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Biphasic calcium phosphate coating on cobalt-base surgical alloy during investment casting

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Abstract The biphasic calcium phosphate (BCP) yields higher bioactivity and efficiency than the Hydroxyapatite (HA) alone. The HA/β-TCP ratio significantly affects BCP bioactivity as well as the extent of BCP resorption. In this study, the BCP coating on ASTM F-75 cobalt base alloy during the investment casting process was investigated. For this purpose, molten metal was poured at 1,470°C into previously coated investment molds preheated to 750, 850, 950, 1,050°C in order to investigate the effect of mold preheating temperatures on coating phase transformations. For in vitro evaluation, samples were immersed in the simulated body fluid (SBF) at 37°C for 4 weeks and characterized by XRD, SEM, EDS, and optical microscopy. The weight percentages of HA and β-TCP of the specimens were calculated to find that the HA/β-TCP ratio significantly depended on the mold preheating temperature as it caused changes in the dissolution behavior of BCP coating and the bone-like apatite precipitation on coating during in vitro evaluation.

1 Introduction

Hydroxyapatite (HA) and beta-tri calcium phosphate (β-TCP) are among the major types of calcium phosphate ceramics used in bone and dental surgery. HA is a more stable phase in biological conditions with the ability to direct chemical bonding to bone while β-TCP is found to be bioresorbable in vivo and is replaced with new bone growth [1, 2]. The combination of HA and β-TCP may produce the biphasic calcium phosphate that yields more bioactivity and efficiency compared to HA alone [3]. The term biphasic calcium phosphate (BCP) was first used by Ellinger et al. [4] to introduce a bioceramic mixture of HA and β-TCP. BCP bioactivity as well as the rate and extent of BCP resorption in clinical conditions are greatly determined by the HA/β-TCP ratio. Ideally, its resorption rate should match that of new bone formation; hence, the HA/β-TCP ratio is a critical controlling parameter. It will be shown that the higher the β-TCP rate, the faster and more extensive its resorption. Crystals in the immediate microenvironment of the implant have been shown to rise to supersaturation with increasing partial dissolution of the HA (or β-TCP), subsequently leading to the precipitation of new apatite crystals [2, 5].

Another important factor during the sintering and coating of BCP on metallic implants is thermal stability of the phases. Some others believe at temperatures higher than 900°C, HA decomposes into β-TCP (Eq. 1) [6] and some other reported 1,200°C as the decomposition temperature [7, 8]:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3\beta - Ca_3(PO_4)_2 + CaO + H_2O \quad (1)$$

Upon decomposition, the HA/β-TCP ratio in the bioceramic changes, which causes the resorption rate to change under clinical conditions [2, 9]. Using wet chemical or solid state methods, BCP ceramics have recently been produced and, subsequently, used to coat metallic substrates by plasma spray [1, 10]. This technique gives rise to the phase transformation in the BCP ceramic, affecting the HA/β-TCP ratio and the bioactivity of the coating.

BCP ceramics cannot be utilized under load-bearing conditions such as hip or knee prosthesis due to their low fraction toughness and other required mechanical properties. However, the strength of the metals and the bioactivity

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of ceramics can be simultaneously exploited by coating bioceramics on metallic implants [6]. It has been shown that calcium phosphate coatings yield higher levels of new bone formation on cementless orthopedic implant interfaces and better biochemical fixation with good clinical results. BCP coatings have exhibited better results in human body applications due to their equilibrated kinetics of resorption and bone substitution. The bioactive behavior of bulk samples reported earlier has been observed in BCP coatings as well [2].

Cobalt-base alloys are widely used for manufacturing orthopedic prosthesis due to their good corrosion resistance, mechanical properties, and biocompatibility [11]. However, metallic biomaterials are classified as bioinert materials since they do not bond with the bone material under clinical conditions and need mechanical locking for their fixation. A number of physical and chemical coating methods have been developed such as plasma spray, electrophoretic deposition, biomimetic process, sol–gel, and thermal spray [12–15]. Surface bioactivation during the fabrication process is economically more desirable as it yields higher product quality with savings in time and energy. Implants are manufactured by such processes as metal forming, powder metallurgy, and casting. Investment casting is a more common process for the fabrication of ASTM F-75 cobalt-base alloy implants [16]. Therefore, surface bioactivation of the implants during investment casting is more attractive. Sohmura et al. [17] introduced a novel method for HA coating on Ti during casting in graphite molds. Other researchers have reported on HA and wollastonite coatings on cobalt-base alloys [18, 19]. To the best of our knowledge, no study has been reported in the literature investigating the possibility of BCP coating on metallic implants during investment casting or the effect of mold preheating temperature on the phase transformation of the coating.

