Production of fine hydroxyapatite films using the well-controlled thermal plasma

Masahiro Kou, Toda Takafumi, Osamu Fukumasa

Graduate School of Science and Engineering, Yamaguchi University,
2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan
Email: fukumasa@plasma.eee.yamaguchi-u.ac.jp
Fax: +81-836-85-9401

Abstract

Hydroxyapatite (HAP)-coated implants on metallic substrates have been used as biomaterials. The problem is that HAP coating on metallic substrates is easily exfoliated at the boundary between HAP and metallic substrates, i.e. titanium (Ti). Therefore, Ti-HAP Functionally Graded Coating (FGC) is considered to improve adhesion of Ti-HAP coatings. In this paper, preparation of Ti-HAP FGC is studied in detail by using the well-controlled DC plasma jet. Properties of Ti-HAP FGC films (i.e. the c-axis orientation, the bond strength and the hardness) are also discussed in relation to spraying conditions.

KEYWORDS; dc plasma jet, plasma spraying, functionally graded coatings, hydroxyapatite.

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 [1, 2]. The reactor can produce a plasma jet with high stability and high thermal efficiency under various operating conditions [2]. So far, we have reported the experimental results on preparation of Ti-Al FGC, β”-alumina film synthesis and of MgO coatings with using this device [3, 4, 5].

By the way, in the recent years with aging society, necessity of artificial bones has been increased. Hydroxyapatite (HAP; Ca_{10} $[PO_4]_6[OH_2]$), 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 coefficients between the ceramic coatings (i.e. HAP) and the metal substrates, residual stress arises at the ceramic/metal interface. This residual stress often causes cracks and reduces the adhesion strength of HAP coatings to the substrate. Therefore, Functionally Graded Coatings (FGC) has been found to improve the adhesion strength.

There are various methods of applying HAP coatings. Most of HAP coatings have been performed by Radio Frequency (RF) thermal plasmas [6]. The adhesion strength tends to increase with increasing the applied RF input power [6.7]. However, HAP is decomposed because RF jet power of HAP coating is high. So, by using DC plasma jet with low power, the increase of mechanical strength can be expected because, in general, velocity of injected powders in DC plasma jet becomes higher than one in RF plasma jet. In addition, the control of RF plasmas jet is not so easy compared with DC plasma jet.

We have undertaken preparation of Ti-HAP FGC films with using the well-controlled DC plasma jet. So far, we have succeeded in preparation of Ti-HAP FGC films. Based on the previous results [8], in this paper we further study improvement of Ti-HAP FGC films (i.e. c-axis orientation, the adhesion strength and the hardness) and briefly discuss the optimum condition for preparation.

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 hight).

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 [1, 2]. Then, a stable plasma jet with high heat capacity is produced under various operating conditions [1, 2].

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_t) is 760 Torr, jet power (W_j) is varied from 3 to 6kW, and the distance from the feed ring exit to the substrate (L) is 70 mm. There are some relationships between the jet power (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. Commercial Ti substrates (3 mm thick) are polished with #180 abrasive papers, washed ultrasonically in acetone, and then dried in air before spraying. To prepare Ti-HAP FGC, powders of Ti (mean diameter 25 μm) and HAP (mean diameter 30 μm) are used. These powders are 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. The cross sections of prepared films are observed using a scanning electron microscope (SEM). The adhesion strength of prepared coating is measured by a bond strength machine. The hardness of prepared films is measured with a Vickers hardness tester.

3. Experimental Results and Discussion

Ti-HAP FGC is prepared on the Ti substrates. To melt HAP powder at the low jet power, HAP powders with small diameter are used compared with a previous one [8]. Therefore, feeding rate of HAP powders in the middle coat becomes higher and process time of HAP coating is longer than one in the previous result [8].

In the present experiment, for preparing three layers Ti-HAP FGC coatings, 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 30s).

(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 60s).

(3) The top coat: HAP is 100 mass% (feeding rate is 0.07 g/min and the typically process time 60s).

