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Journal of Alloys and Compounds 434–435 (2007) 477–480

Journal of ALLOYS AND COMPOUNDS

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Structural and microstructural study of Fe–31Cr–12Co mixture prepared by ball milling

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Abstract

Nanostructured Fe–31Cr–12Co mixture was prepared by high energy ball milling (BM) of elemental Fe, Cr and Co powders. The obtained powders were characterized by X-rays diffraction (XRD) using Rietveld's method. The BM leads to the allotropic transformation of Co from FCC to HCP form during the first hour of milling and the formation of a disordered Fe(Cr, Co) solid solution (SS) with BCC structure after 12 h of milling. The microstructural analysis using the profile fitting shows the nanostructured character of the obtained powders. The diffraction line broadening of the SS is Miller indices dependent and is a consequence of anisotropy in size and strains.

Keywords: Nanostructured materials; Mechanical alloying; Anisotropy

1. Introduction

Nanocrystalline materials have attracted considerable scientific interest because of their new physical, chemical and mechanical properties that are normally attributed to the grain size which is in the nanometer range. BM is one of the techniques which is widely used to synthesize nanostructured powdered materials. This technique is a non-equilibrium process resulting in solid state alloying beyond equilibrium solubility limit and the mechanisms involved in the formation of a broad range of alloys depend on the plastic deformations and hence defects accumulated upon milling. During the repeated severe deformations a continuous change in the shape of the powder particles and a degree of disorder in the lattice occur.

In this study the Fe–31Cr–12Co mixture is synthesized by BM. The XRD patterns of the obtained powders were analyzed using Rietveld refinement. This method, well adapted for the broadening of the diffraction peaks, gives more detailed information on the shape and size of the coherent domains, the microstrains and also the quantitative evaluation of the phases.

2. Experimental

Powder mixture of Fe (99.95 %, 2 μm), Cr and Co (99.90%, −325 mesh) were ball-milled for different times ranged from 1 to 48 h under argon atmosphere, using stainless steel vials and balls in a planetary ball mill type Fritsch Pulverisette 7 at a rotation speed of 500 rpm. The powder to ball weight ratio was 1:35. The progress of phase transformation in the powder mixtures with milling time was followed by XRD using a Siemens D500 diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm). The XRD patterns are fitted using the Maud program [1] based on the Rietveld method [2,3] combined with Fourier analysis. The average estimation of the microstructural parameters (crystallite size and microstrains) was derived from isotropic model [4]. When the profiles broadening are Miller indices $[h\,k\,l]$ dependent, the crystallite size, $\langle L\rangle$, and microstrain, $\langle\sigma^2\rangle^{1/2}$, are evaluated from anisotropic model based on the Popa rules [5]. All the parameters are refined by an iterative least-square minimization.

3. Results

Before milling (Fig. 1), the X-ray diffractogram shows the BCC α-Fe, BCC-Cr and both FCC and HCP Co peaks with lattice parameters $a_{\mathrm{Fe}} = 0.2869$ nm, $a_{\mathrm{Cr}} = 0.2887$ nm, $a_{\mathrm{CoFCC}} = 0.3550$ nm, $a_{\mathrm{CoHCP}} = 0.2500$ nm and $c_{\mathrm{CoHCP}} = 0.4140$ nm, respectively. After 1 h of milling (Fig. 2), the mixture pattern reveals the disappearance of FCC Co peaks and the increase of the intensity of the HCP ones. This can evidently be due to the allotropic transformation of Co from FCC to HCP structure.

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doi:10.1016/j.jallcom.2006.08.111

