Preferred orientation of plasma sprayed hydroxyapatite coatings

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The long-term stability of hydroxyapatite (HA) coatings has been under investigation for a long time. The evaluation of crystallinity is important since a relationship exists between the degree of crystallinity and the degradation by *in vitro* cellular reaction. However, the choice of a representative peak to calculate the crystallinity is the subject of some controversy with the (2 1 1) peak and the (0 0 2) peak being the most commonly analysed peaks. Thus the determination of the degree of crystallinity may be biased due to preferred orientation (texture) in the coatings. Therefore, the dependence of texture on thickness during plasma spraying was investigated by the calculation of a texture coefficient (TC). Experiment results showed that the TC value of the (0 0 2) and (0 0 4) peaks increased with thickness and that the TC value in the (2 1 1) peak decreased. This was caused by a high temperature gradient during spraying and also the growth direction for a hexagonal system. It was observed that appropriately controlled temperature increases during annealing did not bring about notable texture to the recrystallized crystallites. However, if the temperature gradient was high during annealing, notable (0 0 2) texture can exist. The effect of particle size on the texture was also investigated.

1. Introduction

Plasma sprayed hydroxyapatite-Ti composites have been widely used in tooth, joint and hip replacements due to their good biocompatibility and high strength [1–3]. The stability of the hydroxyapatite (HA) coatings with the degree of crystallinity is an area which has received considerable attention [4–6]. The calculation of the degree of crystallinity has been performed differently by different researchers [7–9]. Usually the (2 1 1) or (0 0 2) peaks of the XRD patterns are chosen, their height or area is measured and compared to a standard sample, in order to represent the crystallinity of the coating [8, 9]. The choice of the (2 1 1) or the (0 0 2) peak to be the representative peak for crystallinity makes no difference if the rate of increase in both the (2 1 1) and (0 0 2) peaks are the same. It is known that plasma spraying is a high temperature and rapid cooling process. HA powders injected into a plasma flame are usually partially molten, consisting of a molten outer sphere and an unmelted core [10]. The molten portion can be recrystallized or amorphorized depending on the cooling condition [11]. Thus, crystalline HA in the coating is composed of unmelted HA and recrystallized HA, which gives sharp reflections in the XRD patterns. The growth of recrystallized HA crystallites after spraying is constrained due to the rapid cooling rate and thus the coating contains crystalline matter that contains about 10 times smaller crystallites with respect to the original powder (several hundred nanometres) [1]. Preferred orientation (texture) will be the apparent result of the fast cooling, which means that some peaks increase faster than others in the XRD patterns. If the rate of increase of the (2 1 1) peak and the (0 0 2) peak are different, which means a difference between (2 1 1) and (0 0 2) textures, the two crystallinities calculated by choosing either the (2 1 1) peak or the (0 0 2) peak will be different from each other. In cases like this, the crystallinity of a given coating is variable and comparison of the degree of crystallinity in the coating becomes difficult unless the calculation method is well documented.

In this article, the generation of preferred orientation during the plasma spraying and also in a post-deposition heat treatment was investigated by calculation of the texture coefficient (TC) from X-ray diffraction (XRD) data.

2. Materials and methods

2.1. Starting powder

The hydroxyapatite powder for the coatings was produced in our laboratory. The powder was granulated and sintered at 1250 °C. HA granules of size (1–2 mm)

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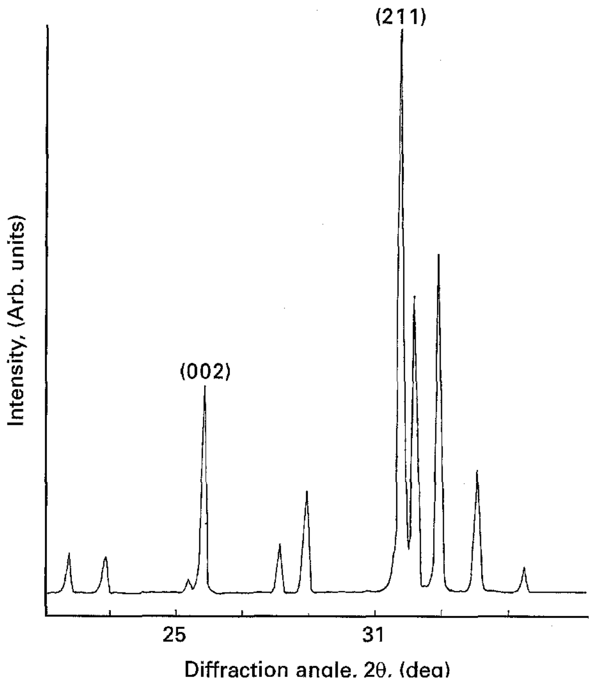

Figure 1 X-ray diffraction pattern of the starting powder, showing that no preferred orientation exists.

were crushed, milled and sieved. A powder with a particle size of 1–50 um (HA50) or 1–180 μm (HA180) was used in the spraying. Coatings prepared for the heat treatment experiment were produced from only powder HA50. X-ray diffraction pattern showed that the starting powder was pure and well-crystallized hydroxyapatite (Fig. 1).

