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Evaluation of Plasma Spray Hydroxy Apatite Coatings on Metallic Materials

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Biocompatible Hydroxy apatite (HAp) coatings on metallic substrate by plasma spray techniques have been developed. Long-term credibility of plasma spray HAp coatings has been evaluated in physiological saline by electrochemical measurements. It was found that the corrosion resisitance of SUS316L based HAp/Ti conbined coatings was excellent even after more than 10 weeks long-term immersion. It was shown that postal heat treatment improved both the crystallinity and corrosion resistance of HAp. By lowering cooling rate during heat treatment process, less cracks produced in HAp coating layer, which lead to higher credibility of HAp during immersion in physiological saline. The ICP results showed that the dissolution level of substrate metallic ions was low and HAp coatings produced in this research can be acceptable as biocompatible materials. Also, the concentration of dissolved ions from HAp coatings with postal heat treatment was lower compared to those from samples without postal heat treatment. The adherence of HAp coatings with Ti substrate and other mechanical properties were also assessed by three-point bending test. The poor adhesion of HAp coating to titanium substrate can be improved by introducing a plasma spray titanium intermediate layer.

Keywords : *Hydroxy apatite, plasma spray technique, biocompatible, EIS, ICP, corrosion resistance, titanium, SUS316L, heat treatment.*

1. Introduction

Hydroxy apatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is well known as a bioactive material since the main inorganic content of bones or teeth is HAp. Although HAp has excellent biocompatibility, its mechanical properties are poor just as other ceramic materials. Therefore, instead of being used as a bulk biocompatible material, HAp has been widely applied as a surface coating on metallic materials to improve their biocompatibility. Plasma spraying is one of the practically and widely used techniques for preparing biocompatible HAp coatings. Compared to other techniques such as sol-gel method, sputter coating, electrophoretic deposition and hot isostatic pressing, HAp coatings obtained by plasma spray process has strong adhesion to metallic substrate, porous coating layer which is big advantage for biomaterials since body fluid can flow into porous HAp coating layer and tissues or bones can grow inside.

The development of plasma spray HAp coating on metallic substrates has been conducted for years in our research lab. It was found that plasma spray HAp coatings on Ti has excellent corrosion resistance.[1)] The stability of HAp powder during plasma spray process can be improved by sintering HAp powder at high temperature.[2)] The crystallinity of HAp coating can be recovered from amorphous HAp obtained right after plasma spraying by applying postal heat treatment at certain temperature.[1)] Besides Ti base HAp plasma spray coatings, developments on other metallic materials based HAp plasma spray coatings were also carried out by us, such as stainless steel. It is well known that stainless steels are being used as materials for implant parts, medical devices and surgical tools. Compared to titanium, stainless steel is also a chemically stable metallic biomaterial in most cases and it is a lower-cost material and easier to fabricate than titanium and its alloys. However, the result of our research showed that when HAp was coated directly onto stainless steel surface by plasma spraying, localized corrosion occurred seriously.[2)] To solve this problem, HAp/titanium combined coatings on SUS316L stainless steel was developed by introducing a plasma spray Ti intermediate layer between HAp and stainless steel substrate.[3)] Good corrosion resistance was obtained by increasing plasma spray current for HAp layer or by shorting the distance between plasma spray gun and coating samples. Long-term immersion test in physiological

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saline showed that plasma spray HAp/titanium coatings on SUS316L had excellent corrosion resistance and were very stable for a long term usage.[4)]

In this study, in order to improve the biocompatibility of amorphous HAp coatings obtained right after plasma spraying, postal heat treatment was conducted. The credibility of HAp/titanium combined coatings and the effect of heat treatment were assessed by electrochemical impedance monitoring in physiological saline for about 10 weeks. Also, conditions during postal heat treatment such as cooling rate were investigated. On the other hand, the adhesion of HAp coating to titanium was also evaluated by three-point bending test.

