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Effect of rapid solidification and heat treatment on Co-20 wt. %Cr alloy for biomedical applications

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Abstract. A series of cobalt-base alloys with different chromium contents (20, 25, 30, 35, 40 and 44 wt. %) were melted into an induction furnace with argon atmosphere and casted into a chill cooper mold. The characterization of samples was carried out with a scanning electron microscope in order to evaluate the effect of chromium additions on microstructure. The resulting microstructure consisted mainly of columnar dendrites with randomly distributed precipitates in primary and secondary dendrite arms. X-ray diffraction patterns in as-cast samples identified the presence of both ε-hcp and the metastable α-fcc cobalt solid solution. As the Cr-content increased, the amount of both interdendrite segregation and precipitates increased too. From the Co-Cr alloys under study, the Co-20 wt. % Cr alloy showed a microstructure nearly free of interdendrite segregation and precipitation therefore was subject to an additional heat treatment to improve elongation from 2.6%, in the as-cast condition to 25.5% in the as-heat treated condition.

1. Introduction

Is well known that cobalt-base alloys are widely used in biomedical applications due to their excellent resistance to corrosion, mechanical properties and biocompatibility. A dental implant and/or prosthetic material suitable must function mechanically without permanent deformation or failure while leaving the biological tissues completely unaltered. Therefore, the materials used for surgical implants must meet principal requirements to perform in the human body: resistance to corrosion by physiological fluids; strong enough to avoid fracture because the normal physiological forces; and finally they must have a high degree of biocompatibility to ensure correct healing after insertion [1, 2]. These features can be achieved with a controlled solidification process and subsequent heat treatments to improve microstructure and mechanical properties of biomedical materials. ASTM F-75 is the most study cobalt-base alloy for biomedical applications and generally is fabricated with the investment casting process. Its standard specification establishes the mechanical properties as follows: yield strength, 450MPa (min); UTS, 650MPA (min); and a minimum ductility of 8% of elongation to fracture [3]. Many investigations has reported that the main defects in the as-cast cobalt alloys are: large grain size, porosity, chemical inhomogeneity and a microstructure with thicker interdendritic zones that may lead to low of mechanical properties of this materials [4,5]. Also, these alloys present the formation of various microstructural features including stacking faults, dislocations and twins which can affect the final properties of the alloys [6, 7]. Finally, recent studies report that precipitates presents in cobalt- base alloys affect the mechanical properties, wear and corrosion resistances [8]. In this work, we present results of solidified Co-20, 25, 30, 35, 40 and 44 wt. %Cr, in order to obtain an optimum as-cast microstructure free of interdendritic zones and a minor amount of precipitates. Also, were proposed a heat treatment to improve mechanical properties of cobalt-chromium alloy for biomedical applications.

2. Experimental procedure

Cobalt-base alloys with different chromium contents (20, 25, 30, 35, 40 and 44 wt. %Cr) were melted in a vacuum induction furnace under an argon atmosphere. Materials with high purity grade were placed into an alumina crucible and the liquid melt was casted in situ by gravity into a chill cooper molds with two isolated faces in order to keep the heat flux in the x-direction. The cooling rate was measured by placing a Pt/Pt-18%Rd thermocouple into the mold reaching values of ~$5X10^3$K/s. The resulting ingots were sectioned longitudinally, mechanically polished and electrolitically etched with 60% HNO_3 and 40% H_2O solution. Microstructure characterization was carried out in a scanning electron microscopy Stereoscan 440 coupled with a wavelength dispersed x-ray microanalysis. X-ray diffraction was performed in a Siemens D-5000 by using a $K_{\alpha\text{-}Co}$ radiation, a scanning angle *(2θ)* from 0 to 120° and a scanning speed of 5min/degree. Hardness HRc measurements were performed in a Matzusawa Hardness tester and mechanical properties were performed in a tensile test Instron machine 1210, using a travel speed of 0.5mm/min. From the experimental results in terms of microstructure, we selected the Co-20 wt. %Cr alloy in order to perform a heat treatment at 750°C during 60 minutes and air cooled.

