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Production of Co-Cr-Mo Biomedical Alloys via Investment Casting Technique

Mehmet Yıldırım[1*], Ali Keleş[1]

[1]Selçuk University, Department of Metallurgical and Materials Engineering, 42075, Selçuklu-Konya, Turkey

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*Correspondence E-mail: ymehmet@selcuk.edu.tr

ABSTRACT Co-Cr-Mo biomedical alloys with three different compositions were produced by investment casting technique from high purity constituents. The structural properties such as phase relationships, microstructures, and hardness of the alloys were studied. The phase relationships of the samples were investigated using x-ray diffraction and the microstructural characterization were performed using light optical microscopy. It was found that the microstructure of the samples was composed of Co-based dendrites (matrix phase) and carbides (second phase particles) precipitated at grain boundaries and interdendritic regions. These carbides act as strengthening particles in such alloys. Moreover, the mean hardness of these three samples were measured as 24.2, 24.5 and 29.6 HRC. The values were found to be in a good agreement with the optimum hardness value given in the ASTM F75 standards.

Keywords: ASTM F75, Co-Cr-Mo Alloys, Investment Casting Technique,

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1. INTRODUCTION

Co-Cr alloys, which are also known as vitallium steels until the beginning of 1930s, were used as candidates for replacing gold in dentistry. Later, they became one of the three main metallic biomaterials used in orthopedic surgery especially as hip prostheses and internal fixators. Co-Cr based alloys can be classified into two main groups: cast Co-Cr-Mo alloys and hot forged Co-Cr-Ni-Mo alloys. Among these two types of alloys, Co-Cr-Mo alloys have been used for many years in dentistry and recently in artificial joint production. Co-Cr-Mo alloys, also known as ASTM F75, contain 58-69 %Co, 26-30 % Cr, 5-7 % Mo and various elements [1-4]. The high Cr content (25-27 wt %) provide biocompatibility and also contribute to corrosion resistance by forming a protective chromium oxide (Cr_2O_3) layer. Moreover, they also exhibit superior mechanical properties by forming metal carbide precipitates through Mo content (5-7 wt %) [5].

Co-Cr-Mo biomedical alloys can be produced by various manufacturing processes such as powder metallurgy, forging and investment casting technique. Among these methods, investment casting technique is the promising method in the production of implants used in orthopedic surgical operations. The main advantage of investment casting technique compared to other methods is that complex shaped parts at very low cost can be produced with dimensions and tolerances very close to the final dimensions.

Co-Cr-Mo biomedical alloys are extensively used in the production of orthopedic implants due to their attractive strength, hardness, toughness, corrosion and wear resistance [6, 7]. It is well-known that Co-Cr-Mo alloys possess low ductility along with cast defects such as micro porosity, chemical inhomogeneity and large grain size in the as-cast state [8-10]. Their poor ductility could be enhanced with proper heat-treatment and alloying additions [11]. In the literature, the effects of alloying additions have been investigated for Co-Cr-Mo alloys. It was noted that addition of Ni enhances ductility and stabilizes Co matrix phase but it has an important allergy problem for human body on biomedical applications [10, 12, 13]. On the other hand, C addition above a certain limit leads to formation of carbide particles at grain boundaries. These particles can be the source of stress concentration resulting in fracture [10]. Moreover, W addition increases γ-Co (FCC)↔ε-

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Co (HCP) allotropic phase transformation temperature and forms W_3C which act as strengthening phase [14].

In this study, it was first aimed to produce Co-Cr-Mo biomedical alloys having different Fe contents by investment casting technique and then investigate their structural properties and hardness. In addition, emphasis was placed on the effect of Fe content on phase relationships on microstructures and hardness since commercially pure alloys may contain Fe amount higher than the optimum content according to ASTM F75 standards [2].

2. EXPERIMENTAL

2.1 Production of the Samples

In this study, Co-Cr-Mo alloys with three different compositions were produced by investment casting technique as shown in Figure 1. This technique with ceramic shell method is performed using the following steps; wax modeling, attachment of multiple parts to wax runner, ceramic shell formation by dipping wax parts in a wet ceramic slurry, removal of wax from the mold by autoclave, sintering of the molds, pre-heating prior to casting and casting steps. As the first step, wax models of the parts were created by wax injection machines using industrial green wax. This step is very important because the surface and dimensional characteristics of the waxes dictate the surface and dimensional properties of the products. Multiple wax models were attached to a wax runner. The wax models were positioned at a proper angle for smooth flow of the melt during casting on the wax runner to prevent the formation of turbulence. Then, two different ceramic slurries were prepared for the ceramic shell formation. Then, wax runner was left to dry at atmospheric conditions. After drying, the wax is removed in an autoclave at 175 °C under 7-8 bar water vapor pressure for 15 minutes leaving the ceramic mold as a residue. Since the ceramic molds did not have sufficient thermal and mechanical strength, they were heated only to a temperature around 700 °C. At this temperature, the ceramic molds were fired for 4 hours in order to be sintered and remove the wax residuals.

