

## Hydroxyapatite Coating Using DC Plasma Jet

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Hydroxyapatite (HAP)-coated implants on metallic substrates have been used as biomaterials. The problem is that the HAP coating on metallic substrates is easily exfoliated at the boundary between HAP and metallic e.g., titanium (Ti) substrates. Therefore, a Ti-HAP functionally graded coating (FGC) is considered to improve the adhesion of Ti-HAP coatings. In this paper, Ti-HAP FGC is tested using a well-controlled DC plasma jet and discussed. It is confirmed that Ti-HAP FGC films with good adhesion within three layers are prepared.

**KEYWORDS:** dc plasma jet, plasma spraying, functionally graded coatings, hydroxyapatite, titanium

## 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. Since thermal plasma processing is, in general, governed by a large number of parameters, the implementation of controls becomes mandatory. To this end, we have developed a thermal plasma reactor based on the forced constricted-type plasma jet generator.<sup>1,2)</sup> The reactor can produce a plasma jet with high stability and high thermal efficiency under various operating conditions.<sup>2)</sup>

Recently, with the advance of the aging society, the necessity of artificial bones has increased. Metallic materials of stainless steel and Ti have been used for the base material of artificial bone. Ti has high mechanical strength and corrosion resistance. However, Ti is a bioinert material and cannot be combined with bone tissue. On the other hand, hydroxyapatite (HAP) ( $\text{Ca}_{10}[\text{PO}_4]_6[\text{OH}_2]$ ), the main component of bone and teeth, is a bioactive material. Plasma-sprayed HAP coatings on Ti substrates have been applied to promote good bonding between living bone and implanted materials. However, due to the large difference in thermal expansion coefficient between the ceramic coating and the metal substrates, residual stress arises at the ceramic/metal interface. This residual stress often causes cracks and reduces the bond strength of the ceramic coatings. Therefore, functionally graded coatings (FGCs) have been demanded to prevent such cracks in the coating.

There are various methods of coating HAP. Most HAP coatings have been prepared using RF plasmas.<sup>3,4)</sup> Bond strength tends to increase with the applied RF input power.<sup>3,4)</sup> However, HAP is decomposed when the RF jet power during HAP coating is high. By using a DC plasma jet with low power, the increase of bond strength can be expected because the

particle velocity in a DC plasma jet is high. In addition, the control of the DC plasma jet is easy compared with the RF plasma jet, and the processing time of spray coatings is short compared with other methods. We have undertaken to confirm the application feasibility of our well-controlled DC plasma jet reactor for preparing Ti-HAP FGC films. So far, we have reported the experimental results on the preparation of Ti-Al FGC,  $\beta''$ -aluminum film and MgO coatings.<sup>5,6,7)</sup> On the basis of those results,<sup>5,6,7)</sup> we hypothesize that dense spray coatings can be prepared under suitable combinations of jet power, ambient pressure and powder conditions. First of all, in this study, we have tried spraying films of FGC and high bond strength under a low jet power condition.<sup>8)</sup>

## 2. Experimental Apparatus and Procedure

A 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 5mm diameter, Cu-insulated constrictor nozzle of 5mm 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 flow of argon (Ar) gas. The plasma jet is produced by DC arc discharge. The insulated constrictor nozzle peculiar to this generator always maintains the arc length constant, and the nozzle wall strongly constricts the arc with the working gas.<sup>1,2,6,7,9)</sup> To prepare Ti-HAP FGC, powders of Ti ( mean particle size of granulated agglomerate is about 30  $\mu\text{m}$  in diameter) and HAP ( mean particle size of granulated agglomerate is about 80  $\mu\text{m}$  in diameter) are used. These powders are injected into

the plasma flow with carrier gas through two capillary feeding ports of the FR. Commercial Ti substrates (0.3 mm thick) are polished with #180 abrasive paper, washed ultrasonically in acetone, and then dried in air before spraying.

