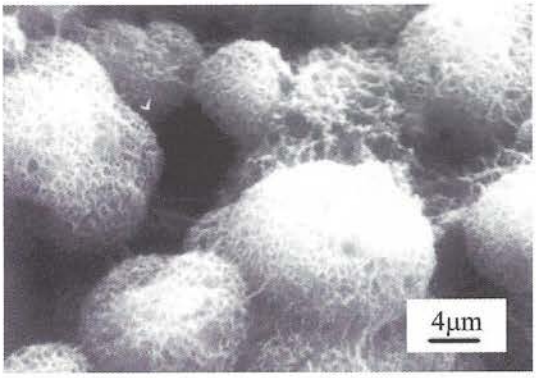
Figure 6 shows surface morphologies of surfaces of Ti coatings before and after surface modification by NaOH solution. A smooth and flattened particle morphology of the as-sprayed coating can be observed in Fig. 6a. Due to the attack of NaOH, fibrous and net-like structure is formed on the coating surface after treatment in the NaOH solution (Fig. 6b).



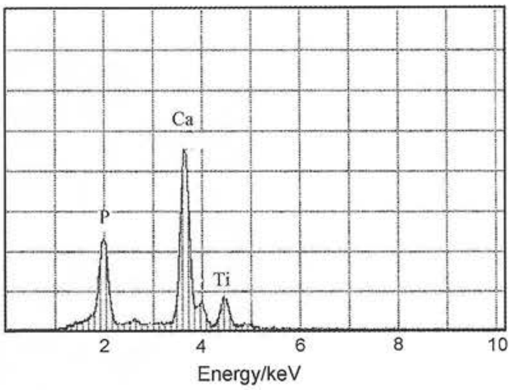
(a) 7 days



(b) EDS of (a)



(c) 14 days

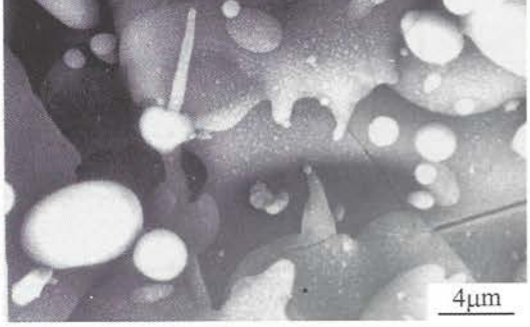


(d) EDS of (c)

Fig. 8. Surface morphologies and EDS of NaOH-modified Ti coatings after immersed in SBF.

The SEM photograph and corresponding energy dispersive spectrum (EDS) of the as-received Ti coating after immersion in the SBF are shown in Fig. 7. No obvious change is distinguished for Ti coating after immersed in SBF for 14 days while comparing Fig. 7a with Fig. 6a. The corresponding EDS indicates that no Ca and P elements appear on the coating.

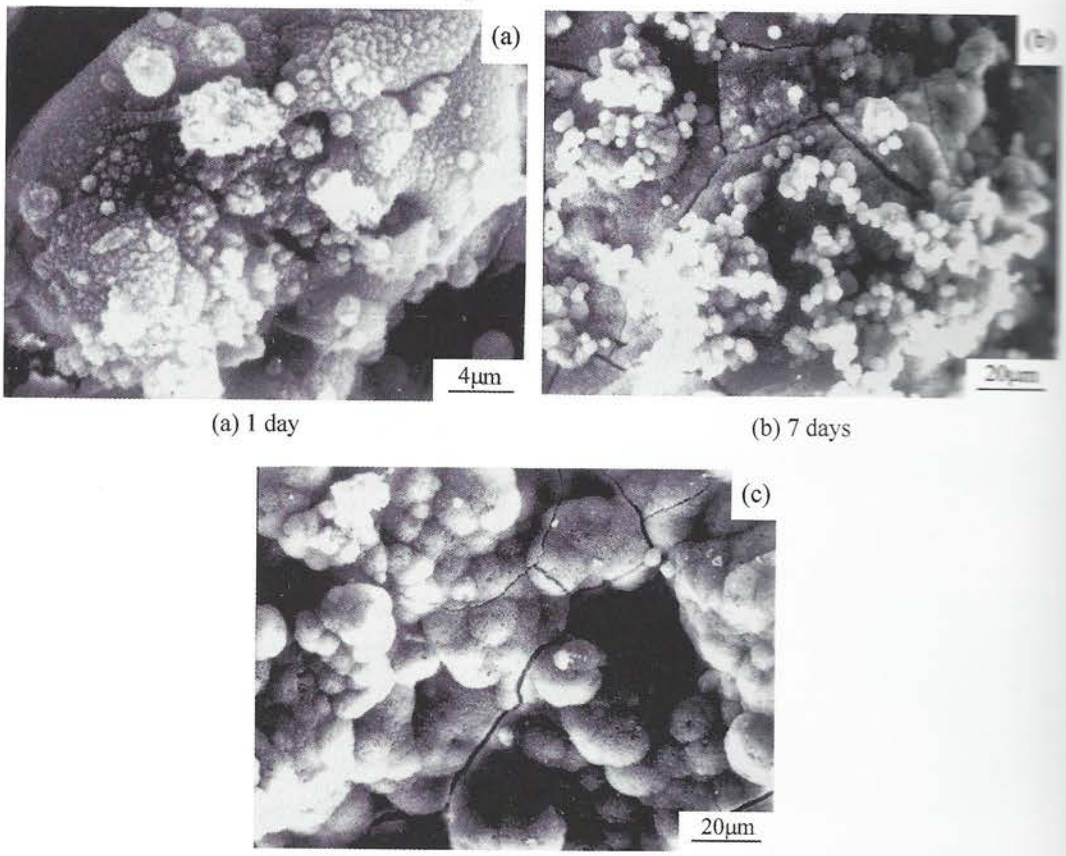
Figure 8 shows the surface morphology of the NaOH-treated Ti coating after being immersed in SBF. Figure 8a shows that there are some spherical particles accumulated on some area of the Ti coating surface after being immersed in SBF for 7 days. The corresponding EDS of Fig. 8a indicates the appearance of Ca and P elements as well as Ti peaks. This means the newly-formed particles on the coating are comprised of Ca and P elements. A continuous Ca-P layer on the surface-modified Ti coating can be observed after immersion in SBF for 14 days (Fig. 8c). The EDS shown in Fig. 8d indicates that the Ca and P peaks are very obvious and the Ti peaks become low, suggesting