3. Results and Discussion

A rapid solidification casting technique was performed to obtain ingots from chill-cast cobalt-chromium alloys because it has been reported that casting parameters have an impact on the mechanical properties, resistance corrosion and biocompatibility on these alloys [9, 10]. The microstructures obtained from chill cast solidification of alloys casted into cooper molds at $5X10^3$K/s cooling rates are shown in Figure 1.

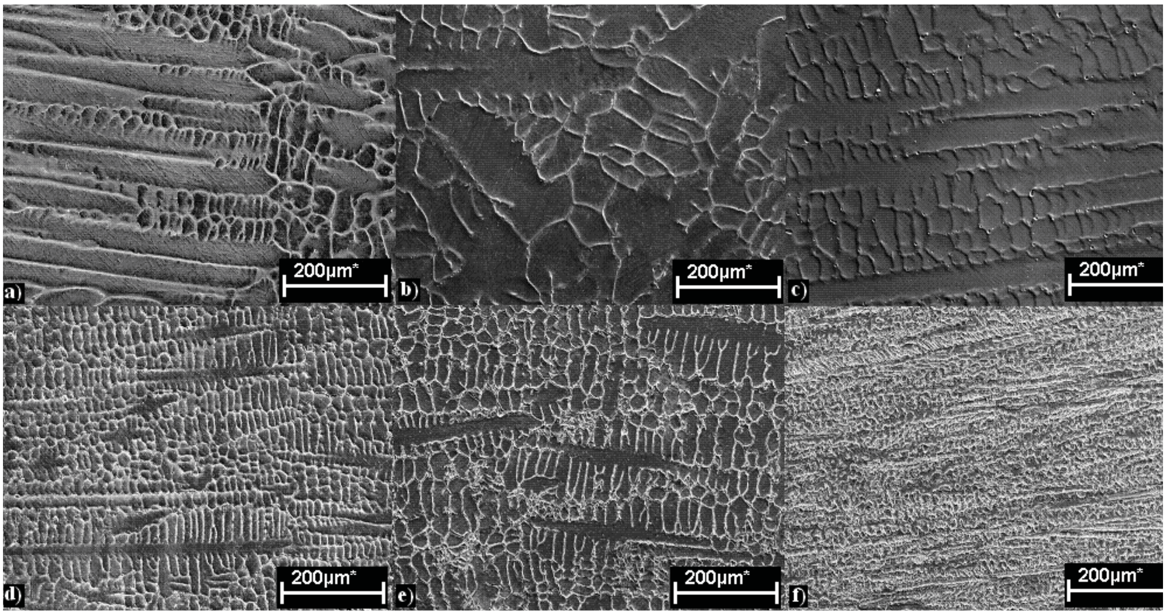

Figure 1. Microstructures observed in chill cast directional solidification of Co-Cr alloys; a) Co-20 wt. %Cr, b) Co-25 wt. %Cr, c) Co-30 wt. %Cr, d) Co-35 wt. %Cr, e) Co-44 wt. %Cr.