Typical example of the spray coating and the result of its composition analysis using EDX are shown in Fig.2, where W_j = 6kW. Figure 2 (a) shows a SEM image of the cross section of the prepared films. On the other hand, figure2 (b), (c), and (d) are the composition analysis of Ca, P and Ti, respectively. Although a few pores are observed in the prepared films, the porosity is about 1%. 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 Ti composition ratio of the prepared films is also carried out with using the photograph shown in Fig.2 (d). Ti component ratio is estimated from the ratio of the area of Ti to the total area of each layer. For example, Ti composition ratio in the middle layer is 33.5at% where spraying is done with powder mixtures of Ti 33mass% and HAP66mass%. For estimation of composition ratio, the same procedure is applied to other two layers. Numerical results of estimation are as follows:

(1) The under layer; Ti is 97.6at%. Film thickness is about 38.6 μm.

(2) The middle layer; Ti is 33.5at% and HAP (Ca) is 43.9at%. Film thickness is about 21.9 μm.

(3) The top layer; Ti is 2.1at% and HAP (Ca) is 95.6at%. Film thickness is about 38.6 μm.

Then, it is confirmed that the three layered Ti-HAP FGC film is prepared successfully.

We have reported that adhesion strength of prepared films is increased with increasing W_j [8]. However, HAP is decomposed when W_j is high. So, in the present experiment, we will spray both the middle coat and the under coat with rather high W_j, i.e. 6kW. After that, we will examine the property of the HAP coating with varying W_j. As a whole, prepared films have the following tendencies. Total film thickness and porosity of prepared films are decreased with increasing Wj. It is thought that prepared films are compressed during HAP coating with increasing Wj. However, it is also confirmed that the three layered Ti-HAP FGC film is prepared successfully.

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

Figure 3 shows XRD patterns of prepared films for three different jet powers. An increase in peak intensities of (002) and (004) peaks, (i.e. 2θ=25.878 and 53.210°, respectively) confirms that the HAP coatings are c-axis oriented. Usually, this point is estimated by the following formula

$$F_{ori} = \{\sum I_c(00l) / \sum I_c\} / \{\sum I_R(00l) / \sum I_R\}, \quad (1)$$

where Σ *I* (00l) is the sum of HAP peak (002) and (004), and Σ *I* is 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 with using eq. (1). The values of F_{ori} are 1.24, 3.24 and 3.53, respectively. The c-axis orientation is increased with increasing W_j. However, tetracalcium (TCP), and calcium oxide (CaO) are also appeared in HAP coatings with increasing $W_{j,}$ (see Figs 3(c) and 3(d)). Therefore, good combination between W_j and HAP powder flow rate is important.

Next, we will test the adhesion strength of the prepared films. It is expected that the adhesion strength of artificial bones with substrate is strong enough and that HAP coating should have long life-time. It is said that, the adhesion strength should be equal to or higher than 10MPa [9].

Figure 4 shows the result of the adhesion strength test for the prepared films (FGC). Although the under coatings are removed from the Ti substrate for all films, prepared three layers (i.e. HAP layer, Ti-HAP layer and Ti layer) are well adhered each other. At any note, with each other the adhesion strength between the prepared film and the substrate increases in its value with increasing W_j. The adhesion strength of prepared films has the necessary value to be used as artificial bones.

Finally, the Vickers hardness of prepared films is discussed. The Vickers hardness is estimated using the following equation:

$$H_v = 1.8544 \times \frac{p}{d^2}, \tag{2}$$

where p is loading and d is the length of the diagonal of the depressed area. The thickness of the sample is necessary more than 1.5 times d. In the present test, d is about 20μm with W_j of 6kW. It is said that the hardness of artificial bones must be higher than 10MPa.

Figure 5 shows jet power dependence of the Vickers hardness of prepared films (FGC). The Vickers hardness is increased with increasing W_j. As is shown clearly in Fig.5, all of the prepared films have the values of hardness much higher than the necessary value (i.e. 10MPa) to be use as artificial dental root.

According to the present results and discussion, it is confirmed that film thickness and porosity of prepared films are decreased with increasing W_j and that mechanical properties (i.e. adhesion strength and hardness) are improved with increasing $W_{j.}$ On the other hand, HAP is decomposed with increasing $W_{j.}$ With increasing $W_{j,}$ jet temperature is increased and its axial distribution is varied (not shown here). Relationship between plasma jet condition and quality of the prepared films is under study. At any note, the present spraying method (i.e. changing spray condition for the top layer coating and other layers coating) is very effective to prepare Ti-HAP FGC.