2.2. Coating

Titanium substrates (of size 12 × 8 × 2 mm) were polished, sandblasted with SiC and cleaned according to ASTM B600–74 before the spraying [12]. A Metco MN system (USA) was used to perform the coating procedure. Coatings with different thickness were produced by varying the spraying parameters.

2.3. Heat treatment

As-deposited coatings were heated in air at 630 °C for 1 h. Two types of heat treatments were performed and the exact experimental conditions are listed in Table I.

2.4. XRD

The structure of the coatings was examined by means of X-ray diffraction (using model D/MAX, made by Rigaku Corporation, Japan). The preferred orientation was evaluated in terms of a texture coefficient (TC) calculated according to the following formula [13]

$$TC_{hkl} = \frac{I^c_{hkl}/I^p_{hkl}}{\frac{1}{n}\sum(I^c_{hkl}/I^p_{hkl})} \qquad (1)$$

TC_{hkl} is the probability intensity of the (h k l) plane being parallel to the surface of the samples. I is the diffraction intensity of the peaks on the XRD patterns. $I_{hkl} = H_{hkl}/H_{211}$. H_{hkl} is the height of the (h k l) peak on the XRD patterns. H_{211} is the height of the (2 1 1) peak on the XRD patterns. n is the number of peaks selected. c is the index for coatings and p is the index for the powder.

Peaks located between 10–60° 2θ on the XRD patterns were chosen to calculate TC. The HA spectrum of the JCPDS card was used as the non-textured standard. The probability intensities of the (h k l) planes parallel to the surface of the HA powder sample is assumed to be 1.

TABLE I Heat treatment schedules

Method I	Temperature of coatings increased at the average rate of 5–10 °C min^{-1}
Method II	Coatings were put into furnace after the furnace temperature had been raised to 630 °C

3. Results

Fig. 2 showed the XRD patterns of HA coatings with and without (0 0 2) preferred orientation. It is known that a TC can be used to evaluate the level of preferred orientation. The higher the TC value, the greater the degree of preferred orientation. Fig. 3 exhibits the dependences of TC on the thickness of the coating. It was observed that both TC_{002} and TC_{004} increased with thickness while TC_{211} decreased with thickness. In addition, a bigger particle size brought about a higher TC_{002} and TC_{004} (Fig. 4). These results indicate that the growth rate of the (0 0 2) and (0 0 4) crystalline planes were much faster than that of the (2 1 1) crystalline plane.

During annealing, coatings heated by method II showed comparatively higher TC_{002} values than that of coatings heated by method I (Fig. 5). An increase in TC_{211} was observed in both heating schedules. An increase in TC_{004} was not observed in any of the heated coatings, which was different from the situation in spraying.

4. Discussion

HA particles injected into a plasma flame are usually partially molten, composed of a molten sphere and unmelted cores [10]. The molten portions recrystallized or amorphorized according to the cooling condition during spraying [11]. Preferred orientation was closely related to the spraying process. It is essential for atoms to gain sufficient energy to move and rearrange from the disordered molten state, in order to subsequently form crystallites. The supply of energy can be met during the spraying of thick coatings because of the higher heat content and lower cooling rate in thick coatings. Notable recrystallization was observed as the thickness of coatings increased [11]. The observed preferred orientation in as-deposited coatings during spraying could only happen in the recrystallization process, which is sensitive to the