In the present work, we have investigated the coating of BCP on ASTM F-75 cobalt-base alloy during investment casting and the effect of mold preheating temperatures on HA/β-TCP ratio. The coating bioactivation is also evaluated in vitro by immersing samples in the simulated body fluid (SBF). It is shown that the HA/β-TCP ratio depends to a large extent on the mold preheating temperature as it gives rise to changes in the dissolution behavior of BCP coating and the bone-like apatite precipitation on coating during in vitro evaluation.

2 Materials and methods

2.1 Specimen preparation

ASTM F-75 cobalt-base alloy was melted in an induction furnace and cast into an investment mold with an internal disk 20 mm in diameter and 5 mm in height. Table 1 shows both the standard chemical composition of the ASTM F-75 cobalt base alloy and the measured chemical composition of the alloy used in this study based on the manufacturer's certificate. The molds were fabricated using phosphate-bonded investment consisting of SiO_2, MgO, and $(NH_4)H_2(PO_4)_2$. Upon drying, the molds were dewaxed at 350°C for 30 min. The cavity walls were coated with moisturized hydroxyapatite (Merck, with an average particle size of 10 μm) using a paintbrush.

Table 1 Standard chemical composition of co-base ASTM F-75 alloy and the casting alloy used

Element	ASTM F-75	Casting alloy
Co	Balance	Balance
Cr	27–30	28.00
Mo	5–7	5.50
Si	1.0	0.35
Mn	1.0	0.35
Ni	1.0	0.35
Fe	0.75	0.75
C	0.35	0.35

Molten metal was poured at 1,470°C into the previously preheated investment molds. To investigate the effect of mold preheating temperatures on coating phase transformations, the molds were preheated to 750, 850, 950, and 1,050°C.

2.2 In vitro evaluation

For in vitro evaluation, a simulated body fluid (SBF) with an ionic concentration nearly equal to that of the human blood plasma was prepared according to Kokubo instructions [20]. The samples were then coated during casting in molds preheated at 750 and 1,050°C, immersed in the simulated body fluid for 1, 2, 3 and 4 weeks at 37°C, and finally held in the water bath at 37°C for 4 weeks. The specimens thus prepared were then washed with deionized water, dried, and stored.

2.3 Characterization methods

X-Ray Diffraction (XRD) (Philips X'Pert-MPD with a Cu Kα wavelength of 1.5418 Å) was used to analyze the phases in both the raw materials and the surface of the coated specimens. The diffractometer was operated at 40 kV and 30 mA at a step size of 0.05. Weight percentages of HA and β-TCP phases in the coatings were calculated using the method proposed by Vallet-Regi et al. [21] and adapted by Raynaud et al. [22]. Scanning Electron Microscopy (SEM) (Phillips XL 30) was used to study the

surfaces of the specimens before and after immersion in SBF. Also to calculate secondary dendrite arm spacing (SDAS) the standard random intercept method was employed and mean value ± standard deviation were statistically calculated. All experiments were conducted at least for $n = 5$. All of the data are expressed as mean ± standard deviation. One-way analysis of variance (ANOVA) was used to compare results. A p value of less than 0.05 was considered statistically significant.

3 Results and discussion

Over the last decades, calcium phosphate coatings have been used for improving the surface bioactivity of metallic implants in dentistry and orthopedic applications. BCP ceramics have shown to be more efficient than other bioceramics because of their equilibrated resorption kinetics and the HA/β-TCP ratio of the coating has proved to be an important factor involved in the surface bioactivation of metallic implants coated by BCP [1].

