Effect of Hydrothermal Treatment on Microstructural Feature and Bonding Strength of Plasma-Sprayed Hydroxyapatite on Ti-6Al-4V

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The effects of hydrothermal treating temperature on bonding strength pertaining to the microstructural evolution of plasma-sprayed hydroxyapatite coatings (HACs) on Ti-6Al-4V substrate were investigated. On the basis of the observed microstructure, the as-sprayed amorphous and impurity phases, such as α-Ca₉(PO₄)₂, Ca₆P₂O₉ and CaO transform into crystalline HA after performing the hydrothermal treatment. Additionally, ultrafine crystallized particles can be recognized that the nucleation and grain growth occur by hydrothermal treatment at elevated temperatures of 175°C and 200°C. Furthermore, the hydrothermal treatment between 100°C and 150°C shows a significant decrease in microcracks, corresponding to an increase in bonding strength. This study reveals that even a small variation of hydrothermal heating temperature under 200°C can cause significant changes of the microstructural morphologies. Combining the experimental results of spraying defects, microstructural evolution and bonding strength, the knowledge of the hydrothermal-treated HACs will be helpful for the understanding and prediction in the biological stability and mechanical stability of HACs in the long-term clinical use.

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Keywords: hydrothermal treatment, plasma-sprayed, hydroxyapatite, crystallinity, area fraction of defects, bonding strength

1. Introduction

With their many outstanding biocompatibility, hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) is one of the most attractive biomaterials used in orthopedics and dentistry.¹ ¹ Clinical application of HA-coated Ti-6Al-4V have high potential to become one of the implants owing to its good bonding with surrounding bone.²³ Among various deposition methods of HA coating on metallic substrates, plasma spraying is a widely used process mainly due to its high deposition rate and good bonding strength of the coatings. However, the main disadvantage of the plasma-sprayed HA coating layer (HACs) is the formation of easily dissolved phases such as tri-calcium phosphate (Ca₃(PO₄)₂, TCP), tetra-calcium phosphate (Ca₄P₂O₉, TP), calcium oxide (CaO) and amorphous HA. Although HACs with fair high content of impurity phases that still exhibit better bonding strength and in vivo shear strength, however, the dissolution rate and the mechanical degradation of HACs for a period of immersion have been recognized.³⁻⁵

The contents of impurity phases and crystallinity are important factors for the long-term stability of the HA coating and its application in clinical use. There are many studies depicted that the phase purity, crystallinity and the adhesive strength of HACs can be improved by post-heat treatment in vacuo or in atmosphere.⁶⁻¹⁰ Nevertheless, in the high temperature interval (800–1000°C) under ambient vacuum atmosphere, the crystalline HA phase starts to decompose, resulting in the formation of TCP and TP phases.³⁻¹¹,¹² Previous reports recognized that the OH⁻ bands of crystalline HA can be easily destroyed and transformed into an unstable oxyapatite (Ca₁₀(PO₄)₆V, V: vacancy) if the materials were treated at elevated temperature without ambient aqueous condition.¹³⁻¹⁴ The crystalline HA tends to become unstable and decompose into TCP and TP. On the basis of the previous investigation, post-heat treatment in the aqueous atmosphere especially with water molecules could accelerate the crystallization of amorphous HA and transform the impurity phases to a stable crystal HA phase, because the water molecules compensate the missing OH⁻ groups from the dehydration of HA.¹⁵⁻¹⁸ Furthermore, not only H₂O molecules, but the treating temperature accompanied by a specific steam pressure (especially in autoclaving treatment) also influenced the crystallization ability of HA. The difficulties of post-treatment without hydrothermal condition including the elimination of impurity phase as well as crystallinity and bonding strength of HACs layer have been recognized. Therefore, the objective of this investigation is to determine the effect of hydrothermal treatment on the above mentioned factors. Moreover, the correlation between surface morphology, microstructure, crystallinity and phase composition pertaining to bonding strength of hydrothermal-treated HACs are also examined.