(a) surface morphology

(b) cross sectional view

Fig. 9. SEM photographs of as-sprayed wollastonite coating.



(a) 1 day (b) 7 days

(c) 21 days

Fig. 10. Surface morphologies of wollastonite coatings after immersed in SBF solution.

that the Ca-P layer has become thicker. Examination of the IR spectrum indicates that the newly formed Ca-P layer is also carbonate-containing apatite. The SBF tests produce the testimony of good bioactivity for the NaOH-treated Ti coating.

Wollastonite Coating

An interest has been aroused in wollastonite ($CaSiO_3$) as a plasma-sprayed coating for biomedical applications. Plasma-sprayed wollastonite coatings were fabricated successfully using ($CaSiO_3$) powder of 20-70 μm diameter. The coating was observed by SEM and was evaluated biologically by an SBF test.

Figure 9 shows the surface morphology and cross sectional view of the as-sprayed wollastonite coating. From Fig. 9a, it can be seen that the coating is comprised of particles which have been molten and few cracks appear in the coating. The cross sectional view of the coating revealed good bonding between coating and substrate (Fig. 9b).

Surface morphologies of the wollastonite coatings after being immersed in SBF solution for 1, 7 and 21 days are shown in Fig. 10. From Fig. 10a, it can be seen that many granular crystallites appear on the surface of the coating after being soaked in SBF for 1 day. After being immersed for 7 and 21 days, the surface of the wollastonite coating is completely covered by a newly-formed dune-like layer (Fig. 10b and c).

Figure 11 shows the thin film X-ray diffractometer (TF-XRD) patterns of the wollastonite coatings before and after being soaked in SBF solution for 1, 7 and 21 days, respectively. From Fig. 11a, it can be seen that the peak ($2\theta = 32^{\circ}$) of the apatite crystalline phase appears in the XRD patterns of the coatings soaked in SBF solution for 1 day, and the peak is very broad resulting from the superfine grains and amorphous phase of apatite. With an increase of the soaking time

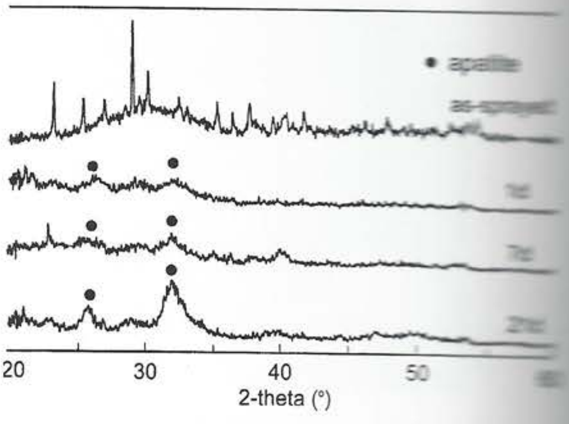


Fig. 11. TF-XRD patterns of wollastonite coatings after immersed in SBF.

the apatite peak became higher and a second strong peak ($2\theta = 26^{\circ}$) of the apatite crystalline phase can be found. It is obvious that the transition of the amorphous to crystalline phase occurred and the crystalline apatite grains became large. The IR spectra also indicate that the apatite formed on the coating surface is carbonate-containing hydroxyapatite similar to the apatite in the bone. It has been pointed out that plasma-sprayed wollastonite possesses excellent bioactivity.

Conclusions

Developments in the field of plasma-sprayed biomedical coatings are presented. The main conclusions are as follows:

(1) Plasma-sprayed HA/Ti composite coatings have been fabricated with improved bonding strength. Good biological properties for the coatings are confirmed by SBF tests and cell cultures.

(2) Plasma-sprayed Ti coating was modified by NaOH solution treatment and bioactivity is obtained.

(3) A new biomedical coating, plasma-sprayed wollastonite coatings has been developed successfully. Excellent bioactivity of wollastonite was testified by SBF tests.

Acknowledgement

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