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Mechanical alloying of biocompatible Co–28Cr–6Mo alloy

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Abstract We report on an alternative route for the synthesis of crystalline Co–28Cr–6Mo alloy, which could be used for surgical implants. Co, Cr and Mo elemental powders, mixed in an adequate weight relation according to ISO Standard 58342-4 (ISO, 1996), were used for the mechanical alloying (MA) of nano-structured Co-alloy. The process was carried out at room temperature in a shaker mixer mill using hardened steel balls and vials as milling media, with a 1:8 ball:powder weight ratio. Crystalline structure characterization of milled powders was carried out by X-ray diffraction in order to analyze the phase transformations as a function of milling time. The aim of this work was to evaluate the alloying mechanism involved in the mechanical alloying of Co–28Cr–6Mo alloy. The evolution of the phase transformations with milling time is reported for each mixture. Results showed that the resultant alloy is a Co-alpha solid solution, successfully obtained by mechanical alloying after a total of 10 h of milling time: first Cr and Mo are mechanically prealloyed for 7 h, and then Co is mixed in for 3 h. In addition, different methods of premixing were studied. The particle size of the powders is reduced with increasing milling time, reaching about 5 μm at 10 h; a longer time promotes the formation of aggregates. The morphology and crystal structure of milled powders as a function of milling time were analyzed by scanning electron microscopy and XR diffraction.

1 Introduction

Of all implant materials, Co–28Cr–6Mo (nominal composition in wt%) alloy demonstrates the most useful balance of strength, fatigue and wear [1] along with resistance to corrosion [2].

A surgical implant, like a dental implant, must be both biologically acceptable to the host and able to withstand the mechanical demands placed upon it. At the present time, porous materials are being considered as a means of providing functional support for dental implants by tissue ingrowth. Co–28Cr–6Mo alloys satisfy the usual requirements for joint replacements; they exhibit good corrosion resistance. However, they tend to corrode over time, releasing Co, Cr and Mo ions into body fluids [3]. The wrought Co–Cr–Mo alloys exhibit superior mechanical and chemical properties compared with the cast alloys due to the finer grain size and more homogenous microstructure [4]. This alloy was chosen because it represents one of the current materials of choice for metallic implants based on over 40 years of clinical application in oral and orthopedic surgery [5]. Its status as a metallic material of choice results from its high strength and corrosion resistance. The excellent in vivo corrosion resistance is an important factor when considering this application since porous metals presents an increased surface area per unit of bulk volume [6].

Generally, this alloy can be easily produced by casting [7]. However, this method requires a special high temperature

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Table 1 Experimental method

Method	Pre-mixture (elements/milling time)	Added element/milling time	Final mixture/total milling time
A	–	–	Co–28Cr–6Mo/1, 3, 5, 7 and 9 h
B	Co–Cr/3 h	Mo/1, 3, 5, 7 and 9 h	Co–28Cr–6Mo/4, 6, 8, 10 and 12 h
C	Co–Mo/3 h	Cr/9 h	Co–28Cr–6Mo/12 h
D	Cr–Mo/7 h	Co/1, 3 and 5 h	Co–28Cr–6Mo/8, 10 and 12 h

furnace, and the final product usually contains large irregular hard particles with interdendritic carbides, which are unwanted impurity phases that cause brittleness [8]. Other methods, like the gravity sintering fabrication technique and metal injection molding, have been developed for Co–Cr–Mo alloy production. This process allows for control of the pore structure, enabling ingrowth of either bone or fibrous tissue [9].

Powder metallurgy and particulate materials processing (abbreviated as P/M^2) refer to a variety of techniques to fabricate engineered products using principles ranging from materials synthesis to industrial engineering. The P/M^2 technologies create particles, control their attributes, consolidate the particles into shapes and heat the shapes to a temperature where the particles bond into a strong product [10]. It is an attractive method because enable to form net shaping bodies, it produces an intrinsic level of porosity, metallurgical structures are usually fine and isotropic, and non-equilibrium compositions are possible [11].