2. Experiments

2.1 Atmospheric plasma spray

Commercial high purity HA powder, with particle sizes ranging from 15 to 40μm, was used in the coating process. Two shapes of bioinert Ti-6Al-4V alloy (ASTM F-136ELI) were used as substrates: cylindrical rods, measuring 25.4 mm in diameter and 55 mm in length, were used for bonding strength measurements; plate specimens, measuring 20 × 15 × 3 mm³, were used for materials characterization and crystallinity measurement. Prior to spraying, their surfaces were degreased to remove organic contaminants and grit-blasted with SiC grit to roughen the surface and then ultrasonic cleaned. The HA powder was carried by high purity argon gas to the plasma torch. HACs with an average thickness of 120 ± 10μm were prepared using the P3 spraying parameters as indicated in Table 1 according to the previous study.¹⁹ During spraying, the substrates were kept at a low temperature by compressed air cooling in order to prevent overheating.

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2.2 Hydrothermal treatment of the HACs

The as-sprayed HACs were hydrothermally treated in an autoclave (Parr 4621, Pressure Vessel). Five hydrothermal treatment temperatures (HT100: 100°C, HT125: 125°C, HT150: 150°C, HT175: 175°C and HT200: 200°C) were employed and held for 6 h, then furnace cooled to room temperature. The temperature deviation of hydrothermal treatment is about ±5°C. Prior to hydrothermal treatment, the autoclave was pre-vacuum in order to remove the residual air reacting with HACs. The cylindrical teflon crucible added deionized water was used as the source of steam in the autoclave, and the pressure at heat treatment temperature that was measured as saturated steam pressure according to a saturated steam table.\(^{20}\) The steam pressures in the autoclave are 0.1 MPa, 0.23 MPa, 0.48 MPa, 0.89 MPa and 1.56 MPa for 100°C, 125°C, 150°C, 175°C and 200°C hydrothermal treatment, respectively. All the HAC specimens were isolated to DI water for the purpose of preventing immersion. Figure 1 shows the schematic apparatus of the autoclave for hydrothermal treatment.

2.3 Materials characterization

2.3.1 Phases and crystallinity analysis

The phase contents of as-received HA powder, as-sprayed HACs, and hydrothermal-treated HA coatings were identified by X-ray diffractometry (XRD, Rigaku D/MAX III. V), using CuK\(\alpha\) radiation, operated at 30 kV, 20 mA with scan speed of 1° (20)/min. To evaluate the degrees of HA crystallinity, the relative index of crystallinity (IOC) was introduced and defined as follows:

\[
IOC = \frac{I_c}{I_o} 
\]

where \(I_c\) and \(I_o\) are the main peak intensities of in HACs and HA powder, respectively. This method assumes that the IOC of the HA powder is 100%. The IOC of as-sprayed and hydrothermal-treated coatings is compared with the HA powder relatively.

2.3.2 Microstructure of the HACs

The surface morphology of the as-sprayed and hydrothermal-treated HACs was examined by secondary electron image (SEI) of scanning electron microscope (SEM, Philips XL-40 FEG). For the measurement of coating thickness and observation of cross-sectional microstructure, the coatings were examined by backscattering electron image (BEI) of SEM. Since both pores and microcracks of the HA coatings affect the mechanical properties, the spraying defects were calculated and defined as the summation of pores and microcracks within the total cross-sectional area of HAC. The continuous photographs in each cross-section of HA coatings were taken for the calculation of spraying defects. The cross-sectional photographs were transferred to computer image files for quantitative analysis by an image analyzer (OPTIMAS 6.0). The mean values of spraying defects of the as-sprayed and hydrothermal-treated specimens were calculated from five specimens (\(n = 5\)) of each group. To avoid inducing extra pores or cracks, the specimens for cross-sectional views were carefully ground and polished.

