

Microstructure of metal carbides in CoCrMo for biocompatible artificial knee joint

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A CoCrMo alloy conforming to the ASTM F75 standard was cast in an industrial environment and the microstructure of the metal carbides was studied. The CoCrMo alloy was characterized by a dendritic structure of a solid solution of chromium and molybdenum in cobalt with interdendritically precipitated carbides. Because of the high chromium content, the dominant phase was $M_{23}C_6$ -type carbides, but chromium-rich carbides can be also of M_7C_3 and M_3C_2 types. The other elements in the alloy lead to M_6C - and MC-type carbides. In the case of low carbon content, formation of metal carbides and intermetallic phases based on the alloying elements and cobalt is limited. The characterization of the samples was achieved by using optical microscopy (OM), field emission scanning electron microscopy (FE-SEM), and energy dispersive spectroscopy (EDS) techniques for a better identification. In this study, the as-cast microstructure was a γ -Co (fcc) dendritic matrix, with precipitation of a secondary phase such as the $M_{23}C_6$ carbides at the grain boundaries and interdendritic zones.

Key words: CoCrMo alloy, ASTM F75, Metal carbides, γ -Co, $M_{23}C_6$, Microstructure.

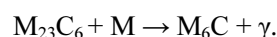
Introduction

Cobalt alloys are widely used as biocompatible alloys, mostly for manufacturing prosthetic implants. An important factor of these materials is the high solubility of the alloying elements in a γ solid solution. This high solubility facilitates not only solution hardening but also controlled decomposition, resulting in stable phases with precipitation hardening [1]. The biocompatible casting alloys can have up to 0.35% of carbon content. Precipitation hardening in such alloys is caused by interdendritic precipitates of the metal carbides of the alloying elements. The contents of chromium (reaching 22 wt.%) and that of the other elements are selected such that the matrix is composed of a solid solution of chromium and molybdenum in cobalt, with an A1(γ) lattice [2-4]. Both molybdenum and tungsten - often present in these alloys-are added to obtain the solution hardening effect. These two elements are usually applied interchangeably [5, 6].

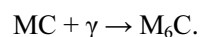
Depending on the concentration of carbon and the alloying elements, the process of precipitation can proceed via a eutectic reaction or simple precipitation [7]. Because of the presence of chromium, $M_{23}C_7$ -type carbides dominate in cobalt-based alloys [7, 8], but chromium-rich carbides can also be of type M_7C_3 and M_3C_2 . The other elements present in the alloy can form

M_6C and MC carbides [7-10]. The most widespread carbide occurring in all cobalt alloys is $M_{23}C_6$. It forms during the solidification of alloys with high chromium-to-carbon ratios and in alloys containing additives of high-melting metals. $M_{23}C_6$ is characterized by a very differentiated morphology [1].

After saturating these alloys, $M_{23}C_6$ -type carbides dissolve in the solid solution or are converted to M_6C according to the equation [9-12].



In cobalt alloys with tungsten and molybdenum concentrations over 4 wt.%, M_6C carbide is often formed instead of $M_{23}C_6$. The former is more stable than the latter and can have a complex chemical composition. A secondary M_6C carbide can also form as a result of the reaction between MC and the solid solution [9-12]:



During aging of the alloys, M_6C carbide can again be converted to $M_{23}C_6$. The formed secondary metal carbide is fine-dispersive, which profitably affects the mechanical properties of the cobalt alloys [2]. M_7C_3 and M_3C_2 carbides are created in cobalt alloys with low chromium contents, and thus, these types of carbides are not formed in biocompatible alloys [1, 4]. The aim of this work was to provide more information on the phases and microstructure of a CoCrMo alloy prepared by investment casting and to evaluate its possible

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transformation during solidification and cooling in an industrial environment.