2. Experimentals

Biocompatible HAp powder was used for preparing the top layer of plasma spray coating. To increase its thermal stability, HAp powder was sintered at 1150˚C for 1 hour. Then, the sintered HAp was crashed into small particles by ball miller and finally screened into powder with a size about 75 μm in diameter by sifter. Pure titanium powder (99%, 45μm) was used for preparing intermediate titanium layer.

The substrate material used for making plasma spray HAp/titanium coatings is SUS316L stainless rod (ф 3.0x50mm). The chemical composition of SUS316L was shown in Table 1. The surface of SUS316L samples were sand-blustered in order to increase the mechanical bonding at titanium/stainless steel interface. All samples were cleaned by ultrasonic wave in acetone before plasma spraying.

Plasma spraying was conducted under air atmosphere. For titanium layer, the thickness was controlled at about 25 μm for getting the best performance as reported.[4)] For HAp layer, plasma spray current was 400 A. The distance between sample and plasma spray gun was set to 12 cm.

According to our previous studies, amorphous HAp combined with some amorphous TCP will be obtained right after plasma spray process. It is known that crystal HAp has better biocompatibility than amorphous HAp. Therefore, postal heat treatment was conducted at 600˚C for some HAp/titanium combined coating samples. Also, cooling rate during heat treatment was changed from 50˚C/h, 100˚C/h and furnace cooling (about 300˚C/h).

The evaluation of stability of plasma spray HAp/titanium coatings on SUS316L was done by continuous monitoring the change of impedance in physiological saline at room temperature for about 10 weeks. At the same time, corrosion potentials for all tested samples were also recorded. 3-electrode configuration was used for electrochemical impedance measurements. Pt sheet and SSE (Ag/AgCl) were used as counter and reference electrode, respectively. A sinusoidal perturbation of 10 mV was applied and the frequency was scanned from 10^5Hz to 10^{-2}Hz. The dissolution of ions from HAp/titanium coating was measured by ICP (Inductively Coupled Plasma). The surface morphology and cross section profile of plasma spray coating samples were observed by scanning electron microscope (SEM). The distribution of main elements such as calcium, titanium in coating layers was analyzed by EPMA.

The adhesion of HAp coating layer to titanium substrate was evaluated by three-point bending test. A plasma spray layer was introduced between HAp layer and titanium substrate as an improvement.

Table 1. Chemical composition of SUS316L (mass%)

	Cr	Ni	Mo	Mn	C	Si	Fe	Co
SUS316L	17.75	14.08	2.77	1.80	0.018	-	Bal.	-

3. Results and discussion

3.1 Effect of postal treatment on the credibility of HAp/titanium combined coatings on SUS316L

It was reported that crystallinity of HAp can be greatly recovered by annealing in the case of plasma spray HAp coated titanium. In this study, postal heat treatment was also applied to HAp/titanium combined coatings on SUS316L stainless steel. X-ray diffraction results showed the crystallinity of HAp was recovered by postal heat treatment at 600˚C for 1 hour. Fig. 1 shows the changes in corrosion resistance obtained from impedance monitoring for HAp/titanium coatings on SUS316L stainless steel. The corrosion resistance for HAp/titanium combined coatings prepared in both conditions was relatively stable during 11 weeks immersion in physiological saline, meaning both of them have good credibility as a biocompatible material. It was also found that the corrosion resistance for samples with postal heat treatment was higher than that without postal heat treatment, which means postal heat treatment can improve not only crystallinity but also credibility of HAp/titanium combined coatings on SUS316L stainless steel.