Then, molten metal was poured into the hot ceramic molds. During this process, Ar gas was blown through the surface of the molten metal to prevent direct exposure of the melt from air. The casting temperature was set as 1585 °C and casting was performed with an induction furnace having 25 kg capacity. After casting, parts were left cooling under ambient condition. The ceramic molds were then broken by vibration or hammer. Finally, individual parts were cut from the runner.

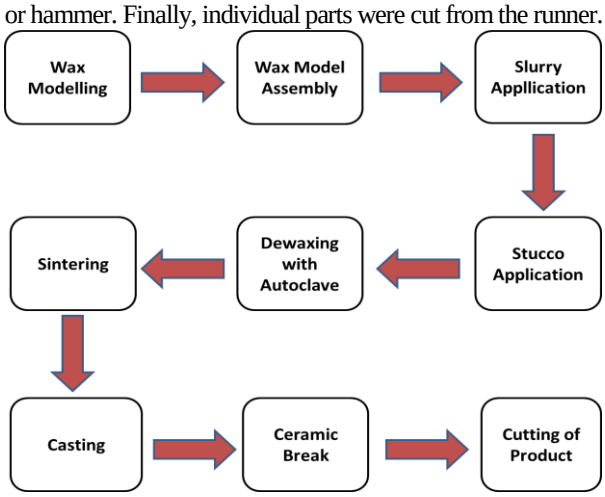


Fig. 1. Schematic pattern of the production of the samples via investment casting technique

2. 2 Characterization

The chemical compositions of the Co-Cr-Mo samples were tested using Oxford Foundry Master Model optical emission spectrometer. The structural characterization, by means of phase analysis and crystal structure, for Co-Cr-Mo alloys produced by the investment casting technique were carried out using X-ray diffraction (XRD) analyses. XRD analyses were conducted using a Bruker D8 Advance model diffractometer with Cu-Kα radiation (λ = 1.54056 Å) and an X-ray source operating voltage of 40 kV. XRD scans were performed in the 2θ range of 25°–100° using a scanning rate of 2°/min. Samples for microstructural examination were mechanically grinded (with 120-1200 grit SiC papers), and then polished with Al_2O_3 suspension. Then, samples were electrolytically etched with chromic acid solution at a voltage of 4 V for 12 s. Rockwell-C hardness measurements were performed using a Digirock RBOV Hardness tester. The mean hardness values were determined by averaging eight measurements obtained for each sample.

3. RESULTS

Table 1. Chemical composition of investigated Co-Cr-Mo samples from optical emission spectroscopy analysis (wt%) and chemical compositions according to the ASTM F75 and ISO 5832-4 Standards

Sample	Co	Cr	Mo	Fe	Ni	W	Mn	C	Si
Sample 1	64.3	28.0	5.5	0.404	0.0775	0.107	0.457	0.206	0.731
Sample 2	64.9	27.6	5.33	0.728	0.0749	0.0868	0.283	0.206	0.673
Sample 3	64.0	28.6	5.0	1.0	0.0945	0.0635	0.298	0.183	0.656
ASTM F75	*balance*	*27-30*	*5-7*	*max. 0.75*	*max. 0.5*	*max.0.2*	*max. 1*	*max. 0.35*	*max. 1*
ISO 5832-4	*balance*	*26.5-30*	*4.5-7*	*max.1*	*max. 1*	*max.*	*max. 1*	*max. 0.35*	*max. 1*

The chemical compositions of the investigated samples are given in Table 1. The results of the chemical analysis of the alloys indicated that the Fe concentration for the Sample # 1 and 2 were below than maximum Fe concentration of ASTM F75 standards [2], while the Fe concentration of the Sample 3 (1 %) was higher than the maximum allowable value (0.75 %). Nevertheless, Sample 3 shows agreement with the ISO 5832-4:2014 [3] standards.

The concentrations of Co, Cr and Mo, on the other hand, were in the designated range specified by ASTM F75 and ISO 5832-4:2014 standards. Furthermore, the amount of Ni, which is an important parameter in these alloys, is less than 0.1% for all three samples. According to the ASTM F75 Standards maximum Ni concentration should be 0.50 %. Although Co-Cr-Mo alloys with high Ni content are used more frequently in leg and arm joints due to their higher load capacity than

that of lower Ni content, high Ni content may lead allergies and poisoning. In addition, especially magnetic resonance (MR) may cause serious problems due to Ni's magnetic property [15].