Experiments are 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 ( $P_r$ ) is 760 Torr, jet power ( $W_j$ ) is approximately 5 kW, and the distance from the feed ring exit to the substrate ( $L$ ) is 60 mm. There are some relationships between the input power (and then  $W_j$ ) 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. The gas flow rate in the present case has been selected to be optimum under a low jet power condition.

Ti, HAP powders and powder mixtures of Ti and HAP are injected into the plasma flow, respectively. The composition ratios of Ti and HAP powders for preparing each film are as follows.

- (1) The undercoat: Ti is 100 at.% (feeding rate is 0.28 g/min).
- (2) The middle coat: Ti is 50 at.% and HAP is 50 at.% (feeding rate is 0.18 g/min).
- (3) The topcoat: HAP is 100 at.% (feeding rate is 0.11 g/min).

Ti-HAP FGC is prepared on the Ti substrates. Typical processing duration times of processes (1)~(3) are 30 s, each.

The prepared films of Ti-HAP FGC are evaluated by X-ray diffraction (XRD) analysis. The surfaces and cross sections of prepared films are observed using a scanning electron microscope (SEM) and an electron probe microanalyzer (EPMA). The bond strength of

prepared films is measured with a bond strength testing machine.

### 3. Experimental Results and Discussion

Figure 2 shows the surface morphology of the HAP coating sprayed at a jet power of 5.3 kW. As spherical powders of HAP are not observed on the surface of the prepared films, HAP particles are concluded to be well melted within the traveling time in the high-temperature plasma flow and jet and that melted HAP particles collided with the substrate and become flat.

Figure 3 shows XRD patterns of prepared films (HAP films) and HAP powders. Usually, HAP is decomposed into tetracalcium phosphate (TTCP), tricalcium phosphate (TCP) and calcium oxide (CaO) on applying a plasma jet with high power. However, decomposed toxic substances, for example, CaO, are not observed under our typical experimental conditions where jet power ( $W_j$ ) is about 5 kW.

The control of the composition ratio and orientation of the films is important for suppressing the dissolution of bioceramics and improving their mechanical strength. Human bone is c-axis oriented, which contributes to the suppression of dissolubility and maintaining toughness. The orientation of the prepared films can be inferred from the change in the peak intensities of the XRD patterns. An increase in HAP (002) and (004) peak intensities ( $2\theta = 25.878$  and  $53.210^\circ$ , respectively) confirms that the HAP is c-axis oriented.<sup>10)</sup> HAP (002) and (004) peak intensities of the prepared films are increased after film formation, and it is confirmed that the HAP of the prepared films are c-axis oriented.

Figure 4 shows XRD patterns of the prepared films (FGC), HAP powders and Ti

powders. Reactions between HAP and Ti particles in contact with each other in the plasma flame might form some titanium-calcium compounds.<sup>3)</sup> However, no clear peaks corresponding to such titanium-calcium compounds are observed in our XRD patterns of the prepared film. The XRD pattern of the prepared film is the same as that of HAP powders. HAP is also not decomposed to toxic substances, similar to the results in Fig. 3. There are no Ti peaks in the prepared films.

Figure 5 shows the results of composition analysis of the prepared film using EPMA. Images (b), (c) and (d) are the results for Ca, P and Ti, respectively. Although a few pores are observed in the prepared film, the porosity is about 4.3 %. Therefore, the HAP layer and Ti layer on the prepared film are well adhered to each other. 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 quantitative analysis of the Ti composition ratio of the prepared films is also carried out using image (d). Namely, the Ti component ratio is estimated from the ratio of the area of Ti to the total area of the middle layer. The Ti composition ratio in the prepared films is 54.9 at.% in the middle layer, which was sprayed with powder mixtures of Ti 50 at.% and HAP 50 at.%. For estimation, the same procedure is applied to the other two layers. Numerical results of estimation are as follows.