Fig. 2 shows the ICP results of dissolution of ions after 11 weeks immersion. The amount of Ni^{2+} ion dissolved from HAp/titanium coating with postal heat treatment was about 1/10 of that from HAp/titanium coating as sprayed. Since the dissolution of all ions decreased after postal heat treatment, it is concluded that postal heat treatment is very effective for preventing dissolution of ions from HAp/ttita-

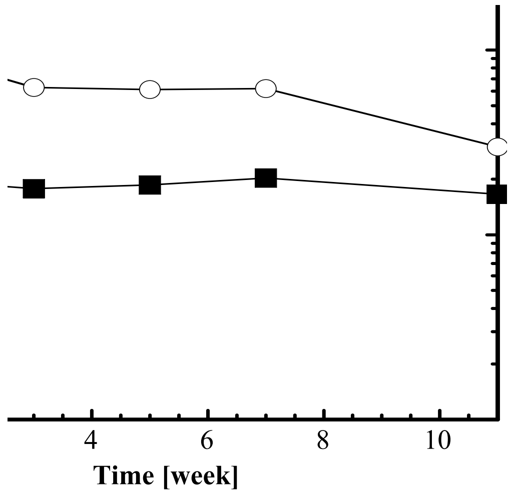


Fig. 1. Changes in corrosion resistance (R_c) for HAp/titanium combined coatings in physiological saline at room temperature.

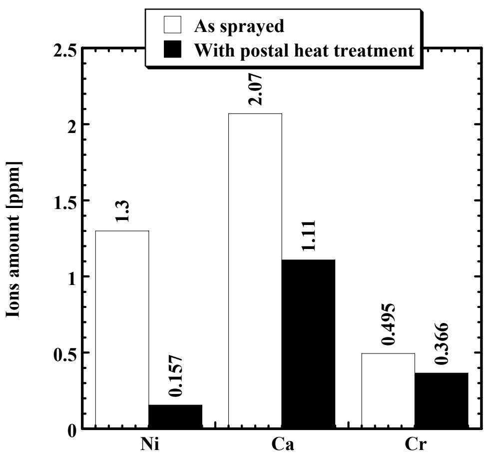


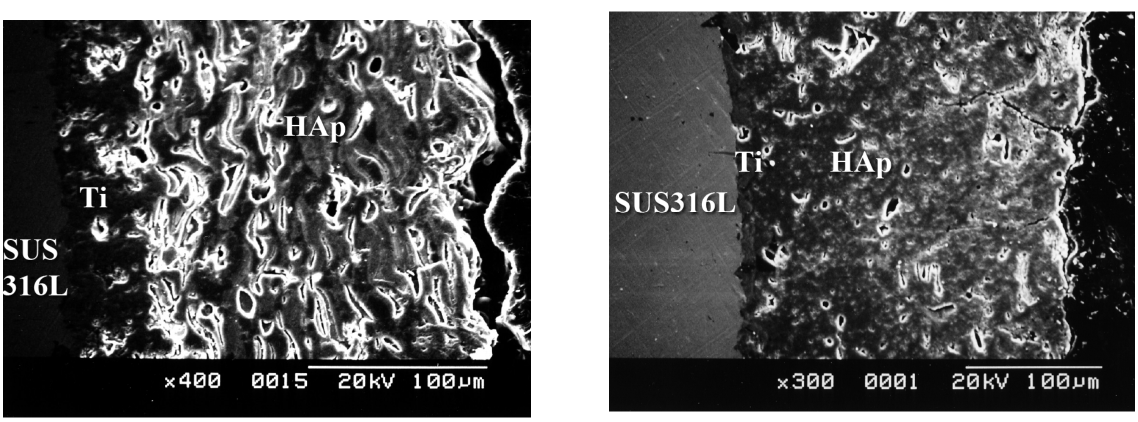
Fig. 2. Results of ICP analysis for plasma spray HAp/titanium coating on SUS316L in physiological saline.

nium combined coatings. This is well correlated with the results from corrosion resistance monitoring (Fig. 1).

SEM observation results are shown in Fig. 3. It can be seen that HAp coating layer became more condensed after postal heat treatment because of the recovery of crystallinity. This may be the reason for showing better corrosion resistance after postal heat treatment. However, cracks occurred at the outside of HAp layer. After 11 weeks immersion in physiological saline, small rusted area was found on the surface of HAp/titanium combined coating samples with postal heat treatment, implying that local corrosion happened possibly due to the existence of cracks.