4. Conclusions

In this paper, we have studied preparation of Ti-HAP Functionally Graded Coating by using a well-controlled DC plasma jet. The characteristics features of prepared HAP coatings are evaluated with varying Wj. The c-axis orientation, adhesion strength and hardness of the prepared films are increased with increasing Wj. However, tetracalcium (TCP), and calcium oxide (CaO) are also appeared in HAP coatings with increasing Wj. It is confirmed that top coat should be prepared with optimum Wj in order to suppress decomposition of HAP. In the futures, for preparing Ti-HAP FGC optimum conditions between jet parameters and spaying conditions are further studied.

5. Acknowledgements

The authors want to thank S. Fujimoto for his support in the experiments. The author (M.K.) also thanks K. Inada (Yamaguchi Prefectural Industrial Technology Institute) for the measurement of the Vickers hardness of prepared films. A part of this work was supported by a Grant-in-Aid for Scientific Research (A) from Japan society for the promotion of science.

References

[1] O. Fukumasa: Oyo Butsuri **67** (1998) 181. [in Japanese]

[2] O. Fukumasa: Thin Solid Films **390** (2001) 37.

[3] K. Osaki, T. Iiboshi, S. Fujimoto, O. Fukumasa and A. Kobayashi: Kouon Gakkaishi **29** (2003) Suppl. 235[in Japanese].

[4] H. Mukunoki, O. Fukumasa and S. Sakiyama: Thin Solid Films **407** (2002) 92.

[5] O. Fukumasa, R. Tagashira, K. Tachino and H. Mukunoki: Surface and Coatings Technology **169-170** (2003) 92.

[6] M. Inagaki, Y. Yokogawa and T. Kameyama: Surface and Coatings Technology **173** (2003) 1.

[7] K.A. Khor, Y.W. Gu, D. Pan and P. Cheang: Biomaterials **25** (2004) 4009.

[8] M. Kurita and O. Fukumasa: Jpn. J. Appl. Phys. **45**(2006)8348.

[9] E Fernandez Maria Daniela Vlad, Maria Montserrat Gel, Jose Lopez, Ricardo Torres, Juan V. Cauich and Marc Bohner: Biomaterials **26**(2005)3393.

Figure Captions

Fig.1 Schematic diagram of the thermal plasma reactor based on the forced constricted type plasma jet generator.

Fig. 2. Composition analysis of prepared film using EDX.

Fig. 3. X-RD patterns of HAP coatings, (a) raw material, (b) coatings at 4kW, (c) coatings 5kW, (d)coatings at 6kW Symbols ○, ● and ▲ mean HAP, TCP and CaO, respectively. Other experimental conditions are as follows: *Pt* = 760Torr, *L* = 70 mm

Fig.4. The adhesion strength of the FGC films versus jet power.

Fig. 5. Vickers hardness of the FGC films versus jet power.