- (1) The under layer: Ti is 98.2 at.%. Film thickness is about 50  $\mu\text{m}$ .
- (2) The middle layer: Ti is 54.9 at.% and HAP (Ca) is 43.9at.%. Film thickness is about 80  $\mu\text{m}$ .
- (3) The top layer: Ti is 3.1 at.% and HAP (Ca) is 95.6 at.%. Film thickness is about 70  $\mu\text{m}$ .

Then, Ti composition ratios are nearly equal to the powder composition ratios for each of the

three layers. It is confirmed that the three-layered Ti-HAP FGC film is well prepared, and that the composition ratios in the prepared films are also well controlled by changing the powder composition ratios. To use the HAP films in artificial bone over a long term, a film thickness within 50~100 $\mu\text{m}$  is necessary. The HAP layer thickness of the prepared FGC film is about 70  $\mu\text{m}$ . The prepared films clearly satisfy the necessary film thickness for artificial bone.

Finally, we test the bond strength of the prepared films. The numerical bond strength is estimated using the following equation:

$$\text{Bond strength (MPa)} = P \text{ (N)} / A \text{ (mm}^2\text{)}, \quad (1)$$

where  $P$  is the tensile breaking load and  $A$  is the area of the prepared film. In general, it is said that the bond strength must be 10 MPa for artificial bones.

Figure 6 shows the results of the bond strength test. For films prepared on the substrates without the blast process, the bond strength is below 10 MPa. In contrast, the bond strength of the films prepared on the substrates with the blast process is higher than that of the films prepared on the substrates without the blast process. Bond strength has a tendency to increase with jet power. For the jet power of 6 kW, some films have a bond strength of 30 MPa at maximum, although the bond strengths of the films are distributed from 10 to 30 MPa. One of the reasons for such a nonuniform result is that the surfaces of blast-processed substrates are irregular. It is also noted that, for all samples, the HAP/Ti interface is not exfoliated whereas the Ti/substrate interface is exfoliated.

In the future, it will be necessary to clarify the relationships between the preprocessing conditions of the substrates and the bond strength, as well as to further study the optimum

conditions of Ti-HAP FGC coatings.

#### 4. Conclusions

The preparation of Ti-HAP FGC using a newly designed thermal plasma reactor was studied. It has been confirmed that the three-layered FGC films are well prepared. The findings are as follows;

- (1) The composition ratio of Ti in prepared films is nearly equal to that of injected powder materials. It would be possible to control the composition ratio of films by changing the composition ratio of powders.
- (2) FGC films can be prepared with a relatively low jet power, i.e., from 4 to 6 kW. Then, products of HAP decomposition do not appear in the films. The prepared films are relatively dense (porosity is about 5%). HAP and Ti grains are adhered together well. The prepared HAP films are c-axis oriented.
- (3) Bond strength increases with increasing plasma jet power. Although the results are preliminary, the bond strength is 30 MPa at maximum with a low jet power of 6 kW. These prepared films have the necessary bond strength for artificial bone.

The obtained films satisfy the necessary conditions for artificial bones. In the future, it may be possible to prepare dense and high-bond-strength Ti-HAP FGC films under optimized combinations of spraying conditions, i.e., jet power, duration and substrate position. We will also perform the clinical test.



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## Reference

- [1] O. Fukumasa: *Oyo Buturi* **67** (1998) 181 [in Japanese].
- [2] O. Fukumasa: *Thin Solid Films* **390** (2001) 37.
- [3] M. Inagaki, Y. Yokogawa and T. Kameyama: *Surf. Coat. Technol.* **173** (2003) 1.
- [4] K. A. Khor, Y. W. Gu, D. Pan and P. Cheang: *Biomaterials* **25** (2004) 4009.
- [5] K. Osaki, T. Iiboshi, S. Fujimoto, O. Fukumasa and A. Kobayashi: *Kouon Gakkaishi* **29** (2003) Suppl. 235[in Japanese].
- [6] H. Mukunoki, O. Fukumasa and S. Sakiyama: *Thin Solid Films* **407** (2002) 92.
- [7] O. Fukumasa, R. Tagashira, K. Tachino and H. Mukunoki: *Surf. Coat. Technol.* **169-170** (2003) 579.
- [8] M. Kurita and O. Fukumasa: *Tech. Meet. Plasma Science and Technology, IEE. Jpn PST-05, 2005*, 53[in Japanese].
- [9] O. Fukumasa and S. Sakiyama: *Surf. Coat. Technol.* **131** (2000) 493.
- [10] M. Inagaki: private communication.