Mechanical alloying (MA) is emerging as an effective, economical and versatile way to produce nanometer-sized powder materials. This process is based on chemical reactions mechanically activated by high-energy ball milling, and it has been successfully applied to obtain different alloys [12, 13]. The Co–28Cr–6Mo powder can be used to produce surgical implants [14] or to obtain composites in order to increase mechanical strength [15].

This work describes the results of experiments, using mechanical alloying as a P/M^2 technique to produce particulate materials, which were performed to examine the possibility of producing Co–28Cr–6Mo (nominal composition in wt%) alloy for surgical implants. It is important to note that in the bibliography consulted, the authors did not find any information about the mechanical alloying of Co base alloys, so we are proposing to use the mechanical alloying technique in order to study the mechanism of mechanical alloying and to modify the properties of the alloy.

2 Experimental part

Co (Sigma–Aldrich, >99.9%), Cr (Sigma–Aldrich, >99.9%) and Mo (Sigma–Aldrich, >99.9%) elemental powders were used as precursors. The raw materials were mixed in the appropriated weight ratio according to the ISO 58342-4 [16]. A total amount of 3.9 g of the powder mixtures, as well as 6 hardened steel balls of 12.7 mm in diameter, were loaded into a steel vial; the mechanical alloying process was carried out at room temperature in air using a shaker mixer/mill machine. The powder-to-ball weight ratio was 1:8. To prevent excessive overheating of the vials, all experiments were carried out by means of cycles of 60 min of milling and 15 min of repose. The maximal milling time tested was 12 h. In order to understand the alloying mechanism, four methods to obtain the Co–28Cr–6Mo alloy were evaluated. In the first method (A), elemental powders of Co, Cr and Mo were mixed together and milled for different times. The other three cases (methods B, C and D) consisted of premixing two of the alloy elements, and the product was added and milled with the third metallic element for different times. The experiments performed are shown in Table 1.

X-ray diffraction (XRD) of the powders was used to follow the phase transformations during the milling process. Samples obtained at different milling times were characterized at room temperature using a Philips X'Pert diffractometer. Diffraction parameters were 2 ranging from 30 to 90° with a step size of 0.02 (2). Cu K_α ($\lambda =$ 1.5418 A) radiation was used in all experiments.

Rietveld refinement was performed on the X ray patterns [17]. This method takes into account all the information collected in a pattern, and it uses a least squares approach to refine a theoretical line profile until it matches the measured profile. It was used to calculate the cell parameter. X-ray data refinement of the patterns was performed using the program MAUD [18].

3 Results and discussion

X-ray powder patterns for a sequence of different milling times for mixed Co–28Cr–6Mo according to method A are shown in Fig. 1. In this method the three elemental powders, Co, Cr and Mo, were mixed together and milled for different times. As expected, the pattern of the powder mixture at time 0 shows only sharp peaks corresponding to the starting metal mixture: Co, Cr and Mo. A mixture of different crystalline structures was found: Co-α (ICDS 76632, BCC), Co-ε (ICDS 76633, HC), a single phase of Cr

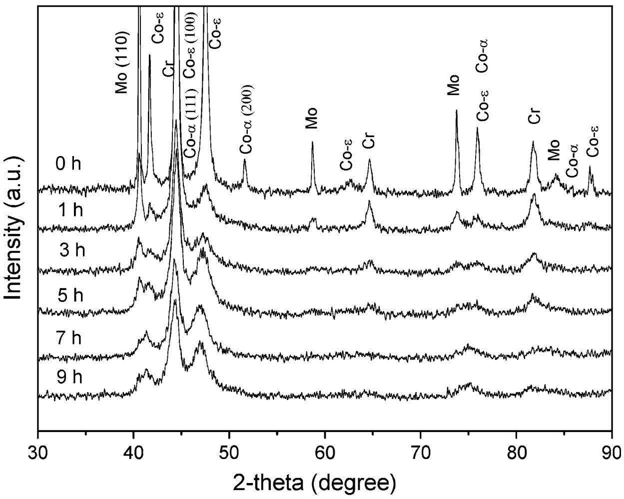

Fig. 1 XRD patterns of powder milled over different milling times (method A)