Figure 1a (optical microscope) shows the cross section of a bioactive coating, in which a homogeneous layer free of pores and voids with a thickness of about 300 μm can be seen. Between this layer and the substrate, a bonding region is also seen in this Figure, which formed due to the solidification of the molten metal under the HA coating on the mold cavity (Fig. 1b). At the beginning of casting, the substrate under the HA layer was as molten metal before the substrate solidified. The as-cast microstructure of the ASTM F-75 consisted of a strongly cored dendritic matrix with carbides distributed across [16]. During solidification, the alloying elements were rejected into the liquid by dendrite growths. Thus, the interdendritic zones (rich in the alloying elements) were the last zones to solidify and transform into $M_{23}C_6$ (M = Cr, Mo) carbides at temperatures around 1,200°C [23]. As observed in Fig. 1b, the dendrite arms progressed into the bioactive layer to form a serrate interface forming a strong mechanical bonding between the coating and the substrate, as schematically shown in Fig. 1c. On the other hand, hydroxyapatite partially melted between the interdendritic zones and the coating on the wall cavity mold to create a strong bonding between the coating and the substrate. These conditions guaranteed a suitable bonding. Figure 1b shows a homogeneous layer, the micro pores less than 1 μm in diameter, and residual mold material particles on the metal surface.

EDS spectrum revealed a surface rich in Ca and P as shown in Fig. 1d. Chromium and molybdenum were also observed in the spectrum, which may be due to the substrate diffusion. The presence of Mg and Si may be due to residual mold materials. The Ca/P ratio of about 1.52 in the EDS spectrum proves the β-TCP existence in the coating.

Theoretically, HA decomposes into other calcium phosphates such as α-TCP and β-TCP at temperatures above 1,200°C [7, 8]. When HA decomposition occurs during coating and sintering, it will significantly affect the physical, chemical, clinical, and biological properties of the BCP ceramic. These phases (α, β-TCP) have different dissolution behaviors so that calcium and phosphorous are released from HA in different manners and quantities.

Figure 2 shows the X-ray diffraction pattern of the surface of the coated samples during investment casting. According to the decomposition reaction (1), HA decomposed to β-TCP because of the mold preheating and the sensible and latent heat rejection from the molten metal

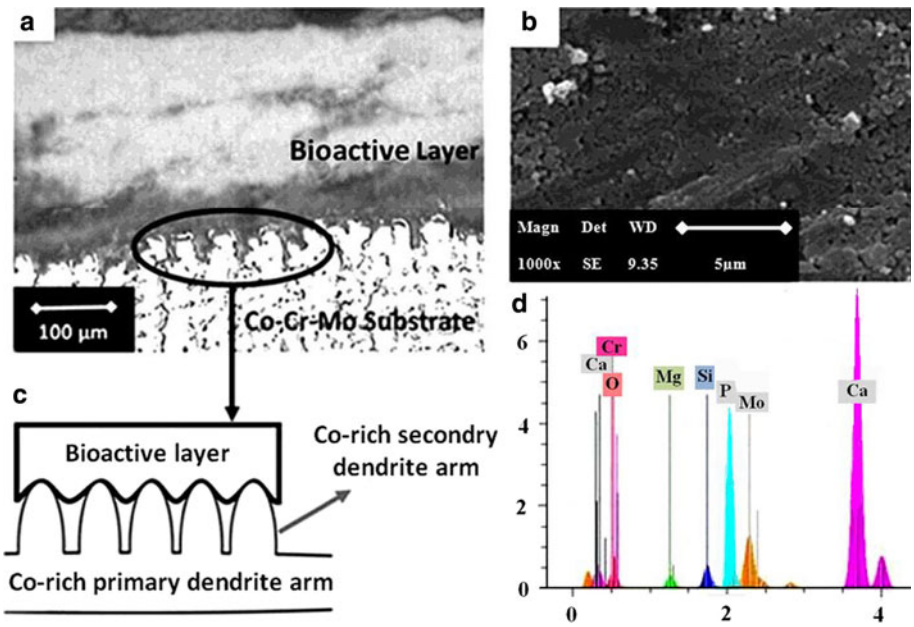

Fig. 1 **a** Cross section optical micrograph of the BCP coating, **b** SEM micrograph of the BCP coating, **c** schematic illustration of the bonding mechanism, and **d** EDS spectrum of the coating