## Figure Captions

Fig.1. Schematic diagram of jet reactor.

Fig.2. Surface morphology of HAP coatings.

Fig.3.XRD patterns: (a) raw HAP powders and (b) prepared films (HAP)

Fig.4.XRD patterns: (a) prepared films (FGC), (b) HAP powders and (c) Ti powders.

Symbols are ○ (HAP) and ◆ (Ti).

Fig. 5. Composition analysis of prepared film using EPMA: (a) SEM images of the prepared film, (b) composition of Ca, (c) composition of P, and (d) composition of Ti.

Fig. 6. Estimated bond strength of the prepared films versus plasma jet power  $W_j$ . Symbols are as follows. ◇, □; Films prepared on substrates without blast process, ▲, ◆, ■: Films prepared on substrates with blast process.

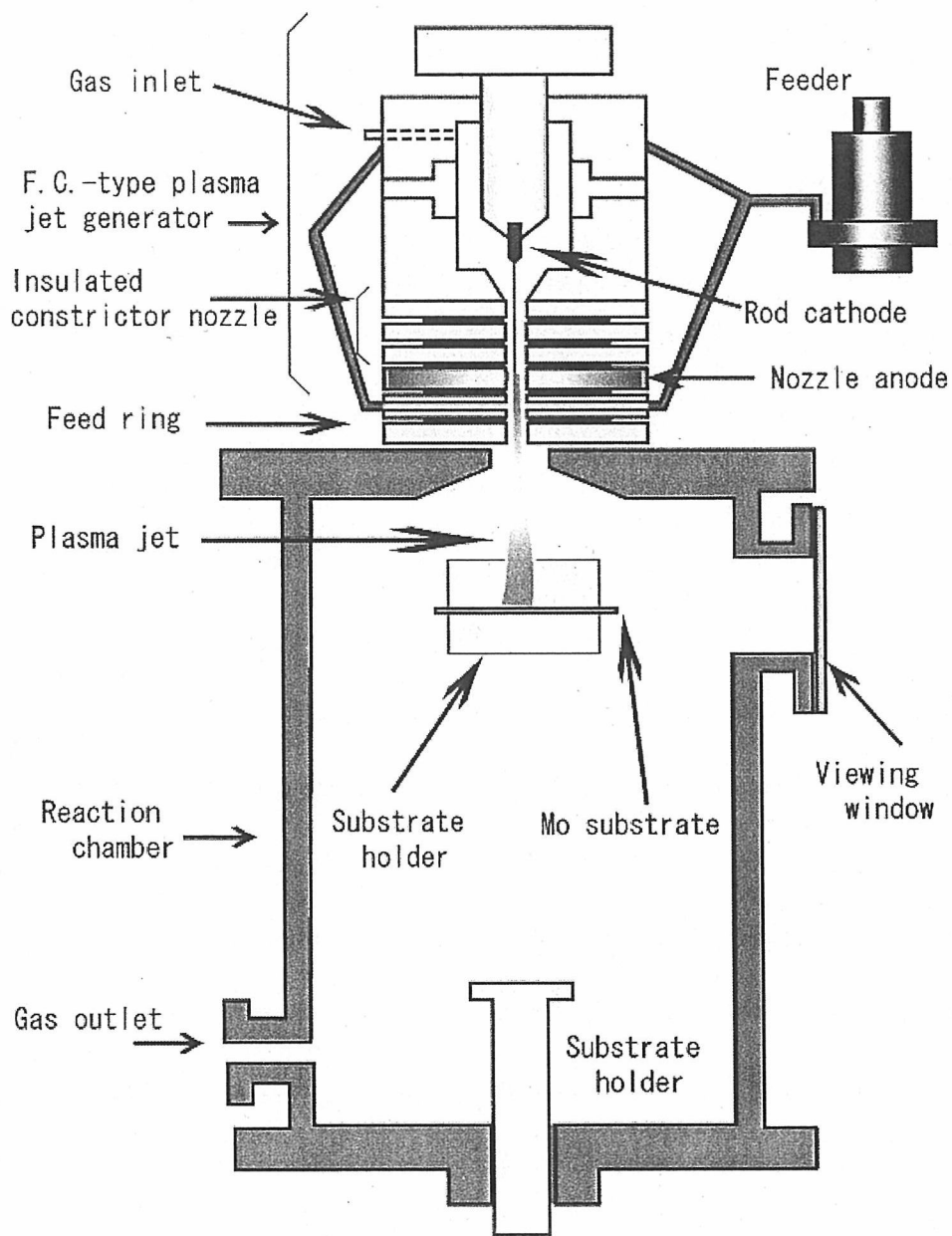
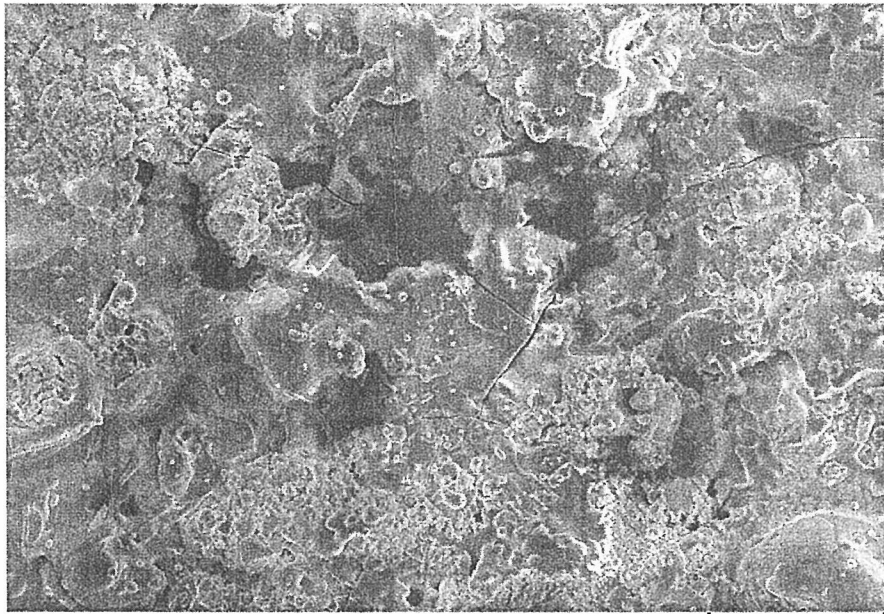


