Transactions of the Materials Research Society of Japan. Vol. 20

Characterization of a hydroxyapatite layer coated upon a Ti-Al_2O_3 composite by radio-frequency plasma spraying

H. Tanizaki[a], A. Otsuka[a], M. Niiyama[a], K. Iwasaki[a],
M. Ueda[b] and A. Motoe[b]

[a]Steel & Technology Development Laboratories, Nisshin Steel,
7-1 Koyashinmachi, Ichikawa, 272 Japan
[b]National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, 305 Japan

A hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAP) layer of about 100 μm in thickness is formed upon a Ti-Al_2O_3 functionally gradient composite substrate by RF-plasma spraying. Though a certain amount of HAP decomposes into $Ca_4O(PO_4)_2$ (4CP) and $Ca_3(PO_4)_2$ (TCP) which are known to be acceptable in a human body, the decomposition into poisonous CaO is suppressed by controlling the substrate temperature. The formation of amorphous phases unstable in the human body is also suppressed. The adhesion strength between the HAP layer and the substrate is about 10 MPa. No biomedically poisonous heavy metal element is detected and cellular growth is observed on the surface of the HAP layer. The HAP layer formed here is expected to be highly biocompatible.

1. INTRODUCTION

Although hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAP) is known to be one of the most promising biocompatible materials, it cannot be used alone for artificial bones and tooth roots because of its poorness in mechanical properties [1]. To compensate this disadvantage, HAP is usually used as a coating material upon a mechanically strong substrate. Various physical and chemical methods have been undertaken for the HAP coating for more than 20 years [2]. Sputtering, flame spraying, direct-current(DC) plasma spraying, radio-frequency(RF) plasma spraying, chemical deposition, electrophoresis, slurry dipping and biomimetic crystal growth are the most popular methods. In the authors' laboratories the RF-plasma spraying method has been selected because of the following reasons.

(1) Adhesion strength between the substrate and HAP is high.
(2) Pores are formed on the surface of the HAP layer, which helps develop strong adhesion with an osteoblast.
(3) Contamination with biochemically poisonous heavy metals can be avoided.

The optimization of the RF-plasma spraying conditions was made in the previous work [3], where Al_2O_3 plates were used as substrates. The experimental results obtained there are summarized as follows.

(1) Only a small part of HAP decomposes into $Ca_4O(PO_4)_2$ (4CP) and $Ca_3(PO_4)_2$ (TCP) if the substrate temperature T_s is kept below about 1300 K.
(2) The amount of 4CP and TCP increases with the in crease in T_s up to about 1400 K.
(3) CaO appears if T_s approaches about 1500 K.
(4) Both the degree of preferred orientation of c-axis of HAP in the normal direction of the coated plane and the porosity increase with increasing cooling rate after the spraying.

Since 4CP and TCP are known to transform back into HAP by means of hydration in the body fluid [4], they are allowed to exist in the coated layer. CaO, on the contrary, is poisonous because it increases pH value. The substrate temperature T_s should then be kept below about 1400 K.

As for the preferred orientation of the c-axis and the porosity, both of them are known to increase biocompatibility [5]. Although higher cooling rate seems to be desirable from these points of view, it must be noted that the higher cooling rate results in the formation of amorphous phases. They are undesirable because of their instability in the human body [6].

In the present work a Ti-Al_2O_3 functionally gradient cylindrical rod [7] is spray-coated with HAP, where the basic information obtained in the previous work [3] is utilized. The composite is planned to be used as an artificial tooth root.