Experimental

The CoCrMo alloy was produced in a vacuum induction furnace, which enabled us to obtain an alloy with a defined chemical composition and prevented oxidation. Melting and casting were conducted under a vacuum of 0.04 mbar. First, the raw materials and molds were prepared. A mold was prepared by using meltable models, which were mainly used in the production of small weight casting of a very smooth surface. A model made of material with a low melting point (such as paraffin or stearin) was gradually covered by layers of the melt, each with different granulometry, until the mold, i.e. shells with 5~7 mm-thick walls, was obtained. The model was melted out, leaving a cavity corresponding exactly to the shape of the desired model. This shell can then be used as a precise casting mold. Cobalt and chromium were first degassed and then annealed at 1000 and 1100 °C, respectively, at pressures of 0.10 ~ 0.20 mbar. Next, these metals were gradually charged into a high-aluminous corundum crucible in the induction vacuum furnace. This material is resistant to corrosion caused by metal charge and dross, as well as to the abrasive effect of the charge.

Melting and casting can be performed under vacuum or in argon atmosphere. If argon is used, it must be extremely pure (99.99%); the pressure in the furnace receptor should be kept below 0.10 Mbar. The mold was preheated to 1050 ~ 1080 °C, and the casting temperature was 1550 ~ 1560 °C. The shell mold material and wall thickness provided controlled cooling, as well as control of the grain size and shape, thus influencing the mechanical characteristics. Monitoring the pressure change, one can observe both the beginning and end of secondary degassing, i.e., the beginning and end of melting and casting in a closed vacuum chamber. This precise vacuum-casting process resulted in samples with precise dimensions and good surfaces, without the need for additional sandblasting.

The bulk chemical composition was measured by wavelength dispersive X-ray fluorescence (WD-XRF, Rigaku, ZSX Primus II). The phase of the as-cast sample was identified using an X-ray diffractometer (XRD, Bruker ASX, D8 Advance, Germany), and XRD patterns were obtained using Cu K α radiation. The preparation of the samples for optical and scanning electron microscopy was carried out using conventional procedures for polishing, from 600-grit SiC paper to 0.05 μ m levigated alumina. Afterwards, the specimens were thoroughly cleaned to remove any polishing residue. Following Szala et al. [13], two different etching techniques were used to reveal the microstructure and to identify secondary phases. A combination of

etchants was selected, which, in the first stage, revealed the dendritic matrix features and, in the second stage, stained the secondary phases [14]. Optical microscopes (OM) from 100 to 400 $\times$ were used to obtain a wide field of view. High magnification was used to identify different phases. The samples were examined by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-7610F microscope. Energy dispersive spectroscopy (EDS) techniques were also employed to obtain a more accurate characterization of the different precipitated phases, even though the EDS technique provided a semi-quantitative analysis. The system used was EDAX (Oxford X-max) equipped with an LN2 free silicon drift detector.

Results and Discussion

Schematic diagrams of the knee joint system and the as-cast artificial femoral component made from the CoCrMo alloy are shown in Fig. 1. Chemical composition of the as-cast CoCrMo alloy sample analyzed by XRF is presented in the Table 1. The obtained alloy follows the ASTM standard (ASTM F75) for casting alloys for surgical implants. The nickel content should be below 1.0 wt%. The as-cast CoCrMo alloy sample had less than 0.2 wt% Ni. It can be seen from the Co-Cr phase diagram [3, 7] that solidification of an alloy containing 31.5 wt% should start at approximately 1420 °C, as shown in Fig. 2. According to the manufacturer's data, the melting point of the alloy is between 1240 to 1350 °C, which indicates that molybdenum and chromium reduced the melting

