Production of high quality Ti-HAP functionally graded coating using well-controlled thermal plasmas

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Plasma sprayed hydroxyapatite (HAP) on metallic substrate have been used as medical implants. Generally, Ti-HAP Functionally Graded Coating (FGC) is made to improve the adhesion strength. In this paper, we make the FGC films under various experimental conditions. The adhesion strength, the Vickers hardness, *c*-axis orientation and the porosity of prepared FGC films are evaluated. The adhesion strength of FGC films has the necessary value to be used as artificial bones. We can control the porosity by varying input jet power and the mean diameter of HAP.

Keywords: DC plasma, jet, plasma spraying, functionally graded coatings, hydroxyapatite, artificial bone

1. Introduction

Thermal plasma processing using a plasma jet with high speed and high heat capacity is one of the most promising methods for spraying materials. In general, thermal plasma processing is, governed by a large number of parameters and implementation of controls becomes mandatory. To this end, we have developed a thermal plasma reactor based on the forced constricted type plasma jet generator [1]. The reactor can produce the plasma jet with high stability and high thermal efficiency for various operating conditions [1]. So far, we have reported the experimental results on preparation of Ti–Al FGC, β"-alumina film synthesis and of MgO coatings using this device [2-4].

By the way, in the recent years with aging society, demand of artificial bones has been increased. HAP ($Ca_{10}[PO_4]_6[OH_2]$), main component of bone and teeth, is called bioactive material. Plasma-sprayed HAP coatings on Ti substrates have been applied to promote good adhesion between human bone and implanted materials. However, due to the large difference in thermal expansion coefficients between the ceramics coating and the metal substrates, residual stress arises at the ceramic/metal interface. This residual stress often causes cracks and reduces the adhesion strength of ceramic coatings. Therefore, FGC films have been demanded to prevent these cracks from coating. In addition, the porous HAP has good bioactivity. It is said that new bone is formed inside of pore.

There are various methods of preparing HAP coatings. Most of HAP coatings have been performed by Radio Frequency (RF) thermal plasmas [5]. The adhesion strength tends to increase with increasing the applied RF jet power [5, 6]. However, HAP is decomposed because RF jet power of HAP coating is high. So, by using DC plasma jet with relatively low power, increasing mechanical strength of HAP coatings can be expected because, in general, velocity of injected HAP powders in DC plasma jet becomes higher than one in RF plasma jet. In addition, the control of RF plasma jet is not so easy compared with DC plasma jet.

We have tried to make the FGC films using the well-controlled DC plasma jet. So far, we have succeeded in the preparation of FGC films. Based on the previous results [7, 8], in this paper, we further discuss preparation of FGC films with varying experimental conditions such as the mean diameter of HAP powder, pressure in the reaction chamber and the input jet power.

2. Experimental apparatus and procedure

Schematic drawing of the plasma jet reactor system used in this study is shown in Fig. 1. The system consists of the forced constricted type plasma jet generator (Cu-nozzle anode of 5 mm diameter, Cu-insulated constrictor nozzle of 5 mm diameter, and rod cathode made of 2% Th–W), the feed ring (FR) (5 mm diameter) with the powder feeder and the reaction chamber (370 mm in width, 390 mm in depth, 610 mm in height).

Experiments are performed under continuous pumping and flowing of argon (Ar) gas. The plasma jet is produced by DC arc discharge. As the insulated constrictor nozzle is set between the nozzle anode and the cathode, arc length is always kept constant, and the nozzle wall strongly constricts the arc with the working gas.