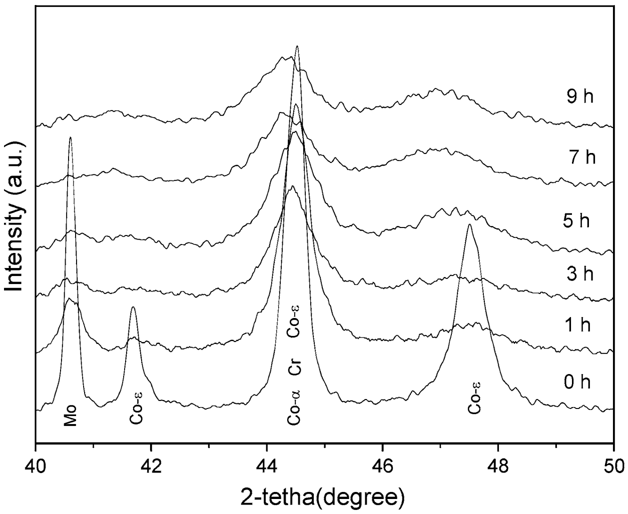

Fig. 2 Amplification of XRD patterns of powder milled during different time periods

(ICDS 44731, FCC) and a cubic phase of Mo (ICDS 76279, FCC).

After the first stage of milling (1 h) the intensity of the (200) reflection peak of Co-α ($2\theta = 51.7°$) dramatically decreased, while the (100) peak of the same structure ($2\theta = 44.41°$) increased. Additionally, an important reduction in the peak intensity of Co-ε (100) occurred at $2\theta = \sim 41°$. After 5 h of milling, it is apparent that the peaks corresponding to Cr disappeared completely, and no other peaks appeared. By observing the increase of the (100) reflection of Co-α, the diminution of the Mo peaks and the disappearance of the Cr peaks, we can say that this event might be due to the partially integration of Mo and Cr into the Co-α phase by deforming it and packing the (111) plane. After deformation of the cubic phase of Co, it tends to the hexagonal structure until saturation. The presence of reflection peaks of Co-ε can be observed in the powder mixed for 9 h. In order to confirm this observation, Rietveld [17] refinement was performed on the XRD patterns and used to calculate the cell parameter of the Co-α phase.

As milling time increased, a peak profile broadening occurred, probably as a result of a particle size refinement and bulk plastic deformation causing the cell parameters to change. At the same time, a peak displacement toward lower 2θ angles can be observed for the mean peak at ~44.5° associated with a distortion of the crystal structure and a variation in the cell parameter of Co, probably as a consequence of lattice strain promoted by the chromium and molybdenum substitution of cobalt in the cubic structure due to the plastic deformation of the cell, especially after 5 h of milling. Figure 2 presents a magnification of the 2θ angles between 40 and 50° for different milling times. In this figure, we can also observe the split of the main peak due to the displacement of just one of the superimposed reflections.

The cell parameters for Co-alpha were also calculated, and a consistent increase in this parameter from 3.5447 to 3.66561 nm with increasing milling time was found from 0 and to 9 h of milling, respectively, confirming the partial insertion hypothesis of some atoms of Mo (2.01 Å atomic radii) and Cr (Co 1.67 Å atomic radii) into the Co-beta phase (1.85 Å atomic radii).

In order to confirm the deformation of the particles associated with the RX diffraction pattern, Fig. 3 presents the SEM micrographs of Co–28Cr–6Mo mixed for different milling times, and changes in the particle shape, from rounded to flaked, and in the surface condition, from rugged to smooth, are associated with the level of deformation of the particles depending on the milling time. This can help to justify the changes in the relative intensities of the peaks in the diffraction pattern.