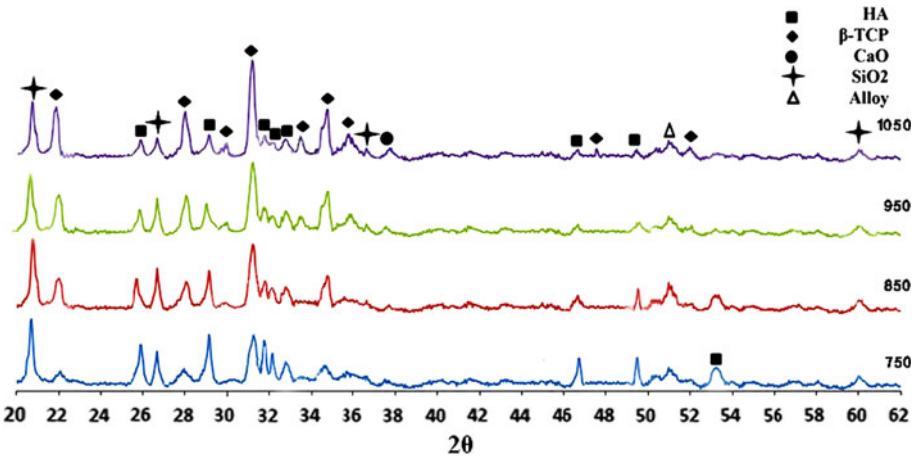

Fig. 2 The XRD pattern of the BCP coating obtained during casting at different mold preheating temperatures

during solidification. This is why the XRD pattern indicated the presence of the BCP coating on the surface of the ASTM F-75 alloy. The presence of the SiO_2 phase on the surface is due to the residual mold materials. Some researchers maintain that the SiO_2 phase must be responsible for the increased apatite formation by immersion in SBF [18]. As previously mentioned, the HA/β-TCP ratio has a significant effect on the rate and extent of coating dissolution. Therefore, we investigated the effect of mold preheating temperature as an important parameter in manufacturing BCP coating during investment casting on HA/β-TCP ratio.

The molten metal was cast at the four different preheating mold temperatures of 750, 850, 950, and 1,050°C. Figure 3 shows the XRD patterns of the coated specimens. The intensity of HA picks gradually decreased while that of β-TCP picks increased with increasing mold preheating temperature. This shows the dominance of HA decomposition with increasing mold preheating temperature, which leads to a lower HA/β-TCP ratio in the bioactive layer.

Figure 3 shows the variations in HA and β-TCP weight percentages versus mold preheating temperature in BCP coatings. HA/β-TCP ratio changed from 70/30 to 20/80

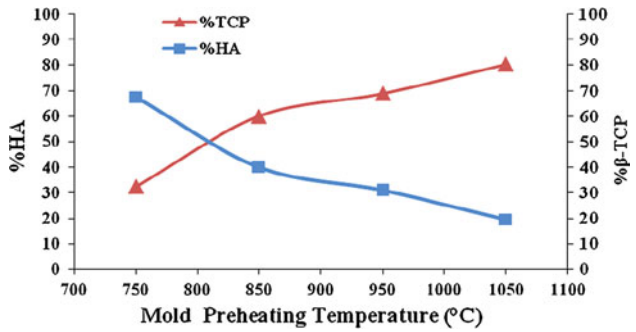

Fig. 3 HA and β-TCP variations versus mold preheating temperature in BCP coatings

when mold temperature increased from 750 to 1,050°C. It is also clear from this Figure that the decomposition reaction of HA significantly increased in molds with preheating temperatures higher than 850°C. In fact, HA in this case

$$Ca_{10}(PO_4)_6(OH)_2 = Ca_{10}(PO_4)_6O_x(OH)_{2(1\geq x)} + xH_2 \qquad 0 \geq x \geq 1 \tag{2}$$

$$Ca_{10}(PO_4)_6O_x(OH)_{2(1\geq x)} = 3Ca_3(PO_4)_2 + CaO + H_2O \qquad 0 \geq x \geq 1 \tag{3}$$

The former step has no significant effect on the properties of HA ceramics, whereas the latter leads to impaired mechanical properties, higher chemical activity, and poorer stability of HA in the human body. Water and HA begin to separate from each other at 900°C. The water is gradually released and oxyapatite $Ca_{10}(PO_4)O_x(OH)_{2(1;x)}$ (HOA) might form with a decreasing amount of OH groups.

Thermal decomposition of HA ceramics was controlled by water diffusion from the reaction zone to the ceramic surface. Different temperatures have been reported for the minimum temperature of HA decomposition, which probably has to do with HA purity, the powdered form of HA, and the conditions under which the decomposition is studied [24]. Increasing mold preheating temperature led to greater expulsion of water and higher HA decomposition.