The XRD patterns of produced Co-Cr-Mo samples were shown in Figure 2. According to the XRD patterns, all the samples were mainly composed of γ-Co phase with a FCC crystal structure [16]. Besides that, presence of low intensity diffraction line corresponding to the (101) plane of ε-Co phase indicated that all samples contain small amount of ε-Co phase with HCP crystal structure [16, 17]. Neither any additional diffraction line nor any shift of the present γ-Co and ε-Co peaks were observed. Nevertheless, Cr has an extended solid solubility in Co and forms a single phase solid solution even at 37 wt% Cr addition [18]. Thus, any diffraction line corresponding to the Cr or Co-Cr intermetallic compounds were observed in XRD analyses.

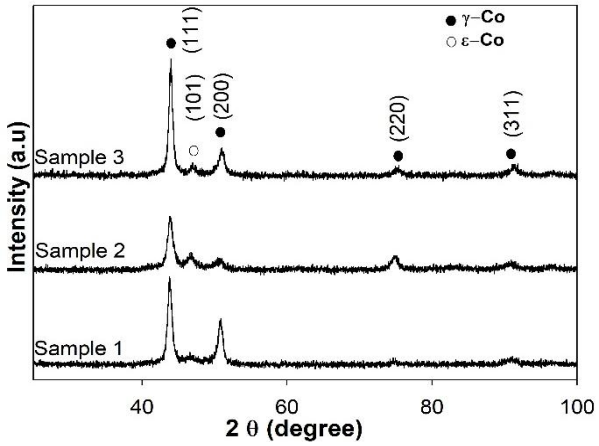
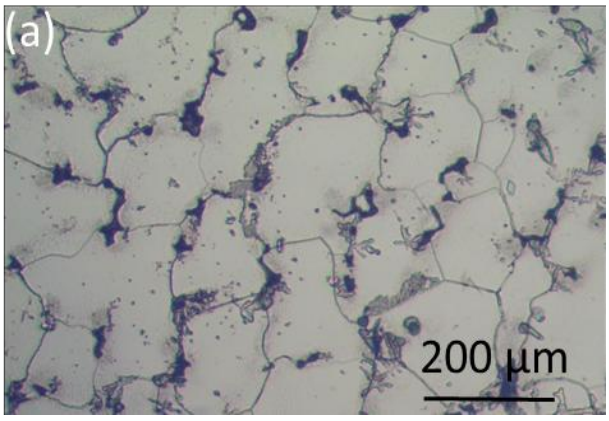
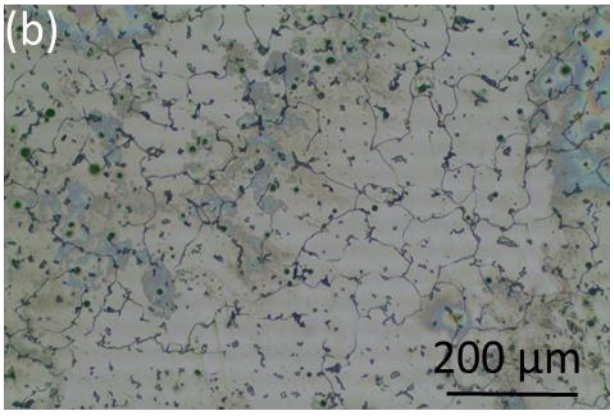


Fig. 2. XRD patterns of Co-Cr-Mo alloys





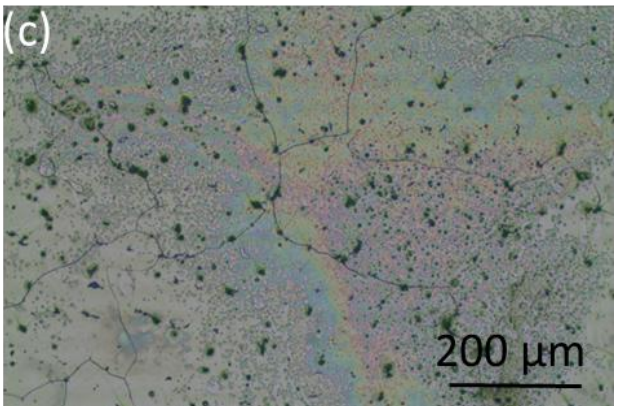


Fig. 3. Optical micrographs of Co-Cr-Mo alloys, (a) Sample 1, (b) Sample (2), and (c) Sample 3