The resulting microstructures in Co-20, 25, 30, 35, 40 and 44 wt. %Cr alloys showed a columnar and/or equiaxed dendrites and, the effect of rapid solidification in cobalt-chromium alloys was observed regarding dendrite arm refinement as the chromium content increases and the extension of solid solubility in the eutectic Co-44 wt. %Cr alloy. From these alloys, we choose the Co-20 wt. %Cr alloy for apply in a heat treatment because its microstructure was nearly free of interdendritic segregation and a minimum of precipitates, see Figure 1a). On the other hand, Co-25 wt. %Cr and Co-30 wt. %Cr alloys have a major amount of precipitates respect to the Co-20 wt. %Cr alloy, Co_3Cr and CoCr precipitates were identified with wavelength dispersed x-ray microanalysis, showing a volume fraction of ~3X10-3, randomly distributed in the cobalt-chromium matrix, see Figure 1b) and Figure 1c). The interdendritic regions thickness was measured in Figure 1a) based on the scale of the micrograph taken by scanning electron microscopy and, the value was of the order of 5-6X10^{-3}mm in both Co-25 wt. %Cr and Co-30 wt. %Cr alloys. As the chromium content increased we can observed the presence of a major quantity of precipitates that corresponded to σ phase. Furthermore, there is an increment of interdenditic segregation and reduction in magnitude of primary dendrite arm spacing. All these features are in agreement with other research [11, 12]. The results obtained in this work showed a reduction or absence of interdendritic segregation and small volume fraction of precipitates in the Co-20 wt. %Cr alloy which is a very important result, consequence of control of microstructure during rapid solidification. Based on present results were obtained various ingots of as-cast Co-20 wt. %Cr alloy and were thermally treated at 750°C during 1 hour and air cooled.

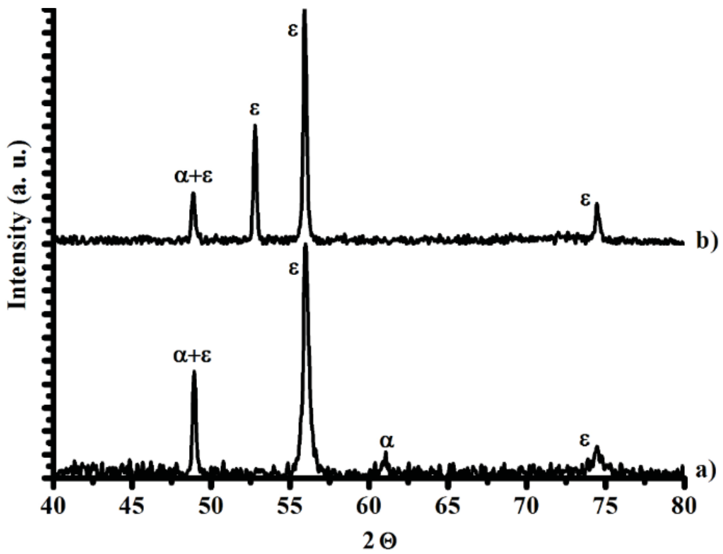

Figure 2. X-ray diffraction pattern: a) as-cast Co-20 wt. % Cr alloy, b) heat treated Co-20 wt. % Cr alloy.

The presence of both α-Co, fcc and ε-Co, hcp phases (metastable alpha -cobalt and epsilon-cobalt, respectively) are confirmed by x-ray diffractometry and shown in Figure 2. It's important to remark that generally cobalt-base alloys consists by a mixture of α-Co/ε-Co phases and, depending of solidification process and/or heat treatments applied to alloy, the α-Co or ε-Co phases are in minor or major percentage (independently of chromium content). Some studies reported an increase of ε-Co, hcp phase from heat treatments applied to cobalt-base alloys due to the promotion of fcc → hcp transformation and, as consequence an increase of mechanical properties in these materials. In

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agreement with those studies, we confirm a mayor presence of ε-Co phase as is seen in Figure 2b), that correspond to the heat treated Co-20 wt. %Cr alloy, in comparison with the diffraction pattern of as-cast Co-20 wt. %Cr alloy shown in Figure 2a). Also, C. Montero and co-workers indicated that the mechanical behavior of these two phase Co-27Cr-5Mo-0.05C alloys have shown that the hardness and yield strength of a 50% hcp alloy can be increase by at least 30% without ductility looses [13]. Those results are in agreement with this study where it was observed an improvement on mechanical properties from heat treated Co-20 wt. %Cr alloy, regarding ductility, we observed an important increase in ductility from 2.8% in the as-cast condition to 25.5% in the heat treated condition as is shown in Figure 3. This is a very important result since these values of elongation only are reported for cobalt-base alloys in as-cast condition (superalloys) with certain nickel percentage or in cobalt-base alloys in forged condition (that contain determined percentage of Ni too), because an amount of nickel is added to these alloys to improve their ductility by stabilizing the α-Co, fcc phase, in spite of the fact that nickel causes skin allergies or cancer in living organisms [14, 15].