2.4 Bonding strength measurement and fractography observation

The bonding strength of the as-sprayed and hydrothermal-treated HACs was tested using a standard tensile adhesion test (ASTM C633) that was especially designed for plasma-sprayed coatings.\(^{21}\) Figure 2 schematizes the representative procedures of the adhesion test. The facings of the loading fixtures were also grit-blasted and attached to the surface of the HACs using special adhesive glue (METCO EP-15) with an adhesive strength of about 60 MPa. The assembly was held perpendicularly and the glue was cured in an oven at 180°C for 2 h. The couples were then subjected to tensile tests at a constant crosshead speed of 0.02 mm/s until failure. Five

![Fig. 1 The schematic apparatus of the autoclave for hydrothermal treatment.](image_url)

![Fig. 2 Representative procedures of ASTM C633 adhesion test: (a) degreased, grit-blasted substrate rod, (b) plasma-sprayed HAC on substrate rod, (c) glue attached on HAC and (d) loading rod attached on substrate rod.](image_url)
specimens of each group were used in the bonding strength measurement, and the data were reported as the mean ± standard deviation (SD). To characterize the fractographs, the optical pictures of the fracture surfaces from bonding strength specimens were scanned as image files in a computer. They were also quantitatively determined by an image analyzer. The fracture morphologies were examined by SEM/BEI to evaluate the mechanisms.

3. Results

3.1 Phases and crystallinity

The diffractograms of the as-received HA powder and as-sprayed HACs are shown in Figs. 3(a) and (b), respectively. As illustrated in Fig. 3(a), as-received HA powder is a well-crystallized single phase of Ca\(_{10}\)(PO\(_4\)_6)(OH)\(_2\) (JCPD 9-432). Apart from the HA phase, a fair amount of the amorphous and impurity phases can be recognized, including α-TCP (α-Ca\(_3\)(PO\(_4\))\(_2\), JCPD 9-348), TP (Ca\(_4\)P\(_2\)O\(_9\), JCPD 25-1137) phases, and some CaO (JCPD 37-1497) phase in the as-sprayed HACs (Fig. 3(b)). Comparing Figs. 3(a) with (b), the difference in the phase composition and crystallinity between HA powder and as-sprayed HACs is evident.

The diffractograms of the hydrothermal-treated HACs in the temperature interval 100–200°C are depicted in Figs. 3(c)–(g). As shown in Figs. 3(b)–(g), the impurity phases in the HACs gradually decrease as the heat treatment temperature increase. Apparently, the increases in coating crystallinity, indicated by the sharpening of the diffraction line (2θ = 31.8), were found for hydrothermal-treated HACs within the temperature range 100–200°C. This finding implies that the HACs further crystallized after hydrothermal treatment. The IOC of as-sprayed and hydrothermal-treated HACs is shown in Fig. 4. Although the crystallinity of as-sprayed HACs shows the lowest value, it should be noted that the highest crystallinity about 84.5% is obtained after heating at 200°C. It is clearly seen from Figs. 3 and 4 that HT200 specimen contains the least impurity phases and the highest crystallinity compared with the other specimens.

3.2 Effect of heating temperature on HACs morphology

The macroscopic morphology feature of hydrothermal-treated HACs could be divided into two groups by different heating temperature ranges of 100–150°C and 175–200°C. Figure 5 shows the typical difference of as-sprayed HACs, HT150 and HT200 sample by SEM. As shown in Fig. 5(a), the as-sprayed HAC is a completely molten coating with accumulated splats and a fair amount of microcracks can be recognized, resulting from the thermal contraction during rapid cooling rate. Figure 5(b) shows surface morphology of the HT150 specimen. Little difference between the as-sprayed and HT150 HACs is observed, whereas microcracks become invisible under the conditions of HT175 and HT200 (Fig. 5(c)).

High magnification evidence as illustrated in Fig. 6(a) shows a significant cracking feature of as-sprayed HACs. It should be noted that a fair amount of ultrafine particles can be observed in the vicinity of cracks after the specimen with hydrothermal treatment as indicated by arrows in Figs. 6(b) and (c); these ultrafine particles tend to become coarse as the heating temperature is raised up. Figures 6(d)–(f) represent the coarsening feature of ultrafine crystal with increasing hydrothermal temperature; it is reasonable to suggest that the microcracks invisible in the macroscopic observation is closely related to this phenomenon.