Besides the initial HA powder parameters, such other factors as volume of the molten metal, pouring temperature, mold preheating temperature, and thickness of HA coating on the mold wall cavities affect the coating phase transformation. The coating of all the specimens in this work had nearly the same thickness of 300 μm. In order to study the effect of mold preheating temperature on phase transformation of the coating, other parameters were kept constant. These parameters affect the cooling rate, thereby influencing both the phase transformation of HA in the coating characterized by β-TCP formation and the microstructure of the substrate characterized by the secondary

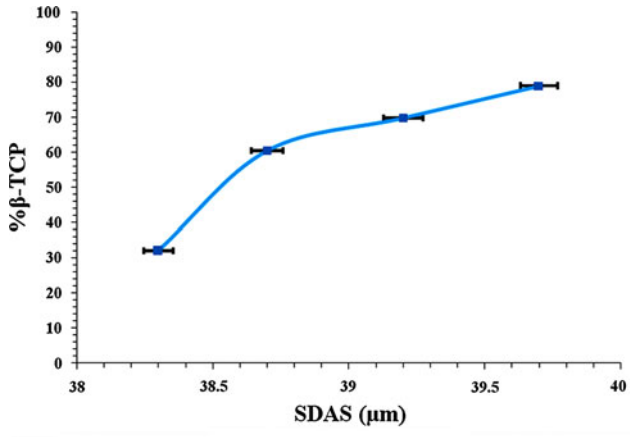

Fig. 4 β-TCP weight percentage variation versus SDAS

dendrite arm spacing (SDAS). By varying the values in these parameters, we were able to determine quantitatively their effects on HA/β-TCP ratio through measuring the SDAS of the substrate using the diagram in Fig. 4.

After the specimens were immersed in SBF, nucleation and growth of bone-like apatites were investigated as the bioactivity criterion for both C750 and C1050 specimens (C750 and C1050 denote the samples cast at 750 and 1,050°C mold preheated temperatures, respectively). Figure 5a and b shows the biological-like apatite formation on C750 specimens after immersion in SBF for 2 and 4 weeks, respectively. Formation of apatite on the surface indicates surface bioactivity.

Figure 5c and d shows the formation of biological apatite on C1050 specimens under the same conditions. Figure 5e shows the bioactive layer before immersion in SBF. As seen, amount of apatite precipitates on the surface of C1050 are higher than those on the corresponding C750 specimens. This is due to the lower HA/β-TCP ratio in the coating of C1050 specimens. Increasing the β-TCP phase in the coating led to the higher solubility of the coating, the release of Ca and P ions, and thereby, to apatite nucleation and growth in vitro and bone formation potential at the implant-tissue interface in clinical conditions.

Comparison of Fig. 5a and c reveals that after immersing the specimens in SBF for 2 weeks, pores formed on the surface while, according to Fig. 1b, the pore size in the coating is less than 1 μm. Formation of these pores proves the solution of coating in vitro condition. As also observed in Fig. 5a and c, the size and number of pores on the surface of C1050 specimens (with a HA/β-TCP ratio of 20/80) are higher than those of C750 specimens (with a