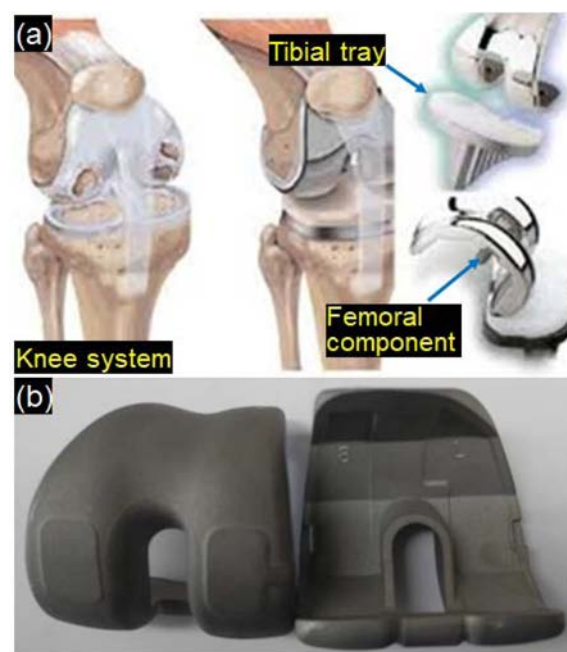
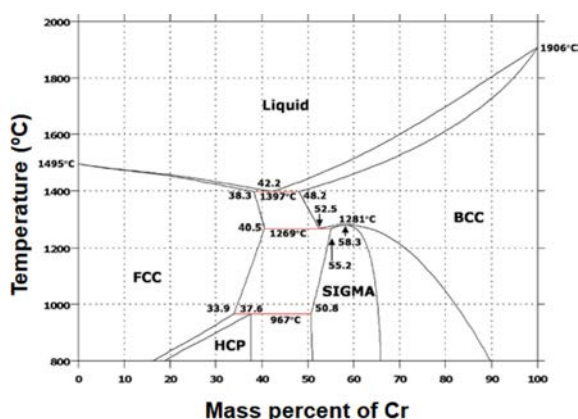
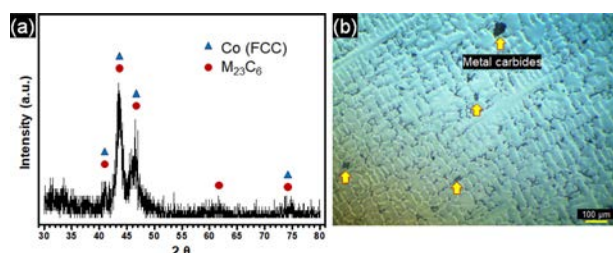


Fig. 1. Schematic diagram of (a) human knee system and (b) artificial femoral part fabricated by investment casting using CoCrMo alloy.

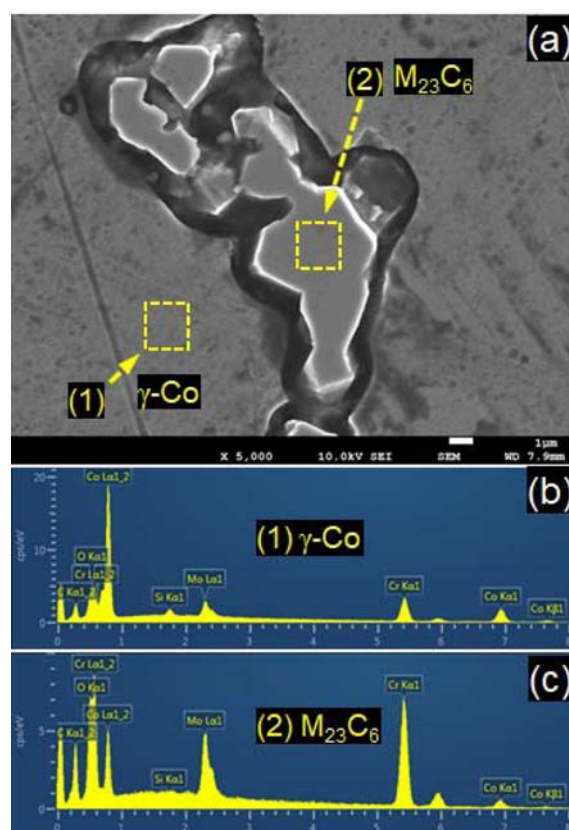
Table 1. Chemical composition of as-cast CoCrMo alloy sample measured by WD-XRF.