The X-ray diffraction patterns of the powders milled for different times using method B are shown in Fig. 4. In this method, Co and Cr were first prealloyed for 3 h, and then Mo was added and milled for different times from 1 to 9 h. In Fig. 4 it is apparent that the most important peak of Mo ($2\theta \sim 40.56°$) never disappears. It is important to remark that this method does not provide a final solid solution because the Mo is out of the solid-solution.

Figure 5 presents the X-ray diffraction pattern of the powder milled for 12 h using method C. In this method, Co and Mo were first prealloyed for 3 h, and then Cr was added and milled for 9 h. For this method we can clearly observe that there is no solid solution between the elemental powders because after 9 h of milling time the presence of the initial precursors can still be observed,

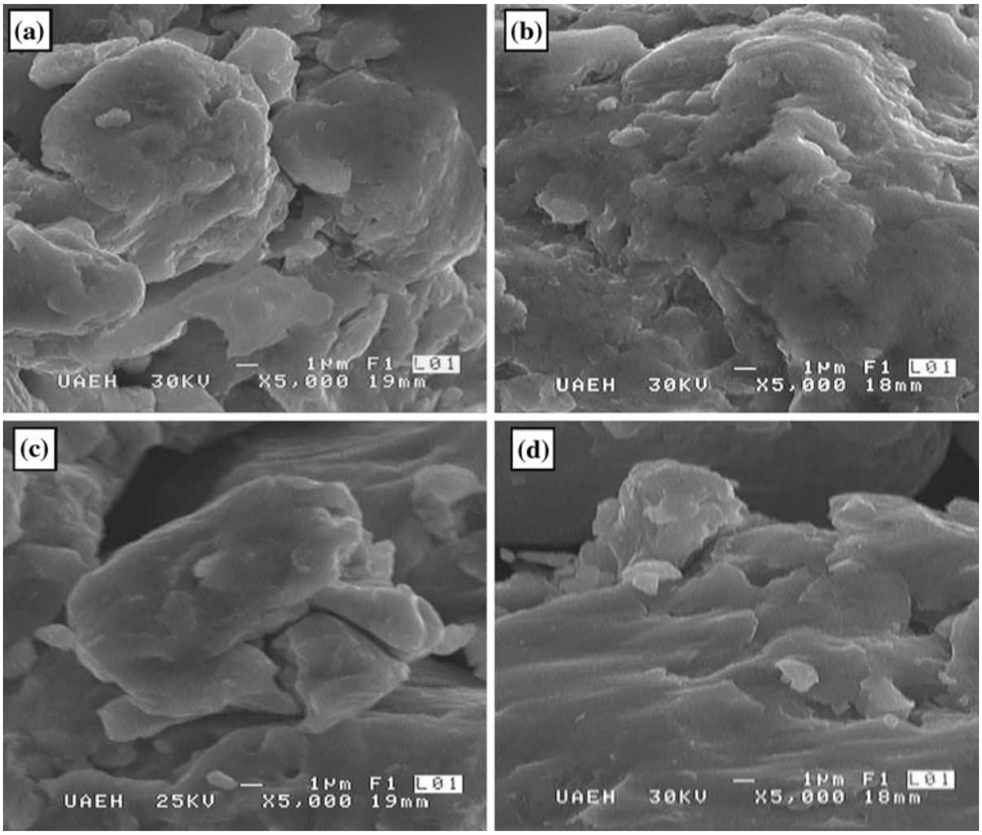

Fig. 3 SEM micrographs of powder mixtures milled at different times: Cr + Mo + Cr at **a** 1 h, **b** 3 h, **c** 7 h and **d** 9 h