The feature of the cross-sectional microstructure of the as-sprayed HAC, HT150 and HT200 specimens is shown in Fig. 7. Compared to as-sprayed HAC (Fig. 7(a)), hydrothermal-treated HACs specimens show a significant decrease in microcrack (Fig. 7(b)). It should be noted that the appearance of the induced inter-lamellar microcracks (at
the lamellar-splat boundaries), indicated by arrows in Fig. 7(c), obviously can be recognized at the specimens with higher hydrothermal temperature (175°C and 200°C). Although very little porosity were found in the sprayed layer, the spraying defects should be defined as the summation of pores and microcracks within a specific cross-sectional area of HAC as shown in Table 2.

3.3 Effect of hydrothermal treatment on bonding strength

The bonding strength of as-sprayed and hydrothermal-treated HACs measured by the tensile adhesion test is shown in Table 2. The bonding strength increases within the temperature of 150°C and tends to decrease from 175 to 200°C. In order to clarify the significant data fluctuation problem, an one-way ANOVA statistical examination as shown in Table 3 ensure the bonding strength actually tends to increase with increasing the heating temperature up to 150°C, whereas the bonding strength markedly decreases with further increasing the heating temperature up to 200°C. These tendencies agree well with the spraying defects data quantitatively shown in Table 2. However, the same method was applied to determine the significant difference among the specimen groups. Statistical significance was defined as p < 0.05 and listed in Table 4. As shown in Tables 2 and 4, the structure of HT125 and HT150 shows fewer microcracks than that of as-sprayed HACs. On the other hand, the evidence of inter-lamellar microcracks as shown in Fig. 7(c) will induce the defects, resulting in the deterioration of bonding strength of HT175 and HT200 specimens.

Figure 8(a) shows the typical fractographs and schematic fracture modes. From the fracture surfaces, both cohesive (co) and adhesive (ad) fracture modes can be recognized. However, although HT100 shows similar bonding strength data as HT175, a significant difference in fracture mode can be recognized. A lamella cracking feature can be found at the cohesive failure region for HT175 and HT200 samples (Fig. 8(b), indicated by arrows). By quantitative analysis of these fractographs, the area fraction of adhesive failure is listed in Table 2. The fracture morphologies on Ti substrate side after pull test were also observed by SEM/BEI as shown in Fig. 9. The fracture morphology of hydrothermal-treated HAC is different from that of as-sprayed specimen; more facet surface can be observed after performing the hydrothermal treatment. Particularly a lamella decoherence of HAC layer can be recognized in HT200.

4. Discussion

4.1 Microstructural evolution by hydrothermal treatment

Many literatures generally exhibit that the HACs possesses both the biological and mechanical stability in surrounding bone tissue as long-term clinical use. Concerning biological stability, increased crystallinity and decreased impurity phase content will improve the dissolution, dissociation and resorption problems of HACs in vivo. In addition, spraying defects will also cause deterioration of biological and mechanical stability in vivo. On the basis of previous investigations, it is difficult to acquire HACs without any macrostructural defects like shrinkage cracks and porosities by the plasma spraying process. In our previous study, better mechanical properties of HACs can be acquired by a higher power condition due to little spraying defects, but the high enthalpy will also induce phase transformation and generate significant increases of amorphous HA and impurity phases. On the other hand, additionally conducting a post heat treatment at 700°C for 1 h in ambient air atmosphere shows the possibility to acquire better coating properties, although the fracture toughness of HA tends to decrease from 0.83 MPa m^{1/2} (as-sprayed) to 0.40 MPa m^{1/2} (heat treatment). It is suitable to suggest that the deterioration could be caused by above mentioned high temperature (700°C) treatment due to the loss of OH⁻ ion.