In addition, lattice parameters of the investigated samples were calculated by applying well-known Bragg's Law and the results were tabulated in Table 2. Pure Co has a lattice parameter of 3.545 Å according to the [16], and the calculated lattice parameters for investigated samples were much higher than that of pure Co. The reason for the higher lattice parameter is the atomic radius differences among constituent elements. Atomic radius of Fe (1.24 Å), Ni (1.25 Å) and Cr (1.25 Å) are very close to that of Co (1.25 Å), while Mo (1.36 Å) and W (1.37 Å) have much higher radius values compared to Co. Normally, the lattice parameter of the FCC γ-Co phase (3.56 Å) in Co-Cr-Mo alloys is very similar to the lattice parameter of pure Co (3.545 Å) [19]. This similarity is due to the almost same atomic radius of Co and Cr. It is well-known that Co is the solvent existing in highest quantity in the alloy (~64%), while Cr is the main solute element (~28%) soluble in Co. Nonetheless, commercially available high purity alloys containing several elements such as Fe, W, Mn, Ni, Si and C were used in this study. Dissolution of these elements increased the lattice parameter of FCC lattice [19]. Nevertheless, when lattice parameters of investigated samples were compared, it was observed that lattice parameter decreased with increasing Fe content. According to the Table 1, amount of Mo and W decreased with increasing Fe content. It is believed that Fe atoms mainly replaced Mo or W atoms in the FCC lattice because Fe, Mo and W all have BCC crystal structure. Moreover, Mo and W have much larger atomic radius compared to Fe and lattice parameter decreased with increasing Fe.

Table 2. Calculated lattice parameters of γ-Co phase in Co-Cr-Mo alloys

Sample	Lattice Parameter (Å)
Sample 1	3.5739
Sample 2	3.5684
Sample 3	3.5600

Figure 3 shows optical micrographs of all produced samples. The microstructures of the investigated samples were consisted of Co dendrites and fine precipitates at grain boundaries and interdendritic zones. All samples showed similar microstructural features with slight differences in size and volume fraction of existing phases. The FCC γ-Co phase is the matrix

phase of the Co-Cr-Mo alloys and the hardness and strength of this alloy are provided by the $M_{23}C_6$ type precipitates. Moreover, some amount of casting defects were also observed for all samples.

The hardness data for all three Co-Cr-Mo alloys are listed in Table 3. The hardness values are increased with Fe content increment in all samples. For Sample 1 and 2, having Fe content of 0.404 and 0.728, respectively, the mean values were close to the lower limit for the required hardness specified in ASTM F75 standard [2]. The lower limit is 25 in HRC where samples 1 and 2 attained hardness values of 24.2 and 24.5 HRC, respectively. Sample 3, on the other hand, suffices the ASTM F75 Standards requirement with 29.6 HRC value [2].

Table 3. Rockwell-C hardness values of Co-Cr-Mo alloys

Sample	HRC
Sample 1	24.2
Sample 2	24.5
Sample 3	29.6

4. CONCLUSION

In this study, biomedical grade Co-Cr-Mo based alloys with chemical compositions per ASTM F75 standard were successfully produced using precision casting technique for orthopedic surgical applications. XRD analyses indicated that all samples had FCC γ-Co single phase. The lattice parameters decreased with increasing Fe content. Finally, the hardness measurements showed that Sample 3 met the ASTM F75 Standards (25 to 35 HRC), whereas Samples 1 and 2 exhibited hardness values very close to the lower limit of the standard.

This study reveals promising properties of the Co-Cr-Mo biomedical alloys. It is predicted that mechanical properties of these alloys at ambient condition can be further enhanced by proper heat-treatment which will control the microstructural features such as Co matrix phase, size, morphology and amount of carbide particles.

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Biographies

Mehmet YILDIRIM was born in Ereğli-Konya, Turkey. He received his BSc. and PhD degrees from Department of Mechanical Engineering, Dokuz Eylul University, İzmir, Turkey in 2004 and from Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey in 2014, respectively. He currently works as an assistant professor at Department of Metallurgical and Materials Engineering, Selcuk University, Konya, Turkey.

E-mail: ymehmet@selcuk.edu.tr

Ali KELEŞ was born in Ilgın-Konya, Turkey. He graduated from Metallurgical and Materials Engineering from Fırat University at Elazığ, Turkey in 2015. He is currently a M.Sc. student at Department of Metallurgical and Materials Engineering, Selçuk University, Konya, Turkey.

E-mail: ali.keles1@outlook.com