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Structural analysis and magnetic properties of solid solutions of Co–Cr system obtained by mechanical alloying

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ABSTRACT

In this paper, a systematic study on the structural and magnetic properties of $\text{Co}_{100-x}\text{Cr}_x$ alloys ($0 < x < 100$, $\Delta x = 10$) obtained by mechanical alloying is presented. Co and Cr elemental powders were used as precursors, and mixed in an adequate weight ratio to obtain $\text{Co}_{1-x}\text{Cr}_x$ ($0 < x < 100$, $\Delta x = 10$). Mechanical milling was carried out at room temperature in a shaker mixer mill using vials and balls of hardened steel as the milling media with a ball:powder weight ratio of 10:1. The mixtures were milled for 7 h. Results shown that after 7 h of milling time, solid solutions based on Co-hcp, Co-fcc and Cr-bcc structures were obtained. The saturation polarization indicated a maximum value of 1.17 T ($144 \text{ Am}^2/\text{kg}$) for the $\text{Co}_{90}\text{Cr}_{10}$, which decreases with the increasing of the Cr content up to $x = 80$, as a consequence of the dilution effect of the magnetic moment which is caused by the Cr content and by the competition between ferromagnetic and antiferromagnetic exchange interactions. The coercivity increases up to 34 kA/m (435 Oe) for $\text{Co}_{40}\text{Cr}_{60}$. For Cr rich compositions, it is observed an important decrease reaching 21 kA/m (272 Oe) for $\text{Co}_{10}\text{Cr}_{90}$, it is related to the grain size and the structural change. Besides, the magnetic anisotropy constant was determined for each composition. Magnetic thermogravimetric analysis allowed to obtain Curie temperatures corresponding to the formation of hcp-Co(Cr) and fcc-Co(Cr) solid solutions.

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1. Introduction

Cobalt-based alloys have been in use since 1907 when Elwood Haynes obtained the first patent on cobalt–chromium compositions [1]. Following this patent, Co–Cr alloys have been of great importance because of their excellent mechanical properties such as wear and corrosion resistance, along with their excellent biocompatibility which permits their use in biomedical devices such as dental and surgical implants [2]. Co–Cr alloys are also the base composition for many steels, high temperature alloys, and magnetic materials [3]. As thin films, these alloys are widely used as magnetic recording media in computer hard discs [4]. Pure cobalt has an hcp crystal structure (ϵ -cobalt) at room temperature that transforms to the fcc structure (α -cobalt) upon heating at 673 K. The wear resistance of cobalt alloys is partially due to a structural transformation that these alloys undergo during mechanical deformation. This transformation can be explained in terms of the metastability of the Co-fcc phase at room temperature which becomes unstable when an external mechanical force or thermal energy is introduced [5]. In addition,

this transformation depends upon alloying elements, such as chromium, molybdenum, and tungsten, that increase the transformation temperature and therefore enhance the stability of the hcp structure [6], whereas elements such as nickel and iron suppress the transformation temperature, yielding stable fcc structures [6,7].

Mechanical alloying (MA) is a material synthesis method that creates a large number of crystal defects and stacking faults due to the severe plastic deformation that results from the high energy supplied to the system [8,9]. This enables structural changes such as allotropic transformations [10–19] that normally only occur at high temperatures [14]. In addition, the magnetic properties of mechanically alloyed materials can be notably influenced by the MA process due to the stresses and defects that are generated during the milling process, together with a consequent grain size reduction that results in an increase of the magnetization and coercivity [20,21]. The aim of this work is to present a systematic study of the crystal structure and magnetic properties of the $\text{Co}_{100-x}\text{Cr}_x$ alloy system with $10 \leq x \leq 90$ and $\Delta x = 10$ synthesized by mechanical alloying, MA.

2. Experimental details

Elemental cobalt powder (Sigma-Aldrich, > 99.9%), with a mean particle size (D_{50}) of 10 μm and elemental chromium

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powder (Sigma-Aldrich, > 99.9%) with a mean particle size (D_{50}) of 30 μm were used as precursors. The elemental powders (Co and Cr) were mixed in the appropriate weight ratio to obtain $\text{Co}_{100-x}\text{Cr}_x$ alloys, where x varies from 10 to 90 with $\Delta x = 10$. A total amount of 5 g of the starting mixtures together with 6 hardened steel balls of 12.7 in diameter mm were loaded into a steel vial with 64.6 cm^3 of volume and milled for 7 h in a high energy ball miller. Hardened steel balls were used as milling media because in several works it have demonstrated that provide enough energy to promote solid state transformation during high energy ball mill in metallic systems [8–24].

The milling process was carried on at room temperature in argon atmosphere using a SPEX 8000D shaker mill. The ball-to-powder weight ratio was 10:1. To prevent excessive overheating of the vials, all experiments were performed using cycles of 90 min of milling followed by 20 min of rest, until achieving 420 min (7 h) of milling time.