Concerning the effects of different treating temperature, ambient atmosphere and pressure will affect the phase transformation condition of HACs with respect to the hydrothermal treatment. An increase in steam pressure...
resulted in a decrease in an activation energy for crystallization\(^{18}\) and improve the crystallinity of HACs. In this study, the saturated steam pressure in autoclave for hydrothermal treatment has been reached to 0.10 MPa for 100°C and 1.56 MPa for 200°C, respectively. As shown in Fig. 4, the highest value of crystallinity was recognized in HT200 specimens. Thus, it is concluded that the crystallization can be acquired at lower heating temperatures by hydrothermal process.

Since the biological stability is strongly dependent on the impurity phases of HACs as one of a harmful factor for mechanical strength \textit{in vivo} or \textit{in vitro}. In addition, Since TCP and TP commonly are easily dissolved compared to the HA phase, this dissolution would cause deterioration of mechanical properties of the coating layer in clinical use, which is attributable to the formation of porosities. Therefore, it is reasonable to suggest that the appearance of Ca\(_3\)(PO\(_4\))\(_2\) and Ca\(_3\)P\(_2\)O\(_9\) phases should be suppressed. On the other hand, it is evident that the microcracks of HACs decrease with increasing the hydrothermal heating temperature from 100 to 150°C, whereas the specimens revealed an apparent increase in spraying defects due to the appearance of inter-lamellar microcracks as the temperature is raised from 150 to 200°C (Table 2). However, for HT100 specimen, it is reasonable to suggest that the hydrothermal temperature could not provide enough energy to enhance meaningful change of microstructure. With respect to the HT125 and HT150 specimens, however, fewer microcracks can be found. It is attributable to the factors including significant crystallization of amorphous, phase transformation from impurity phases into crystalline HA and the formation of crystallized ultrafine particles under saturated steam pressure.

Fig. 6 High magnification of surface morphologies of (a) the as-sprayed HACs, (b) HT100, (c) HT125, (d) HT150, (e) HT175 and (f) HT200. (the arrows: ultrafine particles).
Table 3 Results of one-way ANOVA test of the bonding strength data.

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Note: The number of samples is five \((n = 5)\) in each specimen group. S: Significant difference \((p < 0.05)\), NS: not significant.

Table 4 Results of one-way ANOVA test of the spraying defects data.

<table>
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Note: The number of samples is five \((n = 5)\) in each specimen group. S: Significant difference \((p < 0.05)\), NS: not significant.

Fig. 7 SEM cross-sectional microstructure of (a) the as-sprayed HACs, (b) HT150 and (c) HT200, showing spraying defects including pores and microcracks (Ti: Ti-6Al-4V substrate, HAC: hydroxyapatite coating, E: epoxy, and the arrows: inter-lamellar microcracks).

Table 2 The spraying defects, bonding strength and fractography analysis of HACs.

<table>
<thead>
<tr>
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<th>Spraying defects (%)</th>
<th>Bonding strength (MPa)</th>
<th>Area fraction of adhesive failure (%)</th>
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<td>HACs</td>
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<td>34.1 ± 0.4</td>
<td>36.1 ± 0.9</td>
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<td>HT175</td>
<td>5.1 ± 0.4</td>
<td>34.9 ± 1.0</td>
<td>25.3 ± 1.0</td>
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<td>HT200</td>
<td>6.4 ± 0.5</td>
<td>29.0 ± 1.7</td>
<td>20.8 ± 1.2</td>
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Values are given as mean ± SD, each value was the average of 50 data from five specimens.

Table 3 Results of one-way ANOVA test of the bonding strength data.

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Note: The number of samples is five \((n = 5)\) in each specimen group. S: Significant difference \((p < 0.05)\), NS: not significant.