Fig. 1. Schematic diagram of jet reactor

Masanori Kurita



50  $\mu\text{m}$

Fig.2. Surface morphology of HAP coatings

Masanori Kurit

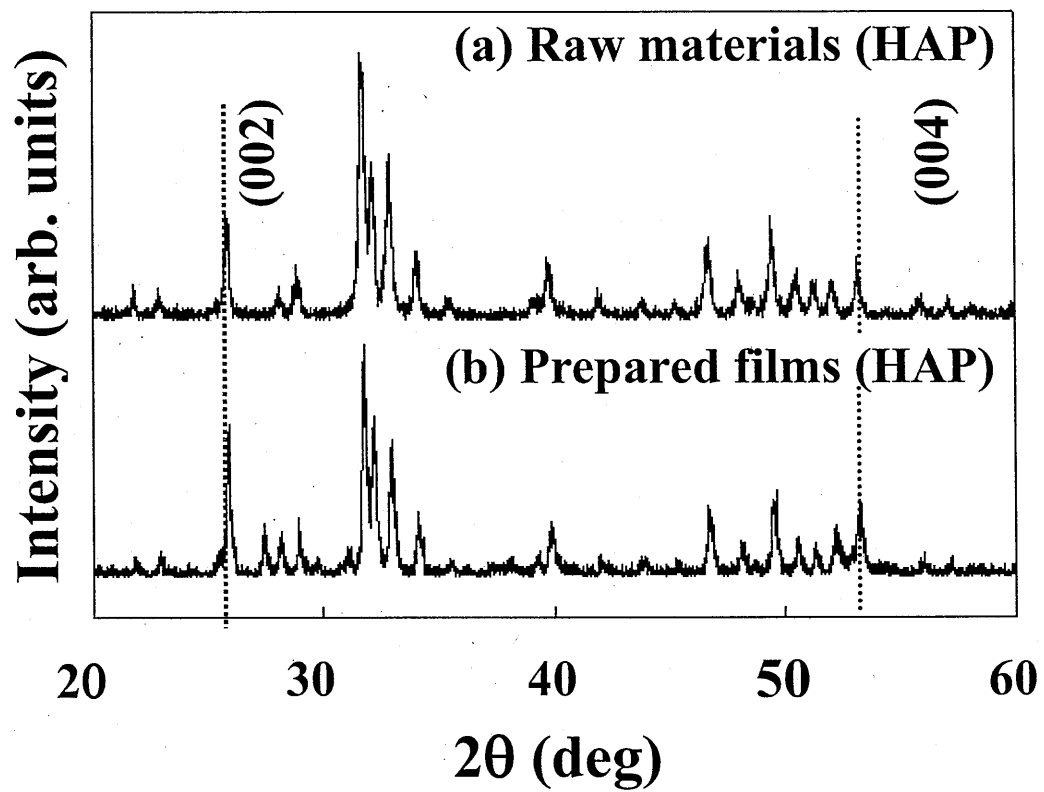


Fig.3. XRD patterns: (a) raw HAP powders and (b) prepared films (HAP).