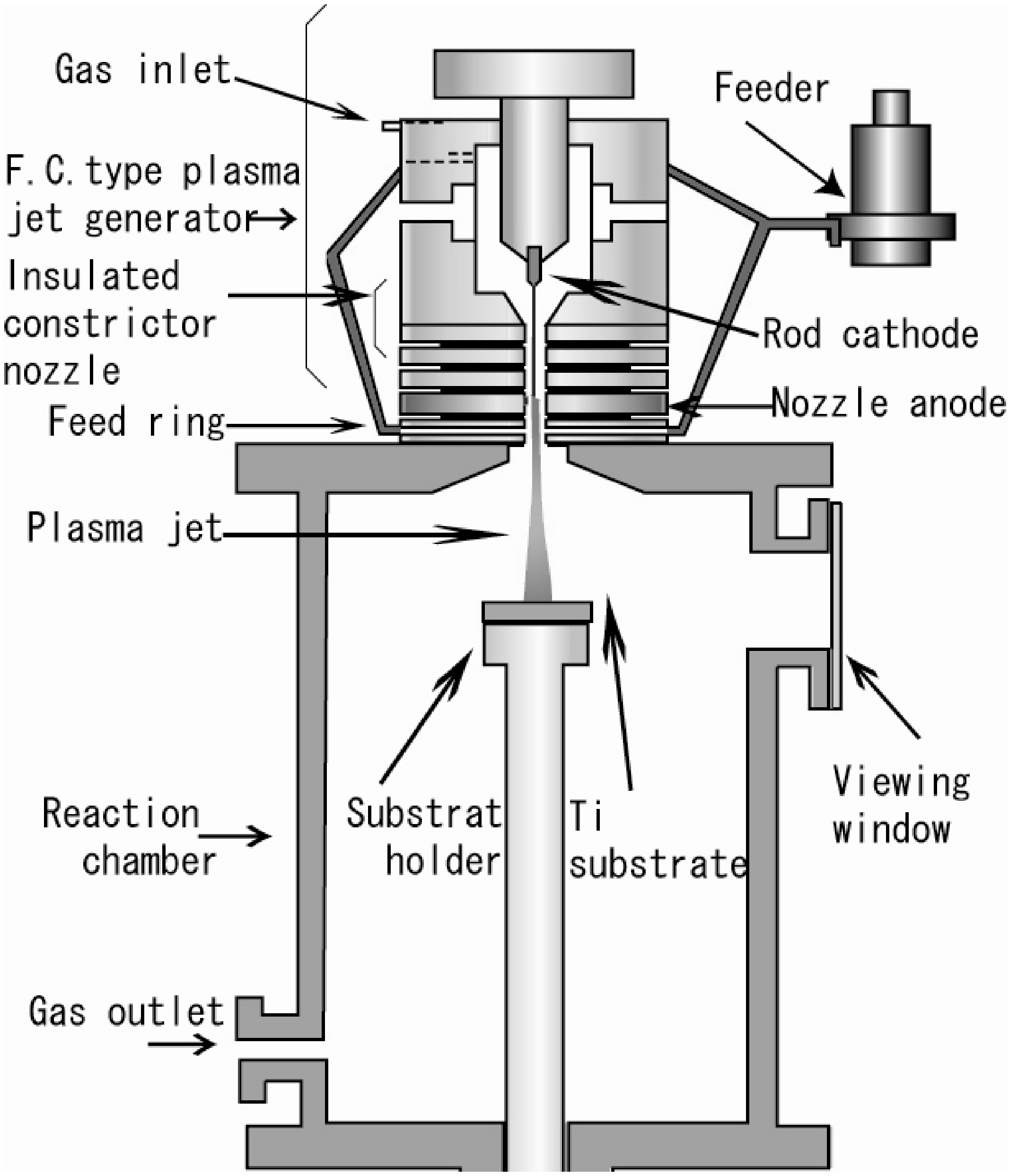