	Co	Cr	Mo	C	Si	Fe	Ni	Mn	Cu	Zn
ASTM (F75) (wt%)	Bal.	27.0 ~ 30.0	5.0 ~ 7.0	0.35 max	1.0 max	0.75 max	1.00 max	1.00 max	—	—
As-cast sample (wt%)	61.60	29.35	5.60	1.25	0.65	0.58	0.20	0.40	0.36	0.10
As-cast sample (at%)	58.77	30.12	3.11	5.55	1.23	0.55	0.18	0.38	0.30	0.08

**Fig. 2.** Two-component phase equilibrium diagram of Co-Cr [3, 7].**Fig. 3.** (a) X-ray diffraction spectrum and (b) optical micrograph of the as-cast CoCrMo alloy sample.

temperature of the current alloy.

Because of the chromium content, the alloy should solidify omitting the eutectic transition at 1397 °C. The γ phase (face-centered cubic (fcc), A1) that solidifies directly from the liquid is stable up to approximately 950 °C, when the martensitic-like transformation to the ϵ phase (hexagonal close-packed (hcp), A3) should start [15]. However, according to the literature data, the γ phase in biocompatible alloys remains stable down to the ambient temperature [1-4]. At lower temperatures, and at chromium concentration ranges such as that of the examined alloy, the eutectoidal decomposition $\epsilon \rightarrow \text{Co}_3\text{Cr} + \text{Co}_2\text{Cr}$ is observed. At higher Cr concentration, the equation is $\text{Co}_2\text{Cr} + \text{Co}_3\text{Cr}_2$, as shown in Fig. 2. It has been found from analysis of Cr-Mo alloys [16] that chromium and molybdenum make a spinoidal mixture. Silicon can react with molybdenum intermetallic phases Mo_5Si_3 and Mo_3Si . The examined material is a multicomponent alloy, and therefore, some complex phases may have been created in its structure that are

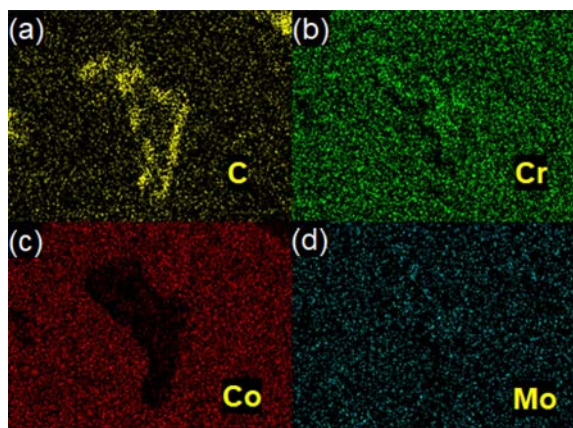
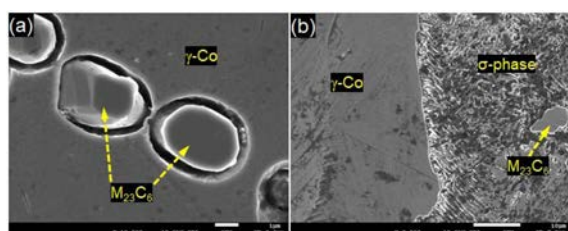
**Fig. 4.** (a) FE-SEM image and (b,c) EDS spectra of blocky M_{23}C_6 type carbide particle formed in the as-cast CoCrMo alloy.

absent in the two-component diagrams.