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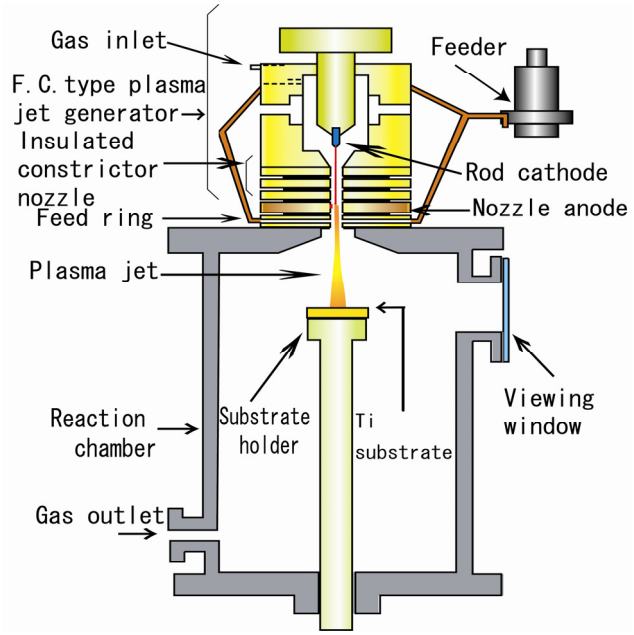

Fig.1 Schematic diagram of the plasma jet reactor.

Then, a stable plasma jet with high heat capacity is produced under various operating conditions. The coefficient of arc voltage fluctuation equals to about 5 %.

Experiments were carried out under the following conditions: working gas (Ar) flow rate is 20 l/min, feed gas (Ar) flow rate is 6 l/min, pressure in the reaction chamber (P_t) is varied 200, 760 Torr, input jet power (W_j) is varied from 4 to 6 kW, and the distance from the feed ring exit to the substrate (L) is varied 70 mm (at 760 Torr), 80 mm (at 200 Torr). There are some relationships between W_j and the gas flow rate of working gas. In general, with increasing input power, working gas flow rate should also increase to maintain stability and high thermal efficiency of the plasma jet. Commercial Ti substrates (3 mm thick) were polished with #180 abrasive papers, washed ultrasonically in acetone, and then dried in air before spraying. To prepare FGC films, powders of Ti (mean diameter of Ti: D_t = 25μm) and HAP (mean diameter of HAP: D_h = 30 μm) were used. These powders were injected into the plasma flow with carrier gas through two capillary feeding ports of the FR.

The prepared films are evaluated by X-ray diffraction (XRD) analysis with Ni-filtered Cu Kα radiation. For qualitative analysis the patterns were recorded in the 20-80° 2θ range (step size 0.01° and 1s counting time for each step). The cross sections of prepared films are observed by using a scanning electron microscope (SEM). The adhesion strength of prepared coating is measured by the adhesion strength machine. The hardness of prepared films is measured with a Vickers hardness tester.

3. Results and Discussion

According to our previous result [8], the quality of FGC films (i.e. the *c*-axis orientation, the adhesion strength and the Vickers hardness) depends on W_j. In addition, the under coat and the middle coat are sprayed with 6kW to improve the adhesion strength. Top coat is sprayed with various experimental conditions to improve the *c*-axis and the porosity.

In general, acceleration and heating of injected powders are influenced by various parameters (W_j, P_t, D_h, L). Therefore, in plasma spraying, the characteristics of the prepared FGC films depend on various parameters (W_j, P_t, D_h, L). When P_t is low, the particle velocity is increased and high temperature region of plasma jet is expanded.

The composition ratios of Ti and HAP powders are as follows:

(1) The under coat: Ti is 100 mass% (feeding rate is 0.28 g/min and the typical process time is 30 s).
(2) The middle coat: Ti is 33 mass% and HAP is 66 mass% (feeding rate is 0.13 g/min and the typically process time is 60 s).
(3) The top coat: HAP is 100 mass% (feeding rate is 0.07 g/min and the typically process time is 60 s).

The FGC film SEM image and the result of its composition analysis using EDX are shown in Fig.2. Experiments are conducted under the following conditions: P_t = 200 Torr, W_j = 6 kW, L = 80 mm. If L is 70 mm at P_t = 200 Torr, Ti substrate is melted by plasma jet. Therefore, L should be 80 mm.

Figure 2 (a) shows a SEM image of the cross section of the prepared films. On the other hand, Figs. 2 (b), (c), and (d) are the composition analysis of Ca, P and Ti, respectively. It is also confirmed that Ti composition is changed along the normal direction, i.e. from the substrate to the surface of the top layer in the prepared film.

The Ti component of prepared films is as follow:

(1) The under layer; Ti is 96.3 at.%.
(2) The middle layer; Ti is 33.9 at.%
(3) The top layer; Ti is 1.9 at.%

Then, it is confirmed that the three layered Ti–HAP FGC film is prepared successfully. The prepared films under low P_t are made the same as one under atmospheric P_t.