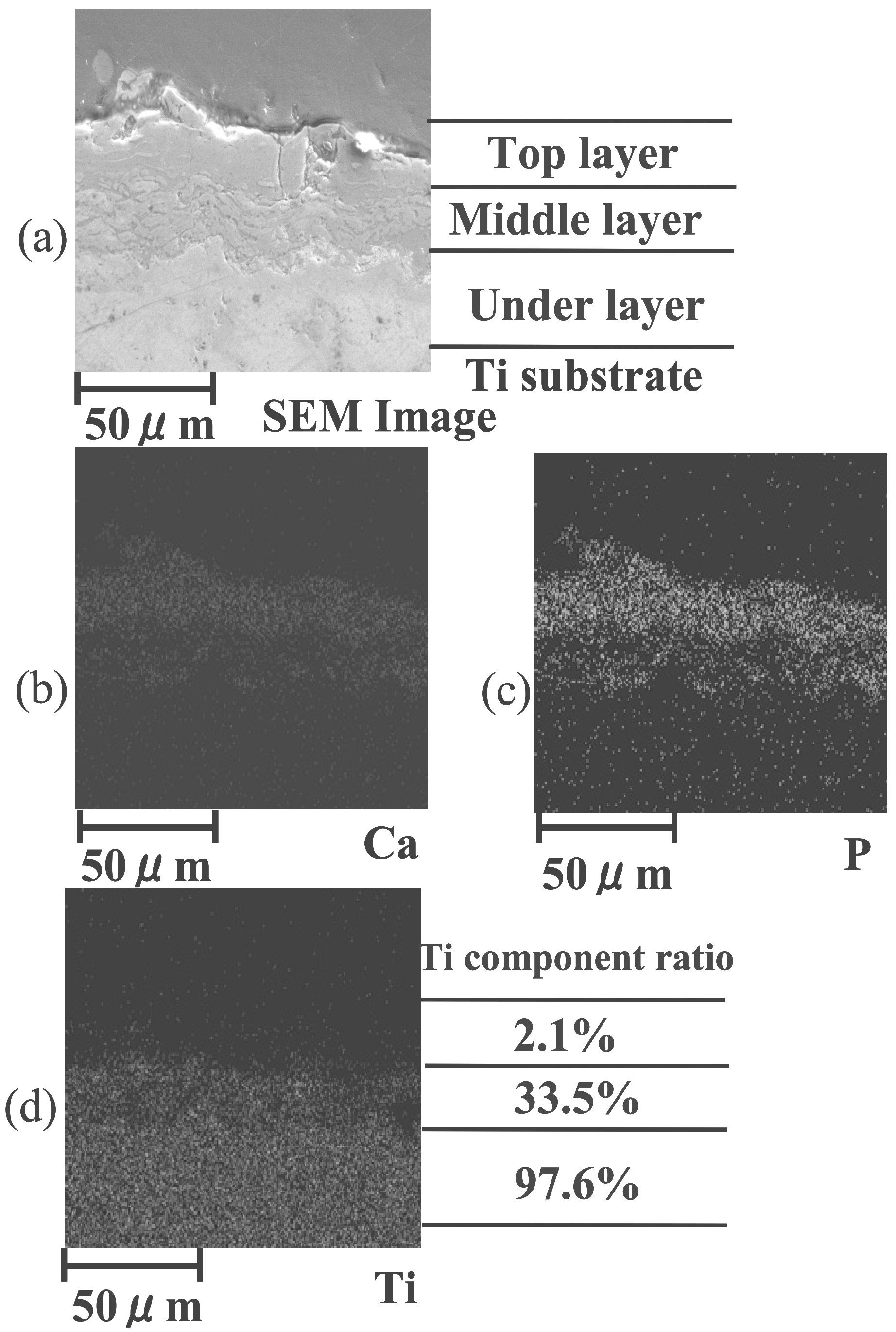

