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EFFECT OF THE CONDITIONS OF A BIOMIMETIC PROCESS ON THE FORMATION OF APATITE ON COBALT BASE ALLOYS

WPŁYW WARUNKÓW PROCESU BIOMIMETYCZNEGO NA FORMOWANIE SIĘ WARSTWY APATYTOWEJ W STOPACH CoCrMo

The effect of the chemical and the heat treatments on the formation of apatite on cobalt based alloys were evaluated. Five cobalt base alloys were used. The metallic samples were chemically treated with KOH or NaOH solutions (0.5, 3 or 5M) at 60°C and heat treated at 600°C. Some experiments were conducted using samples without chemical or heat treatment. The samples were immersed in two different simulated body fluid solutions, one with an ion concentration nearly equal to that of human blood plasma (SBF), and other with 1.5 times that concentration (1.5SBF). After the immersion in the SBF solution a thin ceramic layer containing Ca and P was found on the surface of those samples with a heat treatment, while on those without it mainly compounds containing Ca, O and C were found, regardless of the concentration, alkaline solution or alloy used. After the immersion in a 1.5SBF solution a dense ceramic layer was observed on all the surfaces of the metallic samples treated. The Ca/P ratio obtained indicated a compound formed on the surface of the samples corresponding to a Ca-deficient apatite. The interface was characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX) and X-Ray Diffraction (XRD).

Formowanie się warstwy apatytowej powierzchni stopów kobaltowych w wyniku obróbki cieplno-chemicznej było przedmiotem badań. Stopy takie stosowane są w produkcji protez ortopedycznych lub dentystycznych, zaś powłoka apatytowa sprzyja ich bioaktywności i osteointegracji w środowisku ciała ludzkiego. Przebadano pięć stopów CoCrMo, które poddawano działaniu roztworu KOH i NaOH o 3 różnych stężeniach (0.5, 3 i 5 M) a następnie poddawano obróbce cieplnej w temperaturze 600°C. Na koniec procesu obróbki cieplno-chemicznej zanurzano badane próbki w roztworach symulujących środowisko ciała ludzkiego(skład roztworu zbliżony do składu plazmy krwi ludzkiej) na okres 21 dni. Stosowano 2 typy takich roztworów: roztwór o stężeniu jonów zbliżonym do plazmy krwi (SBF), zaś drugi o stężeniu jonów powiększonym o 50% (1.5SBF). Zastosowanie roztworu

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SBF powodowało powstawanie cienkiej warstwy ceramicznej zawierającej wapń i fosfor gdy próbka podlegała obróbce cieplnej, zaś w przeciwnym wypadku warstwa składała się z wapnia fosforu i tlenu. Zanurzanie w roztworze 1.5 SBF powodowało powstawanie gęstej warstwy ceramicznej na każdej zbadanych próbek. Stosunek Ca/P odpowiadał składowi apatytu z pewnym deficytem wapnia. Badania próbek wykonywano metodami skaningowej mikroskopii elektronowej, oraz metodami rentgenograficznymi (EDX — Energy Dispersive XRay, XRD — XRay Diffraction).

1. Introduction

Due to their high strength and corrosion resistance the titanium and the CoCrMo alloys are used for high load and dental application implants. However, even when these alloys are biocompatible they are not bioactive. The biomimetic process is a relatively recent option which allows the formation of an apatite coating ($A_{10}(BO_4)_6X_2$) on the surface of these alloys permitting them to enhance their bioactivity and osteointegration for these orthopedic and/or dental applications [1, 2, 3]. This process does not present the disadvantages of other methods [4, 5, 6]. Mainly, this process has been studied for Ti and its alloys, tantalum, alumina and composites of biodegradable polymers [3, 7-11]. In the case of Co base alloys some researchers have reported the impossibility to form apatite on the surface of this alloy by using this technique [11]. However, other studies have shown the feasibility of apatite formation on these alloys under other experimental conditions using a biomimetic process [12, 13]. One route to bioactivate metallic materials via this process consists of a chemical treatment in an alkaline solution, followed by a heat treatment and ending with an immersion in a simulated body fluid (SBF) for certain period of time. In the case of the Ti and its alloys this process is well understood and the effect and importance of each stage by using this route has been reported and even the mechanism of apatite formation has been elucidated [3]. However, for the Co base alloys, the effect of these stages has not yet been evaluated due to the disregard of the mechanism of apatite formation on their surfaces. This work studies the effect of the conditions involved in a biomimetic process, heat treatment and the chemical treatment, on the apatite formation on the surface of the cobalt base alloys.