The control of orientation is important for suppressing dissolution of bioceramics and improving mechanical strength. Human bone is *c*-axis oriented, which contributes to the suppression of degradation and maintaining of toughness.

Figure 3 shows XRD patterns of prepared films (FGC) under two different P_t (i.e. (a) 200 Torr, (b) 760 Torr, respectively). An increase in peak intensities of

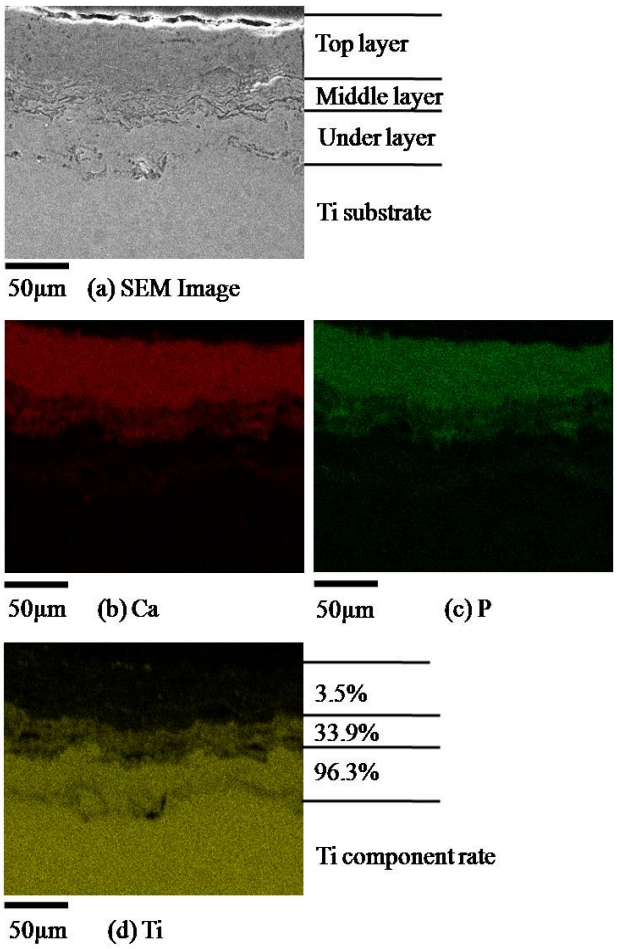

Fig.2 Composition analysis of prepared film using EDX.

(002) and (004) peaks (i.e. $2\theta = 25.878$ and 53.210°, respectively) confirms that the HAP coatings are *c*-axis oriented. Usually, this point is counted by using the following formula

$$F_{orii} = \left\{\sum I_c(00l)/\sum I_c\right\}/\left\{\sum I_R(00l)/\sum I_R\right\} \quad (1)$$

where Σ I (00l) is the sum of HAP peak (002) and (004), and Σ I is the sum of the HAP peak intensity. C and R represent prepared films and raw material.

We calculated relative *c*-axis orientation ratio F_{ori} of prepared films using Eq. (1). The values of F_{ori} were 1.86 in (a), 3.07 in (b), respectively.

It is said that the adhesion strength should be equal to or higher than 10 MPa [9].

Figures 4 and 5 show the results of the adhesion strength test and the Vickers hardness test for the prepared FGC films under two different P_t (P_t = 200, 760 Torr). The Vickers hardness is counted by using the following equation:

$$H_v = 1.8544 \times \frac{p}{d^2} \quad (2)$$

where p is loading and d is the length of the diagonal of the depressed area. The thickness of the sample is necessarily more than 1.5 times d. In the present test, d is about 20 μm with W_j of 6 kW. The adhesion strength of prepared FGC films under atmospheric P_t was higher than that of prepared FGC films under low P_t. In addition, the adhesion strength of prepared FGC films with two different P_t has the necessary value to be used as artificial bones.