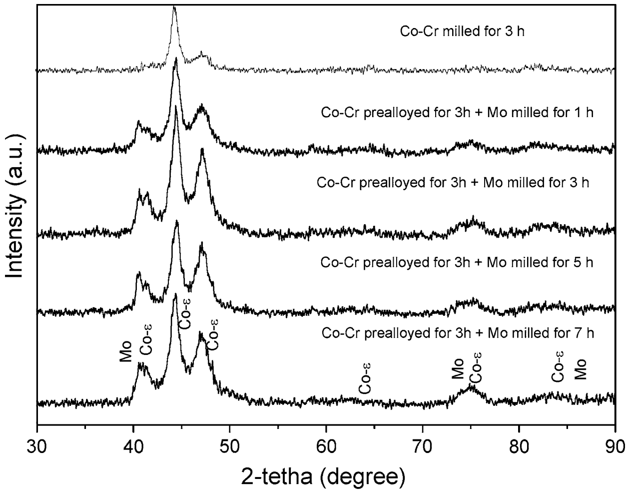

Fig. 4 XRD patterns of powder milled at different times (method B)

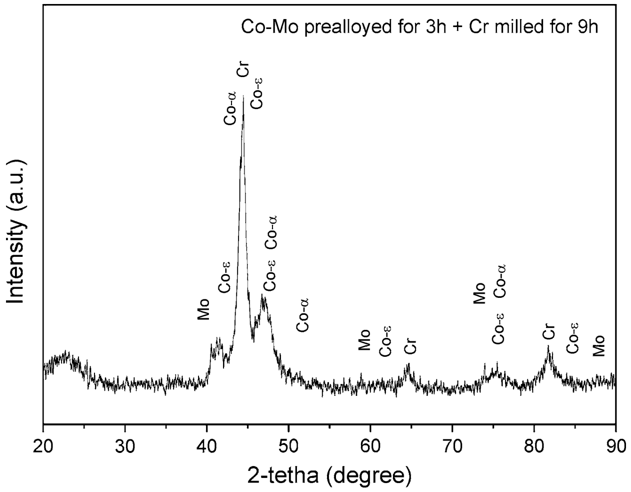

Fig. 5 XRD patterns of powder milled for 12 h (method C)

although with changes in their relative intensities due to the deformation observed using the previous methods.

A different behavior is observed when the order of precursors added is modified; for method D, Cr and Mo were prealloyed for 7 h, and then Co was added and milled for different times from 1 to 5 h. X-ray diffraction patterns for this method are shown in Fig. 6.

In the X-ray patterns shown in Fig. 6, all the peaks tend to form only one peak, which could be related to the mixed Co-based alloy (or solid solution) with small crystallite size, whose cell parameter is on 3.6 Å. A peak displacement toward the left can be observed, which is in accordance with the presence of a mixture between the cubic (α) and hexagonal phases (ε) of Co.

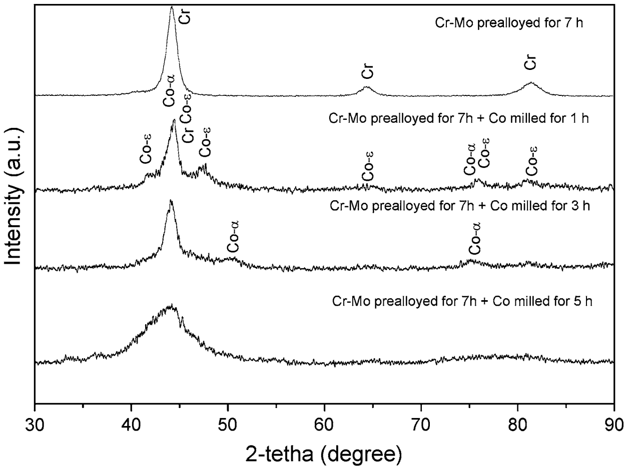

Fig. 6 XRD patterns of powder milled at different times (method D)

In the X-ray patterns for method D for milling times up to 9 h, the presence of reflections peaks of Mo and Cr are not detectable. Thus, we can conclude that there is a solid solution between all the elements mixed. For the application desired, this would be the best option. This method offers the best results.

The variation of cell parameter with milling time was also calculated for Co-α when the mixture was synthesized by method D. Like method A, there is an increase in the cell parameter from 3.5472 to 3.6291 Å for 0 and 12 h of milling time, respectively. This behavior could be due to the insertion of atoms of Mo and Cr into the Co-α phase in order to form a solid solution (Co–28Cr–6Mo alloy).