3.2 The effect of cooling rate on corrosion resistance of HAp/titanium combined coatings

It is considered that the occurrence of cracks after postal heat treatment is mainly due to the thermal stress generated between plasma spray HAp layer and titanium intermediate layer since their thermal expansion coefficients of them are extremely different. In order to easing the thermal stress by drastic change in temperature, the cooling rate at the final step of postal heat treatment was decreased to 100˚C/h or 50˚C/h for some HAp/titanium combined coating samples. Fig. 4 shows the changes in corrosion resistance during immersion in physiological saline for HAp/titanium combined coatings treated at different cooling rates. It can be seen that corrosion resistance of all samples kept at a high value during 10 weeks immersion, meaning they all have good long-term credibility as biocompatible coatings. On the other hand, corrosion resistance for samples annealed at slower cooling rate condition was higher than that of those treated at faster cooling rate. As shown in Fig. 5, SEM observations showed more condensed HAp layer and less cracks for samples treated



(a) As sprayed (b) With postal heat treatment

Fig. 3. Cross section profile for HAp/titanium combined coatings on SUS316L.

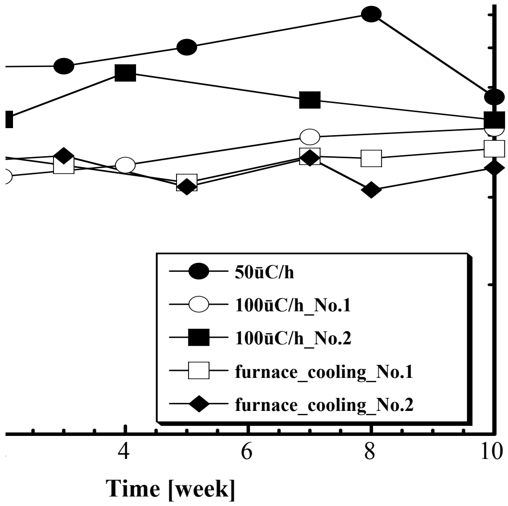


Fig. 4. Changes in corrosion resistance (R_c) for HAp/titanium combined coatings treated at different cooling rate in physiological saline at room temperature.

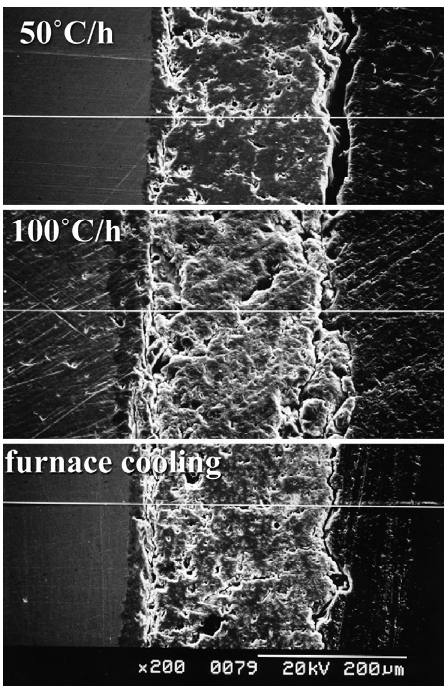


Fig. 5. Cross section profile of plasma spray HAp/titanium coating treated at different cooling rate.

at slower cooling rate. This is consistent to the results from impedance monitoring.

Fig. 6 shows ICP analysis results for HAp/titanium combined coatings treated at different cooling rate. The concentration of nickel ions (Ni^{2+}) in physiological saline after 10 weeks immersion was lower when cooling rate was 50°C/h. This result is well correlated with impedance monitoring and SEM observation. Therefore, it is concluded