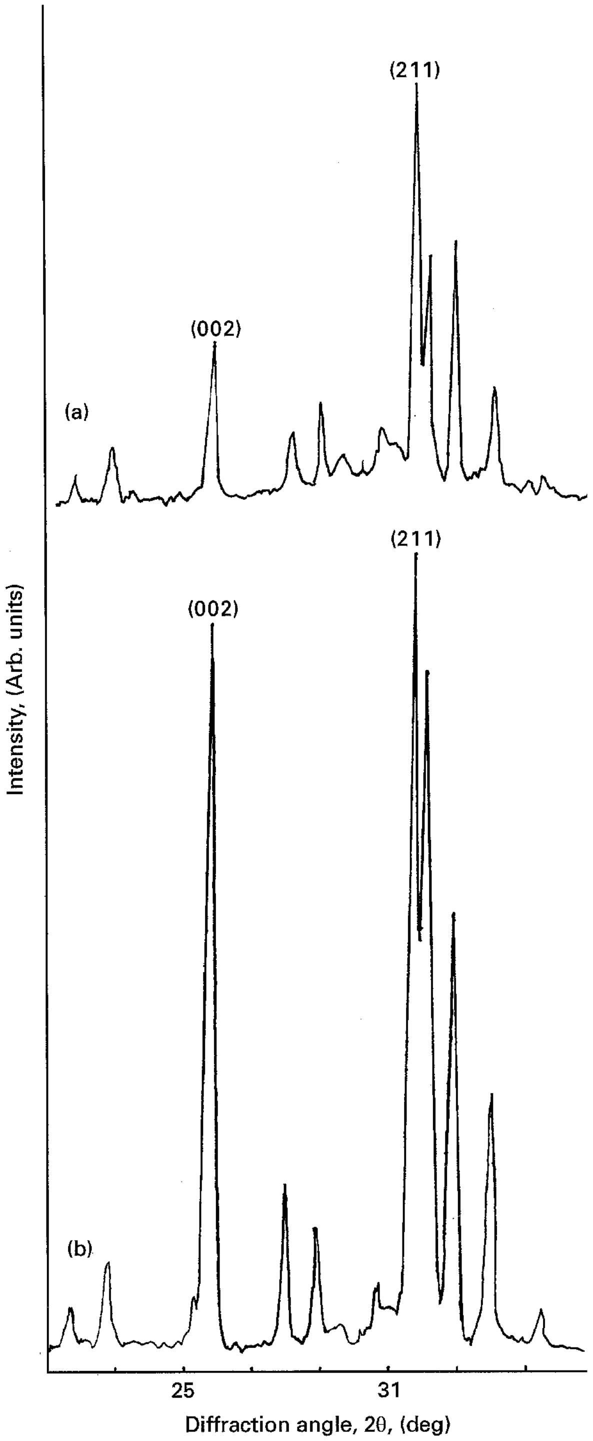

Figure 2 X-ray diffraction patterns of as-received coatings. (a) without preferred orientation in (0 0 2) crystalline plane; (b) characteristic of preferred orientation in (0 0 2) crystalline plane.

thickness of the coatings. Texture created in this manner is known as recrystallization texture. During spraying, heat input occurred at the front surface of the coatings and heat loss occured mainly at the rear surface of the substrates. Heat flux passed through the coating/substrate perpendicularly, and rather a high temperature gradient was built into the coating [11]. Preferred orientation in a polycrystalline mass can arise in a variety of ways. These include the layering of plate-like crystals in sediments and also preferential crystal growth in a definite crystal orientation, due either to growth on an oriented layer, or to growth with a crystal axis parallel to the direction of max-

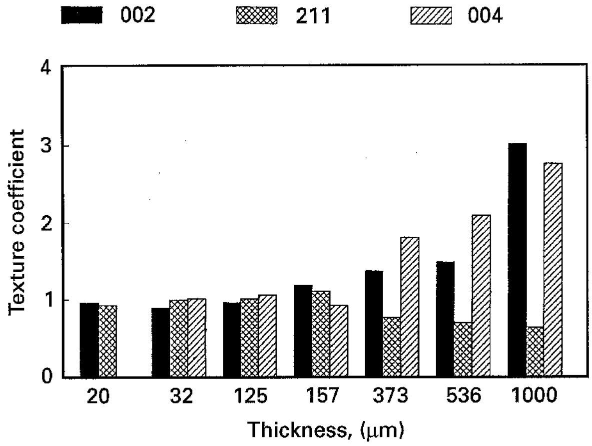

Figure 3 The dependence of TC (texture coefficient) on thickness, showing that TC_{002} and TC_{004} increase with thickness, whereas TC_{211} decreases with thickness. Coatings were prepared by using HA50.

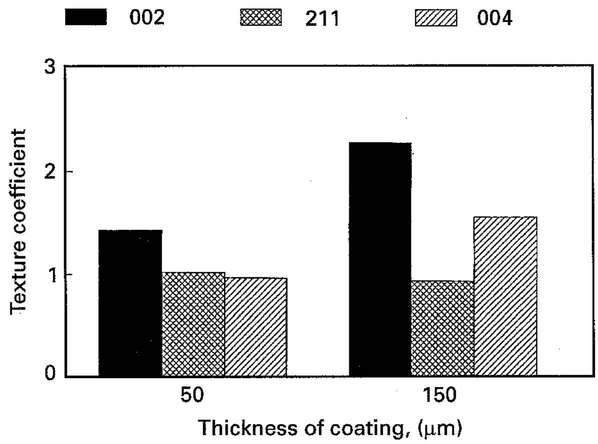

Figure 4 The dependence of TC (texture coefficient) on particle size, showing similar results as Fig. 3 except for the relatively larger TC_{002} and TC_{004} at the same thickness. Coatings were prepared by using HA180.