In order to understand the formation of a complete solid solution using method D, X-ray diffraction patterns for the prealloy of Cr–Mo were obtained and are shown in Fig. 7.

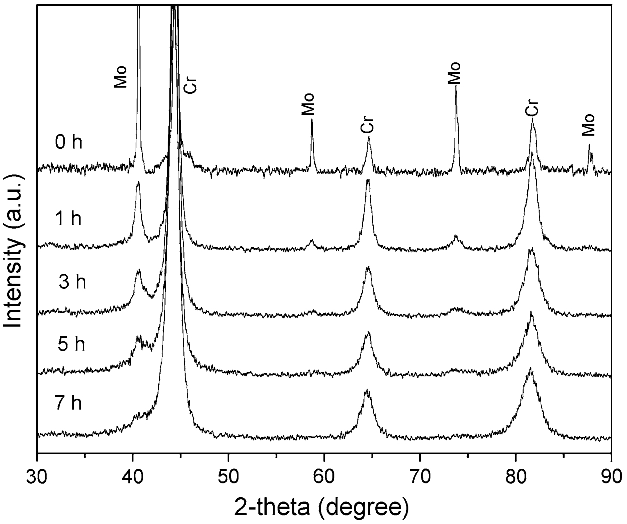

Fig. 7 XRD patterns of Cr–Mo milled during different time periods (method D)

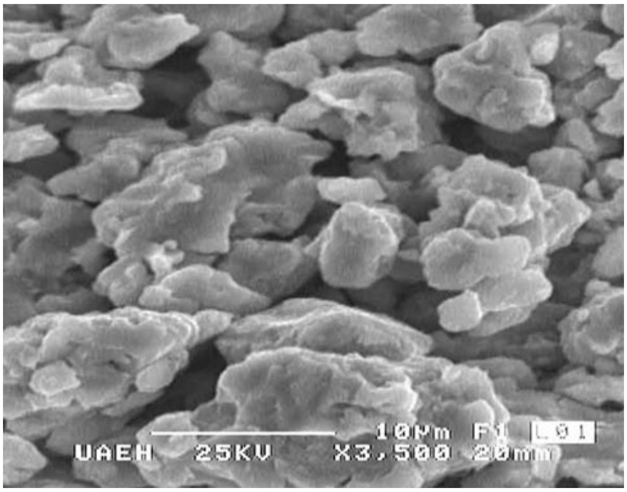

Fig. 8 SEM micrographs of the final powder obtained by method D: prealloyed Cr–Mo for 7 h; then Co was added and milled for 5 h

In Fig. 7 the peak corresponding to Mo diminishes in intensity until it nearly disappears at 7 h of milling, while the peak of Cr remains constant in relative intensity. During milling, Cr peaks remain in the same position, so the Mo atoms are probably inserted into the Cr cell but without affecting its cell parameter; this is in accordance with the total solubility of this element at the concentrations studied. Once the Cr–Mo alloy is obtained, when it is mixed and milled with Mo, a solid solution is formed, which is presented in Fig. 6.

Finally, Fig. 8 shows the SEM micrographs of the solid solution of Co–28Cr–6Mo obtained by method D. In this micrograph the homogenous particles are rounded, with a particle size between 1 and 15 μm.

4 Conclusions

Results obtained show that it is possible to produce a solid solution or alloy with the composition Co–28Cr–6Mo by the mechanical alloying of elemental metallic powders. It was found that there is an important relationship between the order of mixing and milling and the resulting alloy, which may be applied to other similar metallic systems. The successful process to obtain the desired alloy involved making the prealloy of Cr–Mo using high energy milling for 7 h and then mixing it with Co and milling for 3 h. The latter step causes the solid state diffusion of the elements, which depends on the atomic sizes and the structural affinity between the precursor elements. Other methods were studied, but none resulted in the desired alloy.

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