2. Materials and methods

Three alloys, containing low (C_{LC}), medium (C_{MC}) and high levels (C_{HC}) of carbon, were obtained by the investment casting technique. Wax (Swest-USA) and refractory materials (Ransom and Randolph-USA) were used to obtain the investment molds. The molds obtained were sintered at 850°C for one hour. The melting was performed in an induction furnace in argon, pouring the metal at 1600°C in a preheated mold at 960°C. The metallic bars obtained were heat treated at 1224°C for 75 minutes. The forged alloy (F) and that obtained by powder metallurgy (PM) were provided by Carpenter

Technology Co. The chemical analysis of the cast samples was performed by emission spectrophotometry (Lab S, Spectro Analytical Instruments) and direct combustion with infrared detection for carbon (LECO model CS 244-748-000, Leco Corporation). The bars were machined to obtain tensile specimens. The tests were carried out according to the ASTM E8 standard at a crosshead speed of 3 mm/min using an Instron machine model 4206.

The samples were cut to a height of 1.5 mm and ground with silicon carbide papers ranging from 80 to 1200 grit. After this, the samples were washed with water and ethanol, dried by compressed air and stored in a desiccator before testing.

The chemical treatment consisted of the immersion of the samples in 100 ml of an alkaline solution of KOH or NaOH at 0.5, 3M or 5M. This treatment was performed at a constant temperature of 60°C for 24 hours. At the end of this stage the samples were washed with deionised water and dried at 37°C for 24 hours in an incubator (Fisher, model 637D). The heat treatment was performed at 600°C for 1 hour at a heating rate of 10°C/min. Some experiments were conducted using samples without chemical or heat treatment. Finally, an immersion in SBF or 1.5SBF solutions for a 21-day period, was performed. The preparation of the SBF and 1.5SBF solutions was made according to the method described by Oyane [14]. Table 1 shows the ion concentration of the SBF solution, the 1.5SBF solution and the human blood plasma.

TABLE 1

Ionic Concentration

	Concentration (mmol/dm^3)							
	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	HCO3	HPO4^{2-}	SO4$_{2-}$
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5
1.SBF	213.0	7.5	2.3	3.8	223.0	6.3	1.5	0.8
Human blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

At the end of the immersion period the samples were washed with deionised water and stored in a desiccator. These samples were examined using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray analysis (EDX), and X-Ray Diffraction (XRD).

3. Results and discussion

Table 2 shows the results of the chemical analysis of the alloys used, as well as the requirements of the ASTM standards for these alloys. The alloys obtained are within the required range of their respective standard. Table 3 shows the mechanical properties of the alloys used, as well as the requirements of the ASTM standards. For the cast alloys obtained, just the values for the low carbon content cast alloy are below the mechanical requirements of its standard.

TABLE 2

Chemical analysis results [wt%]

	Co	Cr	Mo	Si	Mn	Ni	Fe	C
ASTM F75	Bal.	27–30	5–7	1.00	1.00	1.00	0.75	0.35
Cast Low C (C_{LC})	64.25	28.11	5.77	0.60	0.76	0.26	0.22	0.06
Cast Medium C (C_{MC})	63.12	28.92	5.85	0.76	0.49	0.34	0.34	0.16
Cast High C (C_{HC})	62.76	28.43	6.56	0.78	0.74	0.41	0.12	0.23
ASTM F799	Bal.	27–30	5–7	1.00	1.00	1.00	0.75	0.35
Forged (F)	65.22	27.62	5.39	0.55	0.78	0.04	0.19	0.07
ASTM F1537	Bal.	27–30	5–7	1.00	1.00	1.00	0.75	0.35
Powder Metallurgy (PM)	61.79	29.50	6.60	0.70	0.70	0.14	0.07	0.23

TABLE 3

Mechanical properties

Sample	UTS [MPa]	% Elongation at max. load [%]	% Elongation at break [%]	Yield Strength [MPa]
ASTM F75	655 (min.)	—	8 (min.)	450 (min.)
Cast Low C (C_{LC})	636	15.5	16.15	458.5
Cast Medium C (C_{MC})	724.5	16.6	17.8	528
Cast High C (C_{HC})	744.5	10.4	10.75	574.5
ASTM F799	1172 (min.)	—	12 (min.)	827 (min.)
Forged (F)	1317	—	19.5	1037
ASTM F1537	1172 (min.)	—	12 (min.)	827 (min.)
Powder Metallurgy (PM)	1341	—	17	1041