Fig. 8 Fractographs and schematic representations of (a) the as-sprayed HACs, and (b) HT200 after bonding strength measurement. In all of the HACs, the bonding strength measured was a manifestation of cohesive (co) and adhesive (ad) strength. However, the increase of spraying defects, sum of pores and microcracks, of HT200 degraded the cohesive strength. (L: loading fixture, S: substrate fixture, and the arrows: decoherence HAC lamella).
4.2 Variation of bonding strength by hydrothermal treatment

Figure 10 shows the relationships between bonding strength and spraying defects as a function of hydrothermal temperature. Compared to the as-sprayed and HT100 condition, the bonding strength shows a significant increase up to 150°C, and subsequently decrease from 150 to 200°C. This tendency agrees well with the area fraction of spraying defects discussed in the previous section. The variation of bonding strength in situ was suggested to be governed by (1) the microstructural feature, (2) interface reaction between coating and metal substrate and (3) residual stress of the coating.24–27) However, statistically detailed examination is still needed.27)

From Fig. 3, impurity phases such as TCP and TP can be reduced by hydrothermal treatment, though a few amount of retained CaO phase still can be recognized except for HT200, resulting from the slower reaction rate of CaO phase transformation into HA, compared with the hydrolytic process of Ca₃(PO₄)₂ and Ca₄P₂O₉.17) According to our previous study,3) these impurity phases and the IOC can be apparently improved after performing a high temperature (630°C) heat treatment in vacuo, and the IOC even reached a maximum value at elevated temperatures about 850–900°C. Especially, the IOC value increased from 48.5% to about 70% at 900°C treatment. In this case, however, high temperature treated HA phase will decompose into impurities phases as CaO phase; it should be suppressed due to its detrimental effect for implantation. On the basis of the experimental result in this study, even 150–200°C hydrothermal treatment have already been able to acquire optimum crystallinity as well as high temperature vacuum-heat treatment. As shown in Figs. 3 and 4, the IOC of HACs is improved from 22.9 to 84.5% though it still contains a little CaO impurity phases at 200°C hydrothermal treatment. It is reasonable to suggest that above mentioned improvement in hydrothermal treatment should be correlated with the factors of compensated OH⁻ groups and saturated steam pressure during hydrothermal treatment.

As shown in Fig. 8 that the measured bonding strength of HACs is a combination of adhesive (interface of substrate) and cohesive (within the coating layers themselves) strengths of coating layer. Cohesive strength is dominated by the microstructural feature of coating layer such as crystallinity, porosity, microcrack, lamellar texture, and etc. In contrast, the residual stress and pretreated surface roughness of the substrate greatly affect the adhesive strength.27,28) From the fractographs and the failure mode as shown in Fig. 8, the area fraction of adhesive failure (ad) tend to decrease with increasing temperature as demonstrated in Table 2 and Fig. 10. However, to decrease adhesive failure area fraction represents good bonding at HAC/Ti-substrate interface after hydrothermal treatment. The knowledge of the microstructural evolution and fracture behavior in hydrothermal-treated HACs will be very helpful for the understanding and prediction of the bonding strength. Although the residual stress also might play an important role on the initiation of microcrack, combining the experimental results of spraying defects and bonding strength, the appearance of interlamellar microcracks is the main control factor to cause

Fig. 9 After ASTM C633 test, SEM/BEI of fracture morphology of (a) the as-sprayed HACs, (b) HT150 and (c) HT200, revealing that the failure propagate in the through-thickness direction.
5. Conclusion

The long-term stability of HACs is thought to depend mainly on the crystallinity, phase composition, microstructure, and mechanical properties in vivo. In this study, the post-hydrothermal treatment was performed to improve coating characteristics. The results from this study can be concluded as follow:

(1) Hydrothermal treatment around 150°C actually can promote the transformation of α-TCP, TP, CaO and amorphous of HA coatings to crystalline HA. In this hydrothermal treatment up to 200°C, as increased treating temperature, little impurity phases and higher crystallinity were identified in the HACs.

(2) Ultrafine crystalline particles were observed in the vicinity of microcracks area. Significant nucleation and grain growth was observed at 175°C and 200°C.

(3) Plasma-sprayed-induced microcracks tend to decrease after hydrothermal treatment in the temperature interval 100–150°C, whereas the inter-lamellar microcracks tend to occur as the hydrothermal temperature increases up to 200°C. This is the main control factor to cause deterioration of bonding strength pertaining to the microstructural evolution of HACs.

Acknowledgments

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