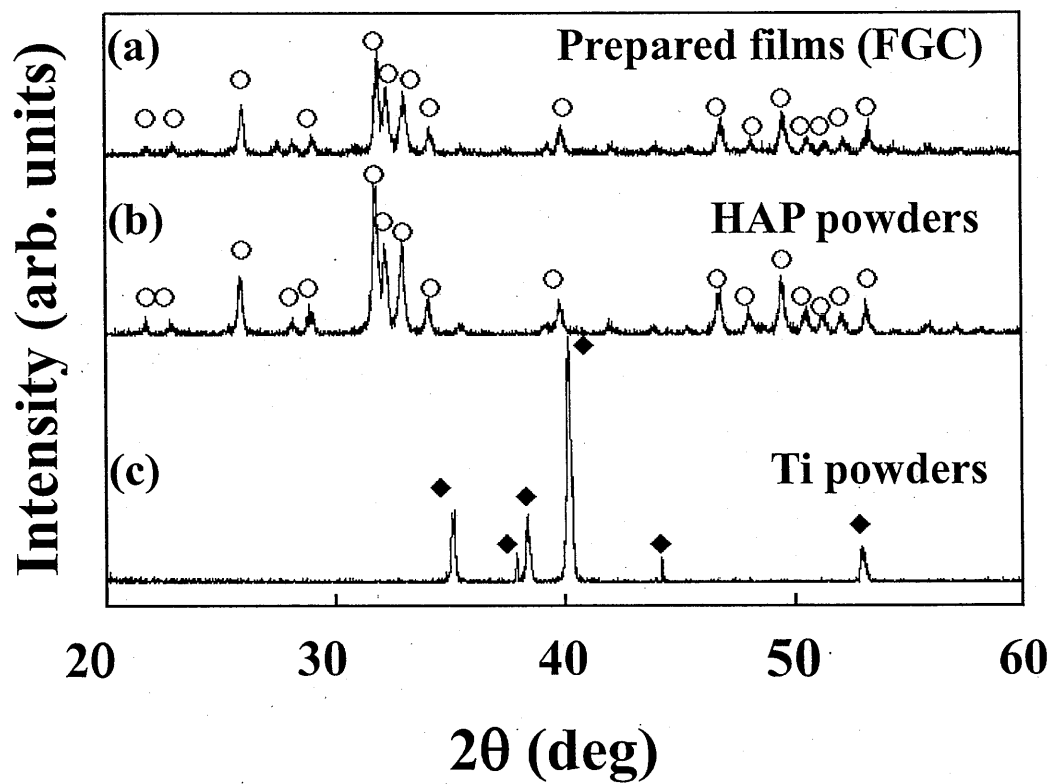


Fig.4. XRD patterns: (a) prepared films (FGC), (b) HAP powders and (c) Ti powders. Symbols are ○ (HAP) and ◆ (Ti).