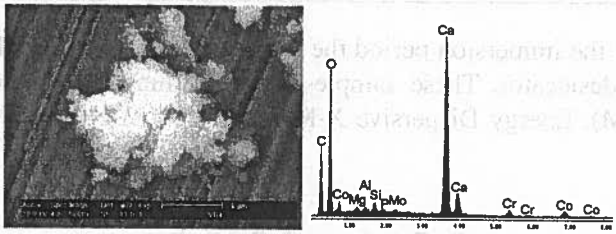

Fig. 1. Medium carbon content cast sample with a chemical treatment in KOH 0.5M, without heat treatment and immersed in SBF

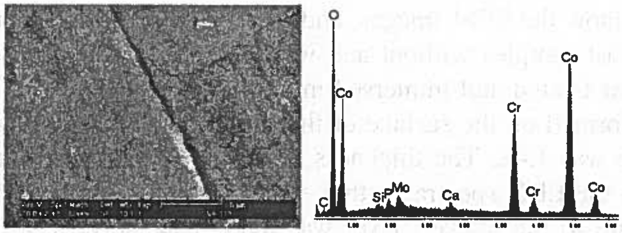

Fig. 2. Medium carbon content cast sample with a chemical treatment, heat- treated and immersed in SBF

Figures 1 and 2 show the SEM images, and their respective EDX analysis, for cast samples. For the sample without heat treatment (Fig. 1), particles consisting mainly of Ca, O and C were found on its unmodified surface. For the sample with heat treatment (Fig. 2), the formation of a thin ceramic layer containing Ca and P with a Ca/P ratio close to that of apatite was appreciated, indicating that the heat treatment has a significant effect. The same type of particles, in the case of samples without heat treatment, and ceramic layers, in the case of samples with heat treatment, were found on the surface of the low and high carbon content cast samples, the forged and the powder metallurgy samples, regardless of the chemical treatment used (agent or concentration).

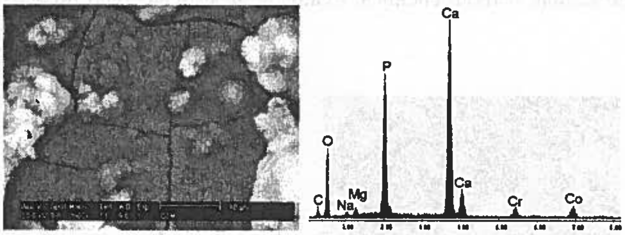

Fig. 3. High carbon content cast sample without chemical treatment, heat- treated and immersed in 1.5SBF

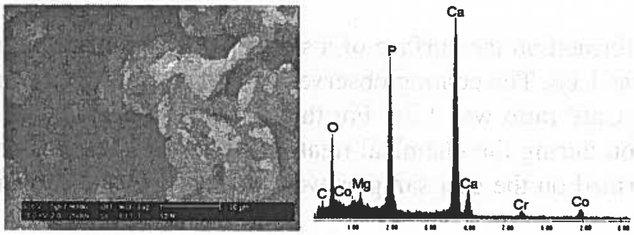

Fig. 4. High carbon content cast sample with a chemical treatment in NaOH 5M, heat-treated and immersed in 1.5SBF

Figures 3 and 4 show the SEM images, and their respective EDX analysis, of the high carbon content cast samples without and with chemical treatment, respectively. Both samples were heat treated and immersed in 1.5SBF for 21 days.

For the coating formed on the surface of the sample without chemical treatment (Fig. 3) the Ca/P ratio was 1.48. The thickness of this layer, inferred from the Co and Cr peak intensity in the EDX spectra, is thin. For a sample with a chemical treatment in NaOH 5M (Figure 4) the thickest layer was found and the Ca/P ratio was 1.27. The Ca/P ratios indicate that the coating formed on the surface of these samples correspond to apatite (1.2 — 1.66). The Ca/P ratio for the hydroxyapatite is 1.67.

Figures 5 and 6 show the SEM images, and their respective EDX analysis, of forged samples without and with chemical treatment, respectively. Both samples were heat-treated and immersed in 1.5SBF for 21 days.