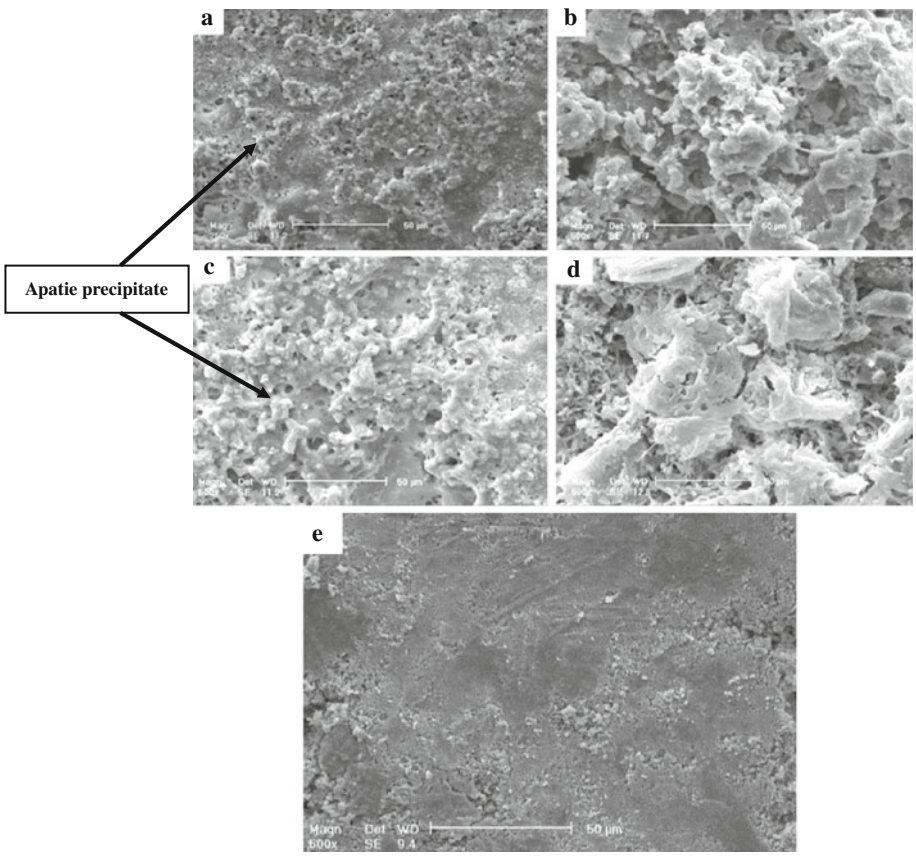

Fig. 5 SEM micrograph of C750 specimens after immersion in SBF for **a** 2 weeks, **b** 4 weeks; and C1050 specimens after immersion in SBF for **c** 2 weeks, **d** 4 weeks and **e** before immersion in SBF

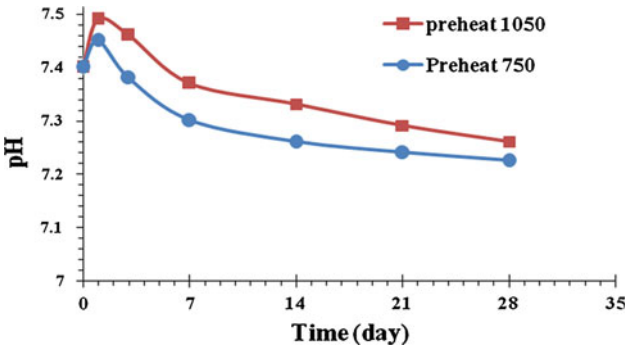

Fig. 6 SBF pH variation versus immersion time for C750 and C1050 samples

HA/β-TCP ratio of 70/30). This confirms the higher solubility of β-TCP ceramics than HA in vitro condition. Since dissolution of the BCP coating can be considered as the dissolution of individual HA and β-TCP crystals, after immersion of the specimens in SBF, the HA/β-TCP ratio increased and the dissolution and biodegradation of the coating in the long run tended toward a constant value. Therefore, the coating can present a controlled dissolution based on its HA/β-TCP ratio.

To compare the dissolution behaviors of C750 and C1050 specimens, the pH variation in SBF versus immersion time was measured (Fig. 6). After immersion of the specimens for 1 day, the pH value increased but then gradually decreased. The increase in pH value might have been due to the ionic exchange between Ca^{2+} ions from the BCP layer and H^{+} ions from the SBF. The following decrease in pH value showed that apatite precipitation started after 1 day [25]. The increase in the pH value of SBF was more pronounced in the C1050 specimens than in the C750 ones. This could be due to the higher β-TCP/HA ratio in the coating of the former. Increasing the tricalcium phosphate content led to a higher release of Ca^{2+} in SBF and, consequently, to a higher pH value due to the high solubility of this phase.

4 Conclusion

In this study, it was shown that it is possible to bioactivate the surface of ASTM F-75 alloy with BCP coating during casting. The coating was bonded to the substrate by mechanical retention. The HA/β-TCP ratio as an important factor involved in the bioactivity of BCP coating depends to a large extent on the mold preheating temperature. The HA/β-TCP ratio changed from 70/30 to 20/80 when the mold preheating temperature increased from 750 to 1,050°C. This caused a change in the dissolution behavior of the BCP coating and the bone-like apatite precipitation on coating during in vitro evaluation.

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