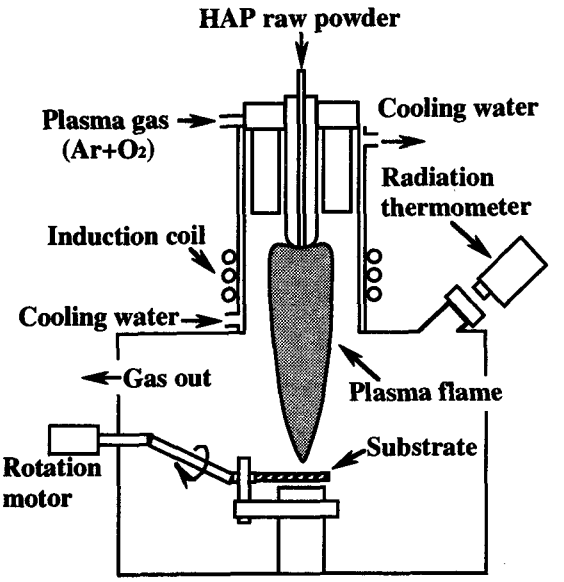

Figure 1. Schematic view of RF-plasma apparatus.

2. EXPERIMENTAL PROCEDURES

A schematic view of the RF- plasma spraying apparatus used here is shown in Figure 1. As for the details of the plasma operation conditions, see ref. [3].

The substrate consists of a cylindrical Ti core rod and a functionally gradient Ti-Al_2O_3 surface layer. The size is about 3 mm in diameter and about 40 mm in length. The Ti/Al_2O_3 ratio decreases from 1 to 0 in the outward radial direction. For the details of its fabrication methods, see ref. [7]. The substrate is held horizontally under the plasma flame and is rotated at 10 rpm to make the spraying homogeneous. The temperature of the substrate surface is measured with a radiation thermometer.

3. EXPERIMENTAL RESULTS AND DISCUSSION

A scanning electron microscopic (SEM) image of a cross section of the spray-coated layer is shown in Figure 2. The coated layer is divide into two different layers. The lower layer near the substrate looks homogeneous and dense.

The formation processes are considered to be as follows by taking the temperature profile during the spraying (Figure 3) into account. As shown schematically in Figure 4, the lower layer is supposed to be formed by the spreading of the melted parts of half-melted HAP particles parallel to the substrate surface. The adhesion between the substrate and this layer is expected to be strong because the melting process is included. As the spraying is continued, the temperature of the substrate surface decreases as shown in Figure 3. In this case the HAP particles are supposed to deposit onto the surface particle by particle without spreading. Then the upper layer consists of the agglomeration of the raw powders and it reveals rough surface and porous structure. The porous surface structure is expected to provide holes into which osteoblast will enter to strengthen the adhesion.

The adhesion strength between the substrate and the sprayed layer is measured to be about 10 MPa by the tensile method [7]. This value is considered to be sufficient for practical use [8].

An example of X-ray diffraction (XRD) patterns of the RF-plasma sprayed layer is shown in Figure 5(a). Although a small part of HAP

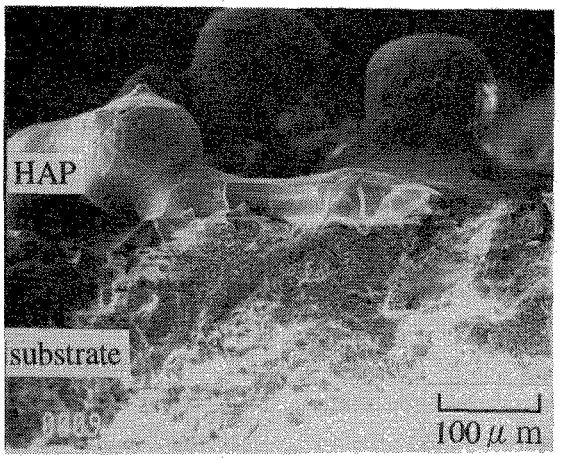

Figure 2. SEM image of cross section of sprayed layer.

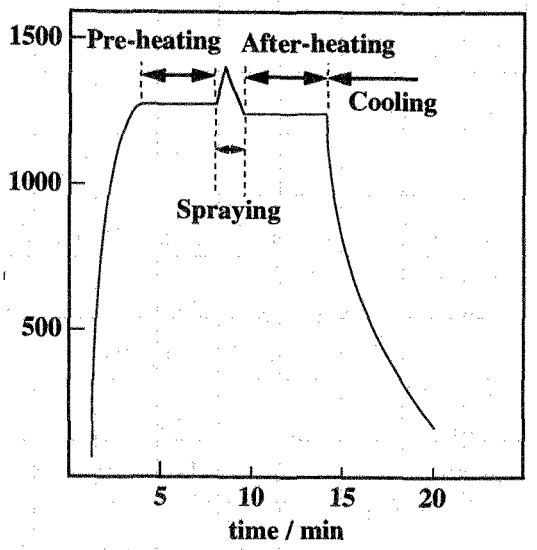

Figure 3. Temperature profile during spraying.