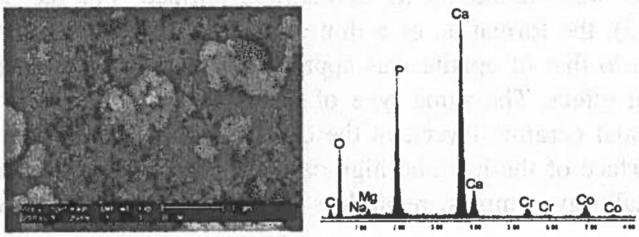

Fig. 5. Forged sample without chemical treatment, heat-treated and immersed in 1.5SBF

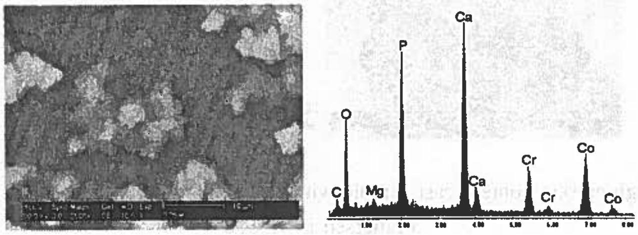

Fig. 6. Forged sample with a chemical treatment in NaOH 5M, heat-treated and immersed in 1.5SBF

For the coating formed on the surface of a sample without chemical treatment (Fig. 5), the Ca/P ratio was 1.68. The coating observed in Figure 6 is thiner than that observed in Figure 5 and its Ca/P ratio was 1.26. For this alloy, as increasing the concentration on the alkali solution during the chemical treatment, the thickness of the layer decreased. The coatings formed on the cast samples were thicker than those formed on the forged samples.

Figures 7 and 8 show the SEM images, and their respective EDX analysis, of the powder metallurgy samples without and with chemical treatment respectively, heat-treated and immersed in 1.5SBF for 21 days.

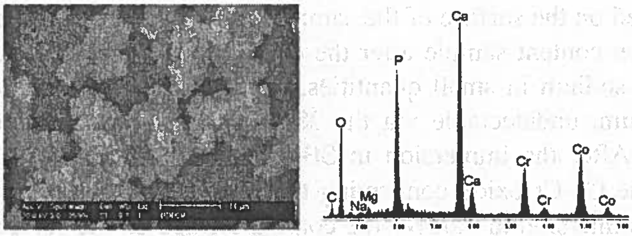

Fig. 7. Powder metallurgy sample without chemical treatment, heat-treated and immersed in 1.5SBF

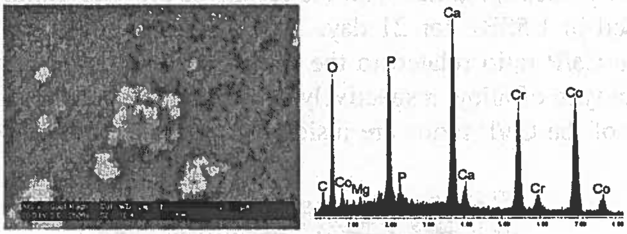

Fig. 8. Powder metallurgy sample with a chemical treatment in NaOH 5M, heat-treated and immersed in 1.5SBF

In Figure 7 a thin coating with a high density of apatite cumulus is observed with a Ca/P ratio of 1.32. Figure 8 presents a thin coating with a low-density of apatite cumulus with a Ca/P ratio of 1.25. The coatings formed on the powder metallurgy samples are thinner than those observed on the cast and forged samples.

The XRD spectra of a medium carbon content sample, analysed at different stages during the biomimetic process is shown in Figure 9.

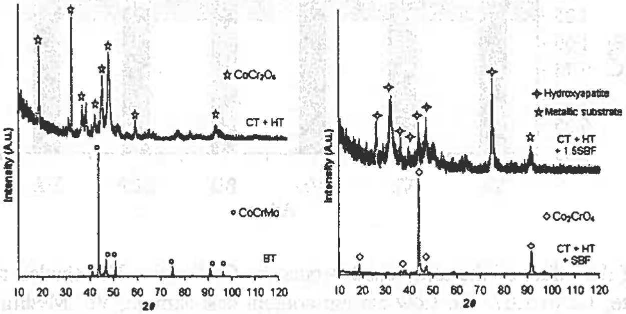

Fig. 9. XRD patterns of a medium carbon content cast sample. BT: Before any treatment. CT: Chemical treatment in NaOH 5M; HT: Heat treatment at 600°C; SBF: 21-day immersion in SBF; 1.5SBF: 21-day immersion in 1.5SBF

Before any treatment, the XRD technique identifies the sample of a CoCrMo alloy as a solid solution. As observed after the chemical and heat treatments a complex CoCr oxide is identified on the surface of the sample. However, the EDX spectra obtained for a medium carbon content sample after the chemical and heat treatments [15] showed the presence of sodium in small quantities, suggesting the formation of a compound containing sodium, undetectable via the XRD method due to the amount in which it was present. After the immersion in SBF, for the heat-treated samples, the XRD detected only the Co-Cr oxide confirming that the coating observed via SEM is very thin. After the immersion in 1.5SBF the coating formed on the surface of the samples is detected by XRD indicating that the layer is considerably thick and identifying it as hydroxyapatite.