The milled powders for different compositions ($\text{Co}_{100-x}\text{Cr}_x$) were characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer, in order to know the phase transformations as a function of the composition and milling time. The diffraction parameters were collected with 2θ ranging from 35° to 120° with a step size of 0.02 and $\text{Co } K_\alpha$ ($\lambda = 1.7889 \text{ \AA}$) radiation. Morphological characterization was performed using a Leica Stereoscan 440 electron microscope operated at 20 kV. The magnetic properties of the milled powders, specifically the saturation polarization (J_s) and coercivity (H_C), were obtained from magnetic hysteresis curves, using a LDJ9600 vibrating magnetometer (VSM) with a maximum applied field of 1.2 MA/m (15 kOe). The magnetic measurements were made on compacted powders at 6.5 g/cm^3 of green density; these compacts were prepared using 0.2 g of each milled powder and pressed into a cylindrical die of 5 mm in diameter. The magnetocrystalline anisotropy was calculated using the collected data from magnetic hysteresis loop, such as is described in the results. In addition, the Curie temperature of the alloys was determined using the magnetic thermogravimetric technique on a TGA/SDTA 851e Mettler-Toledo. These experiments were performed under argon atmosphere at temperatures in the range from 600 K to 1500 K.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of $\text{Co}_{100-x}\text{Cr}_x$ ($10 < x < 90$, $\Delta x = 10$), as a function of the chromium content (x , percentage

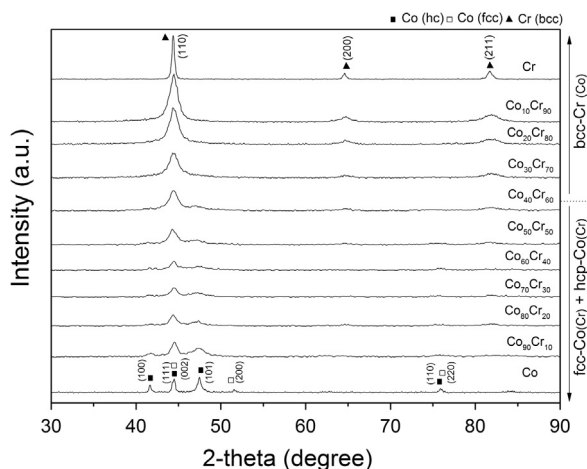


Fig. 1. XRD patterns for $\text{Co}_{100-x}\text{Cr}_x$ ($10 < x < 90$, $\Delta x = 10$) milled for 7 h.

in weight) milled for 7 h. The XRD patterns of the elemental powders, Co and Cr without milling ($x = 0$ and 100% respectively), also presented in this figure, confirm the presence of cobalt with two phases (Co-hcp and Co-fcc) and chromium with one phase (Cr-bcc). After 7 h of milling time for the $\text{Co}_{90}\text{Cr}_{10}$ alloy, the diffusion of Cr into the Co structure has led to the formation of Co(Cr) solid solution, and for this reason, no Cr-bcc reflection peaks are observed in the XDR pattern for this composition. In the XRD of $\text{Co}_{90}\text{Cr}_{10}$ it can be observed the reflection peaks corresponding to fcc-Co phase. Besides, it is evident that the allotropic transformation of Co from hcp to fcc has partially occurred, due to the unique peak of the fcc phase, that does not overlap with any hcp peak, has diminished. The presence of hcp-Co phase can be clearly seen in elemental Co ($x = 0$) confirmed by the presence of the reflection (1 0 2) and (1 0 3) peaks. It is know that this allotropic transformation occurs when the cobalt is subjected to an external mechanical or thermal energy, as a consequence of the accumulation of stacking faults induced during the mechanical milling [9–22]. For this composition a mixture of fcc and hcp is present.

Similar behavior is observed for $\text{Co}_{80}\text{Cr}_{20}$, where Cr peaks have vanished and only it can be observed reflection planes corresponding to a mixture of Co-fcc and Co-hcp phases. However, plane (2 0 0) of the fcc phase appears clearer in this composition, which confirms the preponderance of Co(Cr) with fcc structure. Same case is observed for compositions with x from 0 to 60, in these cases there is a mixture of allotropic phases of Co-fcc and Co-hcp where Cr is inside of both Co structures.

For $\text{Co}_{30}\text{Cr}_{70}$, it can be observed that reflection peaks that belong to cobalt disappear completely, and only peaks corresponding to bcc chromium are observed. This suggests a complete diffusion of cobalt atoms into the chromium structure and thus the formation of the Cr(Co) solid solution with bcc phase. The same behavior is observed for $\text{Co}_{20}\text{Cr}_{80}$ and $\text{Co}_{10}\text{Cr}_{90}$, accompanied by a diminution in the broadening of peaks, which is related to the refinement of the microstructure and the presence of microstrain caused by the introduction of the crystal defects during the mechanical alloying. In this case, the increase of the relative intensity of the peaks is due to the increase of the chromium content.

Besides, the crystal size for each composition was calculated using the Williamson-Hall method, following:

$$B_s \cos \theta = 2\varepsilon \sin \theta + \frac{K\lambda}{D} \tag{1}$$

where B_s is the full-width at half the maximum of the diffraction peak, θ is the Bragg angle, ε is the internal microstrain, λ is the wavelength of the X-ray, D is the crystallite size, K is a constant. B_s can be given as $B_s^2 = B_m^2 - B_c^2$. Where B_s is the width at half the maximum of the silicon powder peak used for calibration and B_m is the evaluated width. In this method $B_s \cos \theta$ is plotted against $2\sin \theta$, ε is the slope and $K\lambda/D$ is the interception [23].

The outcome of the evaluation of crystal size is shown in Fig. 2. In this Figure it is observed a progressive decrease of the crystallite size from 34.49 nm to 10.17 nm for 10 and 70 in wt. of Cr respectively, confirming the stabilization of the Co-fcc phase, where Cr atoms are packet in fcc structure increasing the atomic packing factor (APF), and helping to induce a diminution in the lattice parameters, and also, to produce severe plastic deformations together with accumulation of large amount of structural defects during the milling process. For compositions higher than 70 in wt. of Cr, it is observed an increase of the crystal size, up to 28.89 nm for 90 in wt. of Cr, this can be associated to the presence of Cr-bcc phase and the incorporation of a smaller atom, such as substituting atoms of Co (metallic radii 1.25 \AA) for Cr (metallic radii 1.29 \AA) into the Cr-bcc ($Pm-3m$ structure), whereas the

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