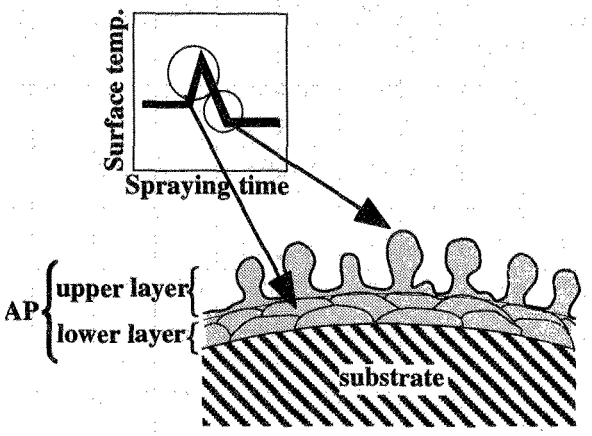

Figure 4. Schematic view of formation processes.

decomposes into 4CP and TCP, no CaO is observed. 4CP and TCP are supposed to be formed mostly in the lower layer because this layer is formed at higher temperatures than the upper one. The background is rather flat, which is to be compared with the case of DC-plasma spraying shown in Figure 5(b) [6]. In the latter case a broad peak seems to exist submerged in the background, which is supposed to correspond to amorphous phases. By comparing these two cases the RF-plasma seems to be preferable to the DC-plasma for avoiding the formation of the amorphous phases.

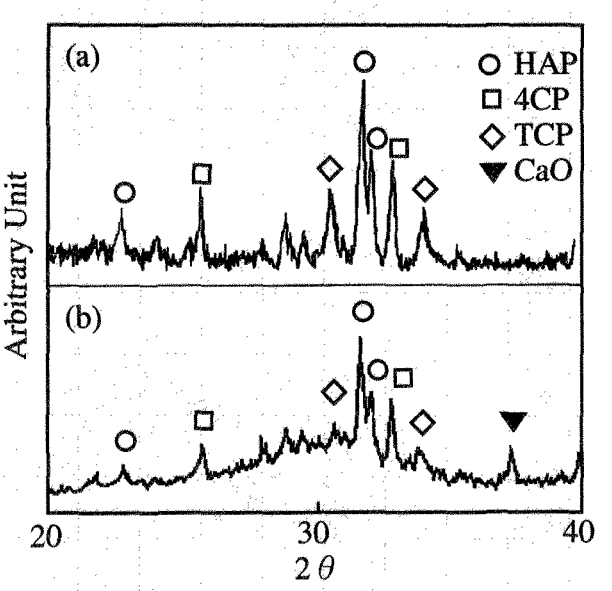

Figure 5. XRD patterns of sprayed layers. (a) RF-plasma spraying. (b) DC-plasma spraying [6].

Figure 6 shows the results of cytotoxicity tests performed for the tooth root produced here (a) and for a standard toxic material, polyurethane film with 0.1% zinc diethyldithiocarbamate(ZDEC) (b). Cellular growth is clearly observed in the former, while all the cells die away in the latter. This is mainly because the absence of electrodes in the RF-plasma spraying avoids the contamination with poisonous heavy metal elements.

The HAP layer produced here consists of a strongly adhesive lower layer and a highly biocompatible upper layer. No poisonous element

is detected and cellular growth is observed. The composite is then expected to be an excellent biomaterials for dental use.