Figures 10 and 11 present graphics with the results of the Ca/P ratios measured on the samples immersed in 1.5SBF for 21 days. These Figures show the general tendency presented for the Ca/P ratio related to the NaOH molarity used during the chemical treatment and the type of alloy, respectively. It is possible to observe that, in all cases, the mean values of the Ca/P ratios are inside the region delimited for the apatite.

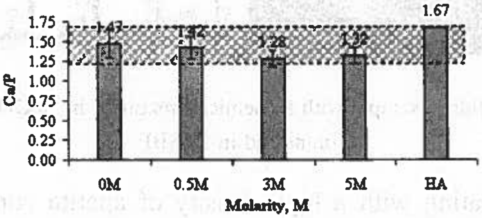

Fig. 10. Results of the effect of the molarity of the NaOH solution versus the Ca/P ratio. The shaded region represents the values for the apatite, 1.2 to 1.67; HA: Hydroxyapatite

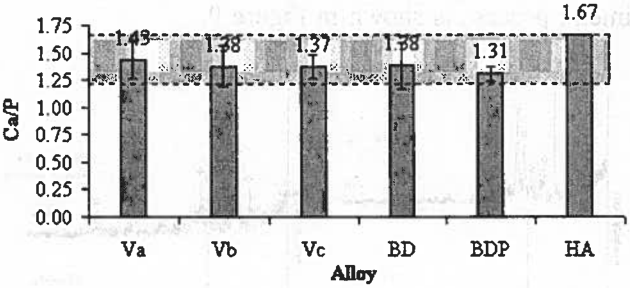

Fig. 11. Results of the effect of the alloy used versus the Ca/P ratio. The shaded region represents the values for the apatite, 1.2 to 1.67. Va: Low carbon content cast sample; Vb: Medium carbon content cast sample; Vc: High carbon content cast sample; BD: Forged alloy; BDP: Powder metallurgy alloy; HA: Hydroxyapatite

From the results of this study it was possible to observe that, in the case when the samples were immersed in SBF, the chemical and heat treatments have a significant effect on the apatite formation on the surface of the Co alloys, regardless of the chemical agent used during the chemical treatment and the type of alloy. The omission of anyone could lead to the formation of a less adherent thin apatite coating [9] or even to promote only the precipitation of small particles of compounds containing Ca, O and C on the surface of the sample. This behaviour may indicate that the chemical and heat treatments modify the surface of the alloy forming a stable compound containg Na. During the immersion in SBF this compound exchanges ions with the SBF increasing the pH of the solution, promoting the nucleation and growing of cristals of apatite on the surface of the alloy. As these nuclei are anchored to the surface of the sample, they provide the adherence to the formation of the coating. For the samples immersed in 1.5SBF the formation of an apatite coating was possible even in the samples without chemical treatment. In the case of the apatite cumulus observed on some samples, they can be formed on the surface of the sample via the precipitation mechanism from the solution. The precipitation mechanism is possible because of the supersaturation of the solution. The surface of the sample can be modified just with a heat treatment to deposite an apatite coating on it with a 1.5SBF solution, but the adherence perceived on the coating is not the same that that for a sample with a chemical and heat treatment.

4. Conclusions

It is possible to form an apatite coating on the surface of a Co based alloy. The results obtained indicated that by using an SBF solution the study of the effect of the chemical and the heat treatments on the formation of apatite on cobalt based alloys was possible. The layers on the alloys analyzed in this work showed that there is not a considerable effect neither of the chemical agent nor concentration used during the chemical treatment in the biomimetic process. Nevertheless, the heat treatment had an important effect when using a SBF solution.. The best coatings were found for the cast samples. The use of a 1.5SBF solution allows the formation of a better apatite coating on the surface of the cobalt base alloys, even if the chemical treatment is omitted. However, the better adhered layers were obtained by the application of both chemical and a heat treatments.

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