Masanori Kurita

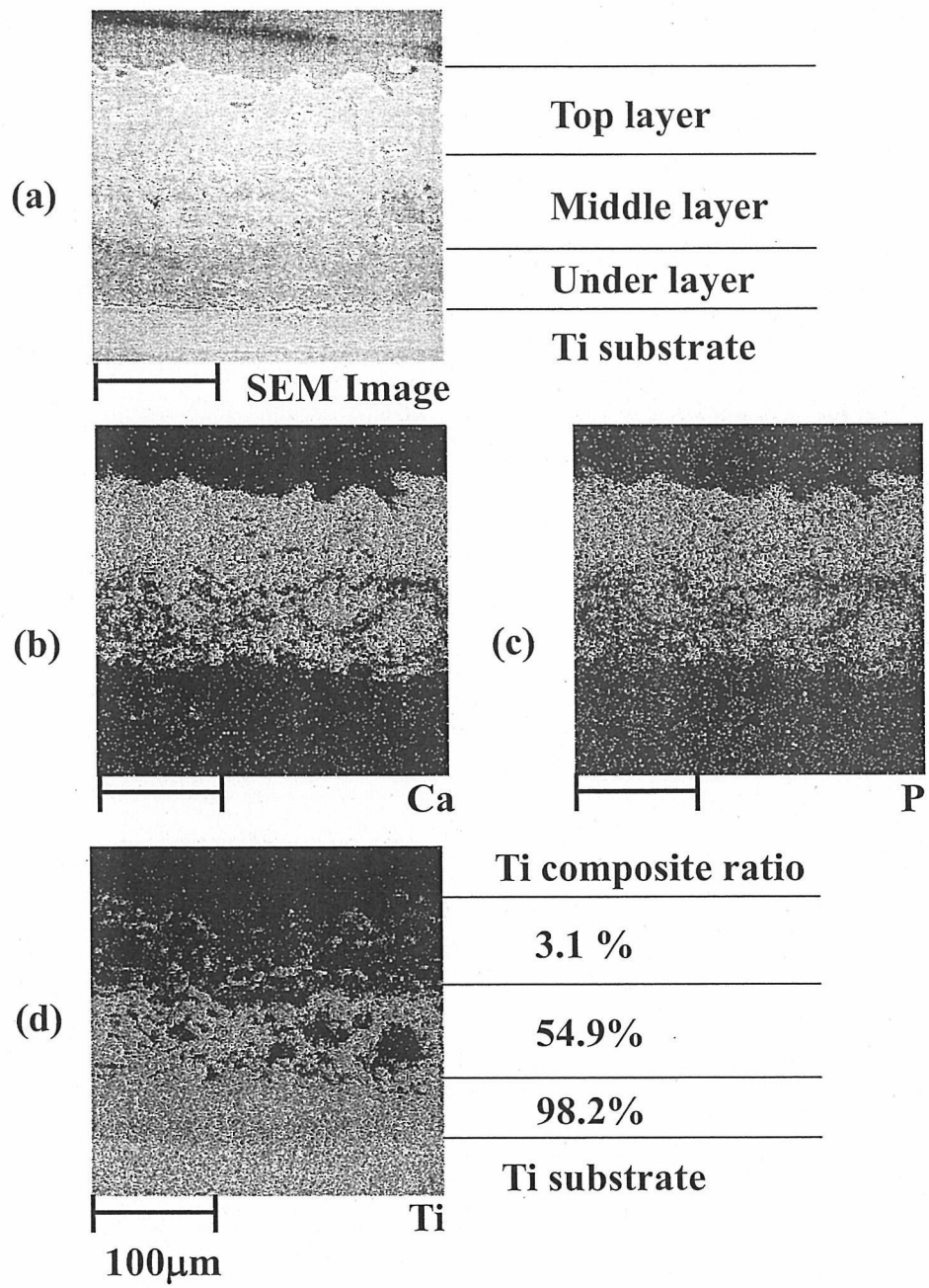


Fig. 5. Composition analysis of prepared films using EPMA.



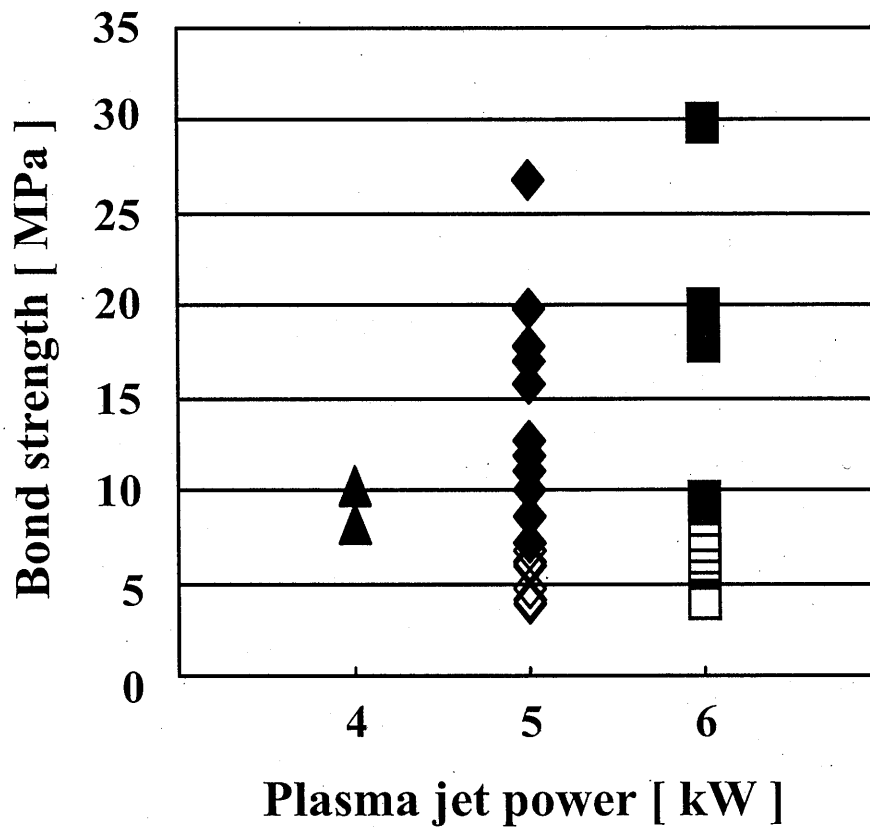


Fig. 6. Estimated bond strength of the prepared films versus plasma jet power  $W_j$ . Symbols are as follows.  $\diamond$ ,  $\square$ : Films prepared on substrates without blast process,  $\blacktriangle$ ,  $\blacklozenge$ ,  $\blacksquare$ : Films prepared on substrates with blast process.