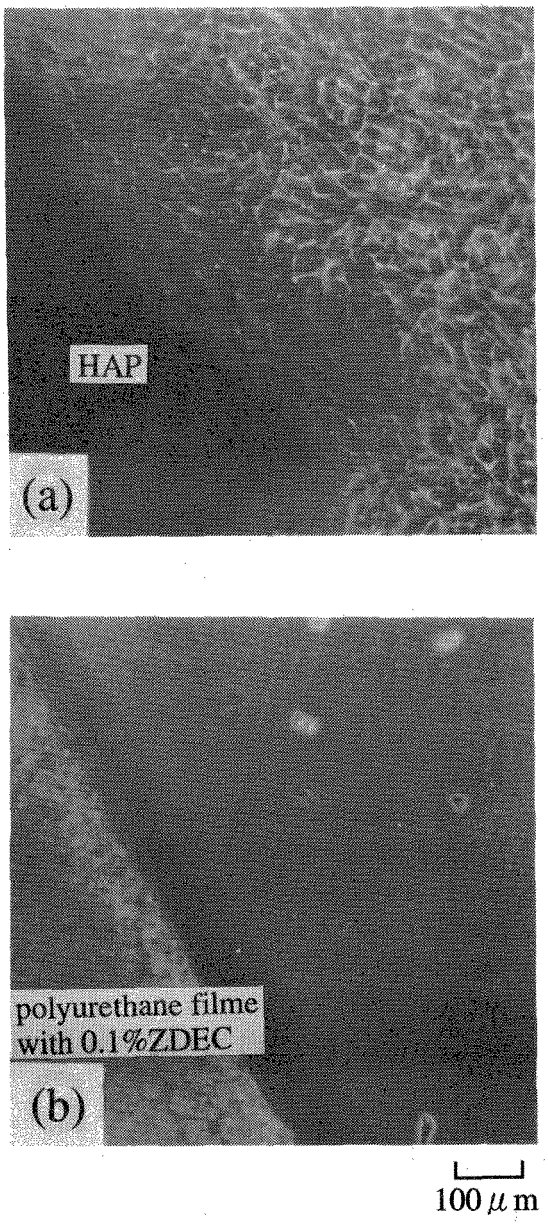

Figure 6. Results of cytotoxicity test. (a) Tooth root produced here. (b) Polyurethane film with 0.1% ZDEC.

ACKNOWLEDGEMENT

This work was conducted in the program "Advanced Chemical Processing Technology", consigned to Advanced Chemical Processing Technology Research Association (ACTA) from New Energy and Industrial Technology Development Organization (NEDO), which was carried out under the Industrial Science and Technology Frontier Program enforced by the Agency of Industrial Science and Technology. Authors would like to express their gratitude to these institutions for supporting this work. Drs. Y. Niwa and Y. Imai of National Institute of Materials and Chemical Research are also acknowledged for their encouragement in performing this work.

REFERENCES

1. Y. Ukegawa, Y. Isobe, K. Furuya, H. Aoki, M. Akao, M. Higashikita and Y. Shin, Orthopaedic Ceram. Implants, 5 (1984) 191.
2. A. Hasegawa, T. Kameyama, A. Motoe, M. Ueda, K. Akashi and K. Fukuda, J. Ceram. Soc. Japan, 100 (1992) 377.
3. K. Ohsaki, H. Tanizaki, K. Iwasaki, M. Ueda, T. Kameyama and K. Fukuda, Proc. 7th Symp. Plasma Sci. Mater., (1994) p. 83.
4. K. Shigeru, T. Oku and S. Takagi, J. Ceram. Soc. Japan, 97 (1989) 101.
5. T. Kameyama, A. Hasegawa, A. Motoe, M. Ueda, K. Akashi and K. Fukuda, Proc. Japan Symp. Plasma Chem., 5 (1992) 257.
6. M. Akao, Proc. Ann. Meeting Jpn. Soc. Mech. Eng., vol. 71, pt. 2 (1994) 472.
7. A. Otsuka, H. Tanizaki, M. Niiyama and K. Iwasaki, in this issue.
8. H.Aoki, M.Akao, M,Higashikata, S.Hasegawa and Y.Ukegawa, Ceramics, 24(1989)614.