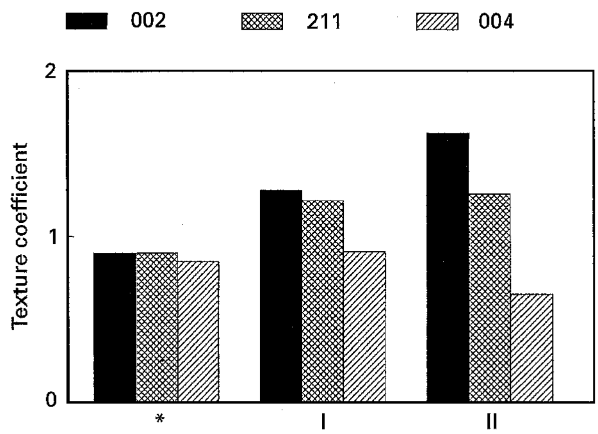

Figure 5 TC of coatings after heat treatment. Coatings treated by method II showed comparatively higher TC_{002} than coatings treated in method I. An increase in TC_{211} was observed in both manners of heating whilst TC_{004} decreased in method II. *, as-deposited coatings.

imum thermal gradient [14]. Thus the rather high temperature gradient in the coatings during spraying was responsible for the occurrence of the observed texture. For HA with a hexagonal crystallographic structure, the (0 0 1) direction is the usual direction for preferred growth, along which crystal planes are most densly populated with atoms. So the (0 0 2) and (0 0 4) crystalline planes whose axes are the (0 0 1) direction would grow preferentially along the direction of heat flux. This explanation is in accordance with the experiment results which showed that the preferred orientation is the (0 0 1) direction during recrystallization by the high TC_{002} and TC_{004} (Figs 3 and 4). As the thickness increased, the cooling rate slowed and the atoms of the lamellae could diffuse at a higher rate and over a longer distance [15] which was beneficial to the recrystallization. Therefore, more preferred crystallites formed per unit volume of the coatings, and the level of preferred orientation became stronger.

Coatings heated by method I did not show any notable increase in TC_{002} compared to that of the coatings heated by method II. This can be explained by the point that during annealing, heat input occurred in all sides of the coating, therefore there existed no obvious temperature gradient in the coating due to the slow temperature increase. The newly formed crystallites distributed randomly and did not exhibit any preferred orientation. The situation was different when the coatings were treated by method II. An initial temperature gradient as high as 1200 °C/100 μm can be created in the coating due to the sudden input of heat from the coating surface and the substrate rear surface. The significant high temperature gradient might be responsible for the high TC_{002} values in coatings heated by method II. However, the mechanism of preferred orientation in post-heat treatment must be different from that in spraying because the types of preferred orientation in both cases are different to some extent.

In fact, the peaks in the XRD patterns reflect the crystalline planes parallel to the surface of the coatings and TC_{hkl} reflects the probability intensity of (h k l) planes being parallel to the coating surface. The dependence of TC_{002} and TC_{211} on thickness changed differently, the former increased with thickness but the latter decreased with thickness, showing that the growth rate of the (0 0 2) plane parallel to the surface of HA coatings was much faster than that of the (2 1 1) plane during plasma spraying. This would result in a difference in the judgement of the degree of crystallinity in the HA coatings by using either (0 0 2) or the (2 1 1) peak as the representative peak. Table II showed an example obtained from the experimental data, in which the crystallinity of coating A (20 μm) and B (373 μm) were represented respectively by the peak height of the (2 1 1) and (0 0 2) peaks compared to the standard. It can be seen in Table II that the crystallinity of coating B was higher than that of coating A as recrystallization proceeded. It can be seen that the ratio of crystallinity B (S_b) to crystallinity A (S_a) calculated from the (2 1 1) peak was 1.87, whilst the ratio changed to 3.33 when calculated from the (0 0 2) peak. This difference in the evaluation of crystallinity may become serious as the difference in texture between the (2 1 1) and (0 0 2) peaks becomes bigger.

TABLE II Example of crystallinities evaluated from the (2 1 1) and the (0 0 2) peaks

Coatings	H_{211}	H_{002}	TC_{211}	TC_{002}
A (20 μm)	45	18	0.93	0.96
B (373 μm)	84	60	0.78	1.38
S_b/S_a[a]	1.87	3.33		
Standard			1	1

[a] S_b: crystallinity of coating B; S_a: crystallinity of coating A.

5. Conclusions

Preferred orientation (texture) was observed in plasma sprayed HA coatings. TC_{002} and TC_{004} increased with thickness whilst TC_{211} decreased with thickness during spraying. Different heating schedules during the annealing may influence the texture of the coatings. The texture of the coatings might affect the evaluation of crystallinity when preferred orientation exists in the chosen representative peaks.

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