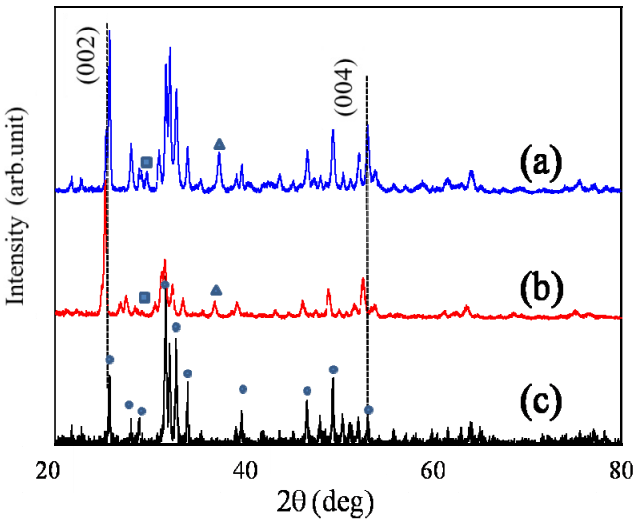

Fig.3 XRD patterns of the FGC films. (a) coatings at 200 Torr, (b) coatings at 760 Torr, (c), raw material, Symbols ●, ■ and ▲ mean HAP, TCP and CaO, respectively. Other experimental conditions are as follows: W_j = 6 kW, L = (a): 70, (b): 80 mm.

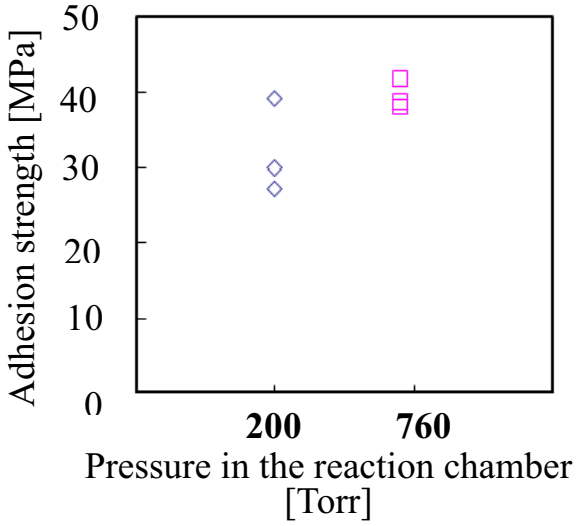

Fig.4 The adhesion strength of the FGC films versus P_t. Other experimental conditions are as follows: W_j = 6 kW, L = 70mm: 200Torr, 80 mm: 760Torr

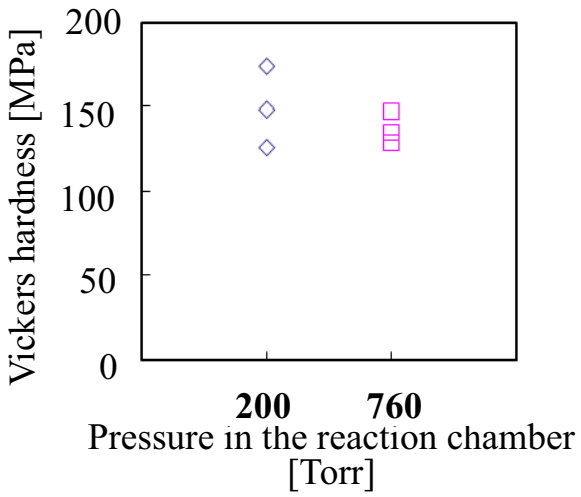

Fig.5 Vickers hardness of the FGC films versus P_t.

Average value of the Vickers hardness at low P_t and atmospheric P_t were 149 MPa and 137 MPa, respectively. The Vickers hardness of prepared FGC films with different two P_t was about the same value.

According to these results, we think that prepared FGC films with varying P_t have sufficient mechanical strength as artificial bone.

The porosity is one of important parameters for the artificial bone materials. If apatite is porous, the neonatal bone is formed inside the pore. In addition, mechanical strength becomes high.

Therefore, we try to increase the porosity by varying W_j and D_h.

Figure 6 shows SEM images of prepared FGC films. The porosities of HAP layers were 1.0% in (a), 6.5% in (b), 8.9% in (c), respectively. According to this result, the porosity was increased with decreasing W_j. At the same W_j, the porosity was increased with enlarging D_h. We could control the porosity of HAP layer by varying W_j and D_h.