The identification of the crystal phases present in the matrix was initially carried out using XRD analysis of the as-cast CoCrMo alloy sample, and the results are shown in Fig. 3(a), which reveals the prominent diffraction lines of γ -Co (fcc) and M_{23}C_6 carbide. The optical microscopy (OM) photographs of the as-cast structure of CoCrMo alloy sample are presented in Fig. 3(b). Fine metal carbides with homogeneous distribution can be observed in Fig. 3(b). The alloy microstructure usually consists of chromium and molybdenum carbides, which are globular, and when such globules are homogeneously distributed, they improve the mechanical characteristics of a CoCrMo alloy. The Cr_7C_3 carbides are eutectic with the Co solid solution, whereas the Cr_{23}C_6 carbides precipitate in a fishbone shape [17]. The microstructure observed by OM consisted of a dendritic matrix with precipitates at the grain

Table 2. Chemical composition of two region in Fig. 4(a) determined using EDS microanalysis

Region	C	Co	Cr	Mo	Si
(1)	11.95	56.28	26.25	3.12	1.56
(2)	31.32	12.45	50.84	5.44	–

**Fig. 5.** EDS mapping images of blocky $M_{23}C_6$ -type carbide particle of Fig. 4(a).**Fig. 6.** FE-SEM image of (a) blocky $M_{23}C_6$ particles and (b) σ phase in the as-cast CoCrMo alloy.

boundaries and interdendritic zones, which agrees well with the microstructure reported in the literature for these types of alloys in the as-cast condition [1-5]. Also, the presence of intrinsic casting-method defects such as micropores, shown in Fig. 3(d), were detected, which were probably due to the high pouring temperature.

Fig. 4 shows the FE-SEM micrograph and EDS spectra of the alloy, showing an interdendritic light-gray blocky $M_{23}C_6$ -type carbide phase and a γ -Co matrix. The chemical compositions of the two regions shown in Fig. 4(b,c) were determined using EDS microanalysis, and the results are shown in Table 2. This feature would result from a partial γ -Co + C $\rightarrow$ $M_{23}C_6$ reaction during the cooling process. Fig. 5 shows digital EDS compositional maps obtained from Fig. 4(a), which indicate that the core of the particle ($M_{23}C_6$ region) was richer in Cr and C, but had less Co than the γ -Co matrix. Carbide precipitates at the grain boundaries and interdendritic regions are the major strengthening mechanism in the as-cast condition, but dislocation interactions with stacking fault intersections are also a strengthening mechanism [18]. The coarse blocky carbides shown in Fig. 4 play an important role

as sources of dislocations and stacking faults when stresses are applied [19]. Because of the intrinsic low cooling rates of the manufacturing process, two carbide morphologies can coexist, a blocky type and pearlitic type, as a result of the eutectoid reaction [20].

Fig. 6(a) shows FE-SEM images with different phases identified. Fig. 6(a) shows $M_{23}C_6$ blocky particles and Fig. 6(b) shows the magnified σ -phase region. Regarding the σ phase, Ramirez et al. [21] stated that this phase is present in both individual particles and as part of a binary eutectic within the γ -Co (fcc) matrix. In this work, the σ phase was found both as individual particles and precipitated over the $M_{23}C_6$ which may corroborate the established transformation relationship between these phases [7, 22]. However, for some of the fine lamellae cellular colonies that were observed at the grain boundaries or at adjacent region shown in Fig. 6(a), further investigation is required to establish their formation mechanism, because there was no clear evidence in the present work to suggest that they grew by a discontinuous reaction. These colonies may have otherwise originated from eutectoid precipitation, a mechanism that has already been proposed to explain lamellar formation in CoCrMo alloys [23].

Summary

An as-cast CoCrMo alloy fabricated by investment casting was found to have a dendritic microstructure of solid solution γ -Co with reinforcing phases precipitated in interdendritic spaces. The OM, FE-SEM, and EDS analyses showed that the phases present in the as-cast alloy were well identified as γ -Co, the σ phase, and $M_{23}C_6$ carbide, respectively. The $M_{23}C_6$ carbide phase presented a blocky-type particle morphology. The $M_{23}C_6$ -type carbides and intermetallic σ phase were detected at grain boundaries and in interdendritic zones. The nature of the precipitates indicates their creation as a result of a eutectic transformation, which is probably related to segregation of the components in front of the solidification front. Further investigation is required to establish their formation mechanism, because there was no clear evidence to affirm whether they grew by a discontinuous reaction or originated from a eutectoid reaction.

Acknowledgements

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