Table 1. Mechanical properties of as-cast and heat treated Co-20 wt. %Cr alloy.

Co-20%Cr alloy	UTS (MPa)	σ_y (MPa)	% Elongation	Hardness (Rc)
As-cast	357.09	240	2.6	18
Heat treated	596.243	325	25.5	24

Furthermore, various authors reported that nickel produce allergic reactions in human bodies, women mainly [16,17]. Table 1, show the results of mechanical testing made to as-cast and heat treated Co-20 wt. %Cr alloys. Hardness measurements are reported in Table 1 and we can note that as-cast alloy exhibit hardness value of 18HRc which is inferior to 24HRc value measured in heat treated sample.

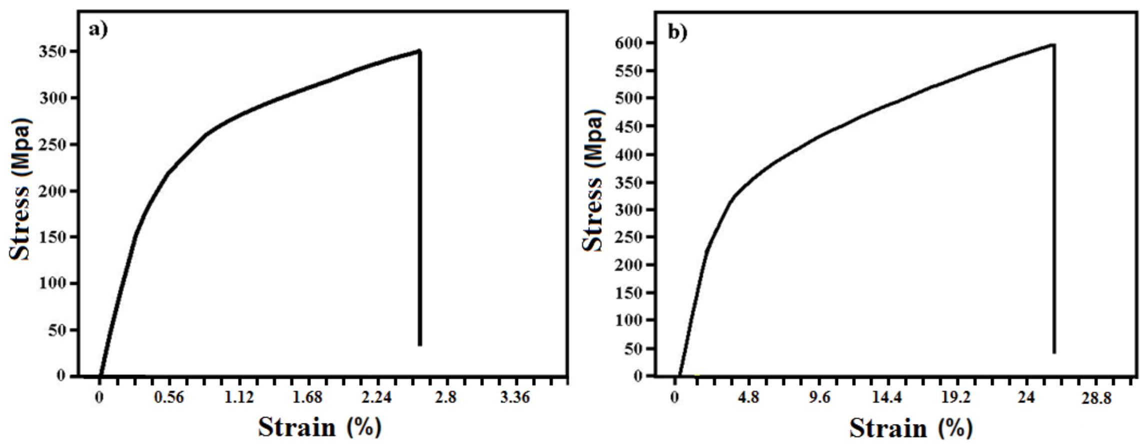

Figure 3. Stress-Strain curves of a) as-cast Co-20 wt. %Cr alloy, b) heat treated Co-20 wt. %Cr alloy.

Furthermore, ultimate tensile strength values exhibited by as-cast and heat treated alloys were slightly below to the lower limit for cobalt-base alloys. But is important to remark that the ASTM-F75 standard specification establishes the mechanical properties as follows: yield strength, 450MPa (min), UTS, 650MPA (min) and minimum ductility of 8% elongation to fracture and some researchers are in agreement with variation in mechanical properties data, particularity in ductility [3]. Beyond that, today there are greatest efforts to understand the complexity of cobalt-based alloys, for example, martensitic transformation mentioned above that been closely related with stacking faults and twins, which have a direct impact on mechanical properties as ductility and strengthening of these materials [18,19]. For this reason, is necessary to elaborate a controlled solidification process that permit to obtain a better characteristics in both microstructural (minimum precipitates and reduction or absence interdendritic segregation) and mechanical features in cobalt alloys. Since, it has been reported that even the materials employed in cast process and temperature of mold during casting are determinant in improving the mechanical properties of these materials [5,20,21]. The materials used in this investigation were selected carefully.