In this study, we have confirmed that the FGC films are made successfully under various splaying conditions. The qualities of prepared FGC films with different two P_t are nearly the same value. However, adhesion strength and c-axis orientation of the films in low P_t are not so good although velocity of injected particles in low P_t is faster than those in atmospheric P_t. Heating of injected particles may influence these results. Optimum combination of spraying parameters is now under study.

In addition, we are now trying in vitro test using simulated body fluid (SBF). It is confirmed that HAP grows on surface of the prepared FGC films soaked in SBF. Details are now under study.

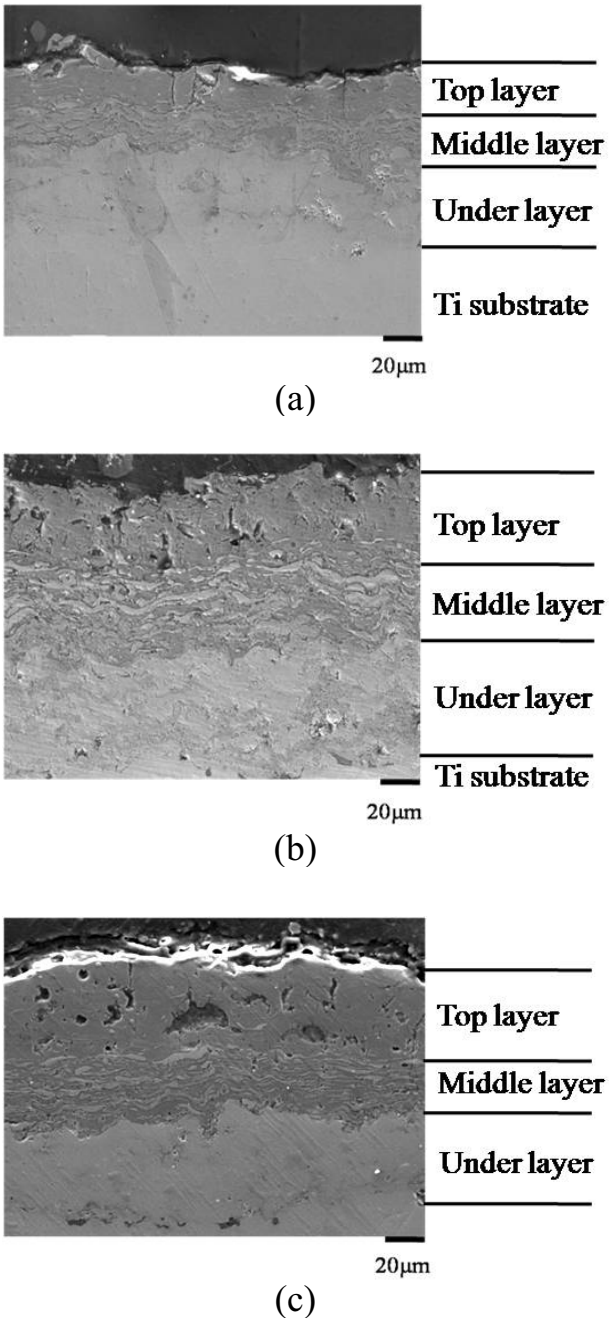

Fig.6 SEM images of prepared film (FGC). (a) W_j = 6 kW, D_h = 30μm, (b) W_j = 4 kW, D_h = 30μm, (c) W_j = 4 kW, D_h = 85μm.

4. Conclusions

In this paper, we have studied preparation of Ti/HAP FGC films by using a well-controlled DC plasma jet. The characteristics of prepared films are evaluated with varying P_t and D_h. The strength of prepared FGC films with two different P_t has the necessary value to be used as artificial bones. For Vickers hardness both FGC films under low P_t and one under atmospheric P_t have sufficient strength. Therefore, we have confirmed that the FGC films can be prepared at various experimental

conditions. We need to optimize spraying conditions of top coat to apply as the artificial bone. In the future, we further study biocompatibility evaluation of the films soaked in SBF.

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