Gas inlet
F.C. type plasma
jet generator
Insulated
constrictor
nozzle
Feed ring
Feeder
Rod cathode
Nozzle anode
Plasma jet
Reaction
chamber
Substrat
holder
Ti
substrate
Viewing
window
Gas outlet

Fig.1



(a)
Top layer
Middle layer
Under layer
Ti substrate
50 μ m
SEM Image
(b)
50 μ m
Ca
(c)
50 μ m
P
(d)
Ti component ratio
2.1%
33.5%
97.6%
50 μ m
Ti

Fig.2

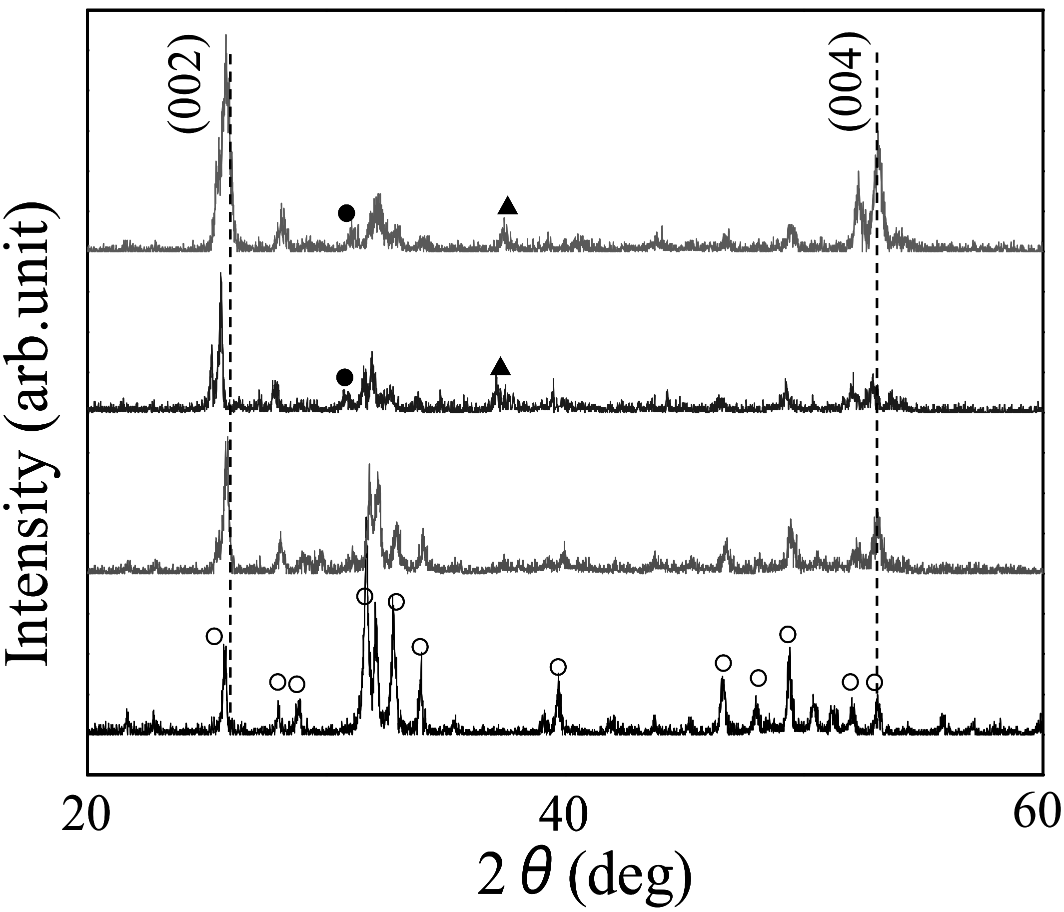


Fig.3

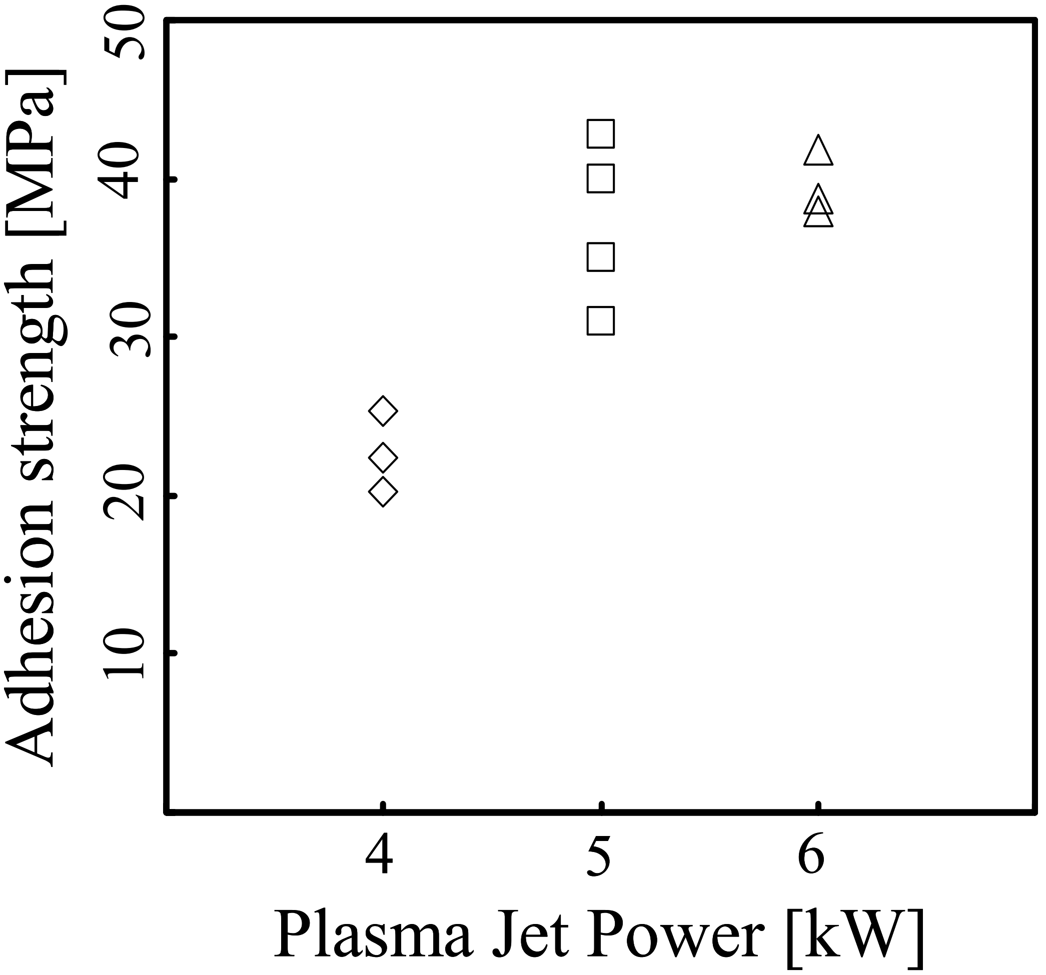


Fig.4

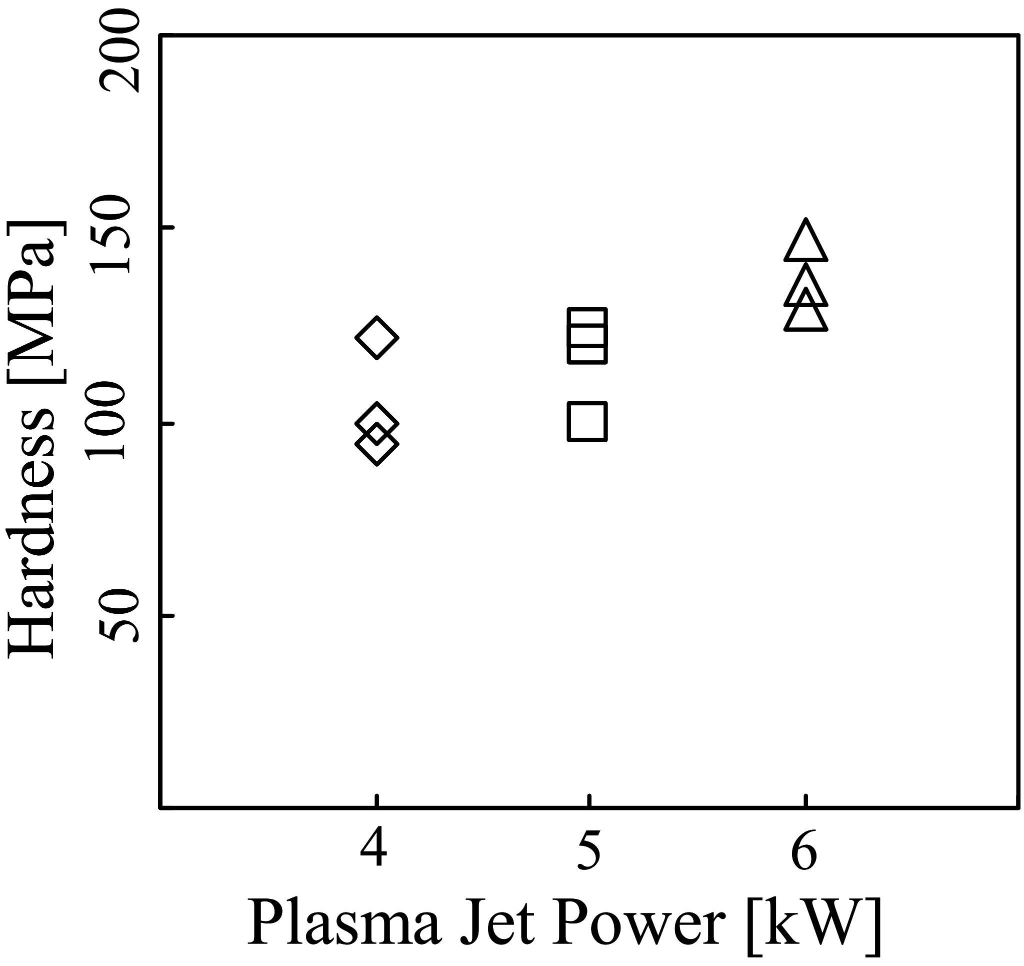


Fig.5