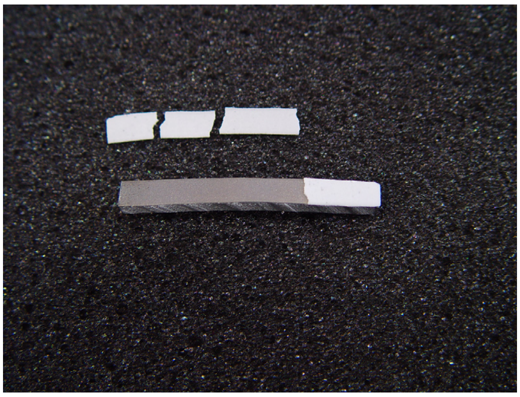
Fig. 6. Results of ICP analysis for plasma spray HAp/titanium coating on SUS316L prepared at different cooling rate.

that by lowering cooling rate during postal heat treatment, thermal stress can be eased and therefore, less cracks occurred in HAp layer. No rusted area was observed after 10 weeks immersion, which means that local corrosion resulted from cracks in HAp layer has been prevented.

3.3 Adhesion of HAp coating layer to titanium substrate

As a biocompatible coating, it is very important that the bonding between coating layer and substrate material is strong enough. In this study, the adhesion of HAp coating layer to titanium substrate was evaluated by three-point bending test. Fig. 7 shows samples of plasma spray HAp coating on pure titanium after the tests. In the case of HAp coating on titanium without postal heat treatment, peeling off of HAp layer was only observed near load concentration area (the central of sample), meaning HAp coating layer had good adhesion to titanium substrate. On the other hand, however, very poor adhesion of HAp coating layer to titanium substrate after postal heat treatment was observed as shown in Fig. 7 (b). Although the surface of titanium was sand blusted before HAp plasma spraying, the mechanical interlocking between HAp coating layer and titanium substrate was not strong enough to endure the thermal stress occurred during postal heat treatment. To solve this problem, a thin titanium intermediate layer was introduced by plasma spraying. Fig. 8 shows plasma spray HAp coating samples with induced plasma spray titanium layer after three-point bending tests. It can be seen that the peeling off HAp coating layer for samples with heat treatment only happened at load concentration area, indicating that a strong bonding between plasma spray HAp coating layer and titanium substrate has been achieved. Compared to Fig. 7 (b), it is concluded that the

(a) HAp coating on titanium as sprayed



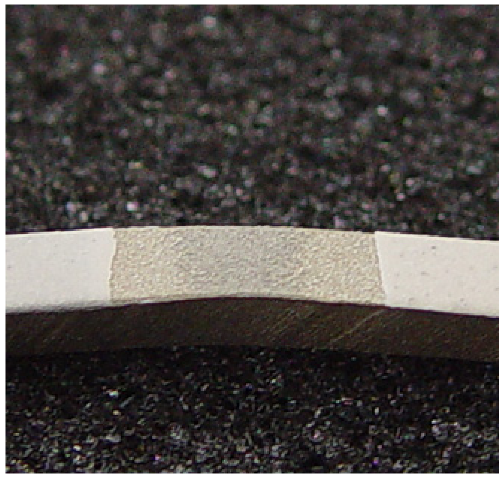
(b) HAp coating on titanium with heat treatment

Fig. 7. Plasma spray HAp coating on titanium after three point bending tests.

adhesion of plasma spray HAp coating layer (especially after postal heat treatment) to titanium substrate can be greatly improved by introducing a plasma spray titanium intermediate layer between them.

4. Conclusions

Biocompatible plasma spray HAp/titanium combined coating on SUS316L with Long-term credibility has been developed in this study. Postal heat treatment can improve not only crystallinity but also credibility of HAp/titanium combined coatings on SUS316L stainless steel. Local corrosion for HAp/titanium coating with postal heat treatment can be prevented by lowering down cooling rate. It was found that plasma titanium intermediate layer played an important role not only in improving corrosion resistance of SUS316L substrate but also in increasing the adhesion of HAp coating layer to metallic substrate.



(a) HAp coating on titanium as sprayed

(b) HAp coating on titanium with heat treatment

Fig. 8. Plasma spray HAp coating with plasma spray titanium intermediate layer on titanium after three point bending tests.

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