4. Conclusions

The results in this work showed that microstructures obtained from casting of Co-20, 25, 30, 35, 40 and 44 wt. %Cr alloys presented columnar and/or equiaxed dendrites of α-Co, fcc metastable phase and ε-Co, hcp phase. The effect of rapid solidification is present with the reduction of interdendritic segregation, minimum amount of precipitates and a notorious extension of solid solution that is evident in Co-44 wt. %Cr alloy. This is an encouraging result because we can obtained near free intedendritic segregation microstructure and a few precipitates in Co-20 wt. %Cr alloy at a cooling rate of $5X10^3$K/s. Therefore, an improvement in ductility was obtain in the Co-20 wt. %Cr alloy increasing from 2.6% in the as-cast condition to 25.5% after heat treatment. This response in the mechanical properties of alloy was consequence of fcc → hcp transformation that promotes an increase of ε-Co, hcp phase which was confirmed by X-ray diffraction patterns.

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References

[1] Lee S H, Nomura N and Chiba A 2008 *Mater. Trans. JIM*. **49**, 260.
[2] Granchi D, Ciapetti G, Stea S, Savarino L, Filippini F, Sudanese A, Zinghi G and Montanaro L 1999 *Biomaterials*. **20**, 1079.
[3] Gomez M, Mancha H, Salinas A, Rodriguez J L, Escobedo J, Castro M and Mendez M 1997 *J. Biomed. Mater. Res.* **34**, 157.
[4] Giacchi J V, Morando C N, Fornaro O and Palacio H A 2011 *Mater. Charact*. **62**, 53.
[5] Kaiser R, Williamson K, O'brien C and Browne D J 2013 *Metall. Mater. Trans. A* **44**, 5333.
[6] Saldivar-Garcia A J and Lopez H F 2004 *Metall. Mater. Trans. A* **35**, 2517.
[7] Lashgari H R, Zangeneh Sh, Hasanabadi F and Saghafi M 2010 *Mater. Sci. Eng*. **527**, 4082.
[8] Narushima T, Mineta S, Kurihara Y and Ueda K 2013 *JOM* **65**, 489.
[9] Ramírez-Vidaurri L E, Castro-Román M, Herrera-Trejo M, García-López C V and Almanza-Casas E 2009 *J. Mater. Process. Technol.* **209**, 1681.
[10] Kaiser R, Browne D and Williamson K 2011 *Mater Sci. Eng.* **27**, 1.
[11] Rosenthal R, Cardoso B R, Bott I S, Paranhos R P R and Carvalho E A 2010 *J. Mater. Sci.* **45**, 4021.
[12] Mineta S, Namba S, Yoneda T, Ueda K and Narushima T 2010 *Metall. Mater. Trans. A.* **41** 494.
[13] Montero-Ocampo C, Juarez R and Salinas A *2002 Metall. Mater. Trans. A.* **33**, 22329.
[14] Jiang W H, Guan H R and Hu Z Q 1999 *Metall. Mater. Trans. A.* **30**, 2251.
[15] Yamanaka K, Mori M and Chiba A 2012 *Metall. Mater. Trans. A.* **43**, 5243.
[16] Roash M 2007 *Dent. Clin. N. Am.* **51**, 603.
[17] Niinomi M 2002 *Metall. Mater. Trans. A.* **33**, 477.
[18] Khlebnikova Y V, Rodionov D P, Sazonova V A, Tabatchikova T I, Antonova O V, Turkhan Y E and Kazantsev V A 2007 *Phys. MET. Metallography (USSR)*. **103**, 609.
[19] López H F and Saldívar-García A J 2008 *Metall. Mater. Trans. A.* **39**, 8.
[20] Montero C, Talavera M and Lopez H 1999 *Metall. Mater. Trans. A.* **30**, 611.
[21] Ghazvinizadeh H, Meratian M, Kermanpur A, Fathi M H and Minouei H 2010 *IJE Trans. A.* **24**, 49.