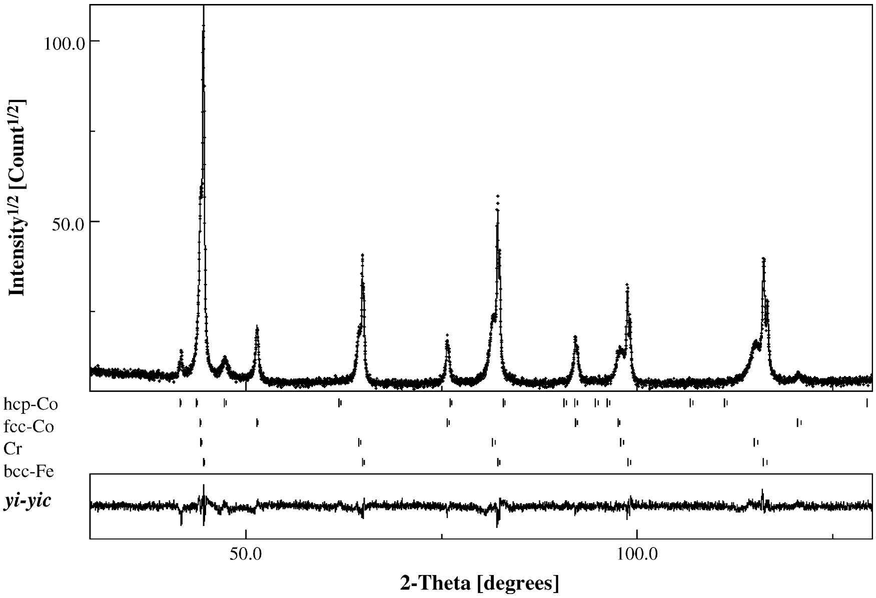

Fig. 1. Rietveld refinement for XRD pattern of Fe–31Cr–12Co mixture before milling. The difference between experimental (dots) and calculated (full line) patterns is given below.

Since FCC-Co is a metastable phase at room temperature, it becomes unstable when external mechanical and thermal energy is introduced. The lattice parameters of all the phases are nearly unchanged ($a_{\mathrm{Fe}} = 0.2870$ nm, $a_{\mathrm{Cr}} = 0.2882$ nm, $a_{\mathrm{CoHCP}} = 0.2505$ nm, $c_{\mathrm{CoHCP}} = 0.4116$ nm). After 6h of milling (Fig. 3), the best Rietveld refinement is obtained when the model consists of two phases with spherical grains: BCC α-Fe and BCC-Cr with lattice parameters $a_1 = 0.2873$ nm and $a_2 = 0.2880$ nm, respectively. Indeed, it is important to emphasize the very small difference of lattice parameters but the refinement by means of a single BCC component does not allow to well describe the experimental pattern. However, after 12 h of milling (Fig. 4), the XRD pattern is fitted with a single BCC phase having a lattice parameter close to $a = 0.2877$ nm. Hence, the disappearance of the elemental powders peaks is correlated to the formation of a disordered Fe(Cr, Co) SS with BCC structure. The broadening of the Bragg peaks is due to the reduction of the crystallite size and the increase of microstrains upon milling.

Fig. 5 displays the XRD pattern of the Fe–31Cr–12Co milled during 24 h and analyzed with the isotropic (Fig. 5a) and anisotropic (Fig. 5b) models. It is clear that the best Rietveld refinement is obtained with the anisotropic model suggesting an anisotropy distribution of microstructural parameters. The crystallite size, $\langle L\rangle$, and microstrain, $\langle\sigma^2\rangle^{1/2}$, for different $[h\,k\,l]$ directions versus milling time are plotted in (Fig. 6). The $\langle L_{110}\rangle$

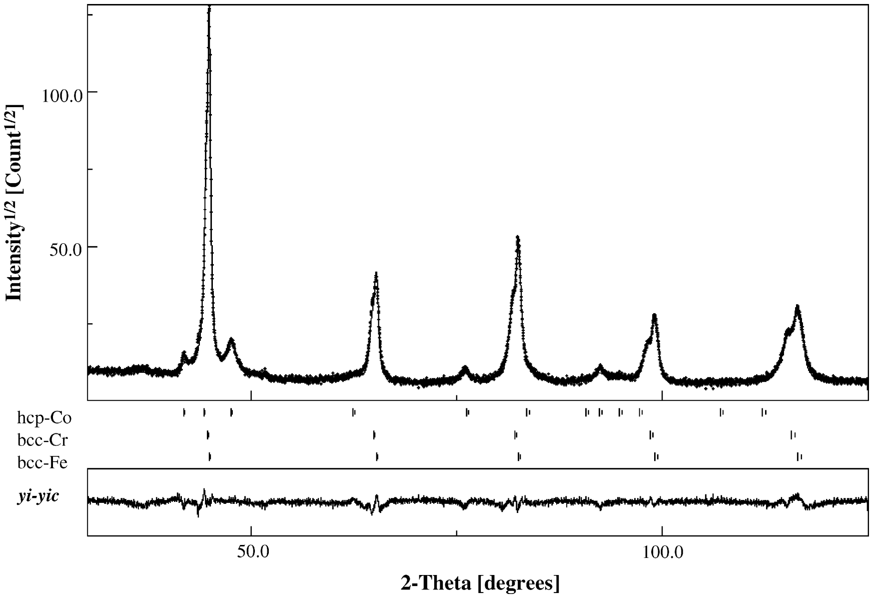

Fig. 2. Rietveld refinement for XRD pattern of Fe–31Cr–12Co mixture after 1 h of milling.

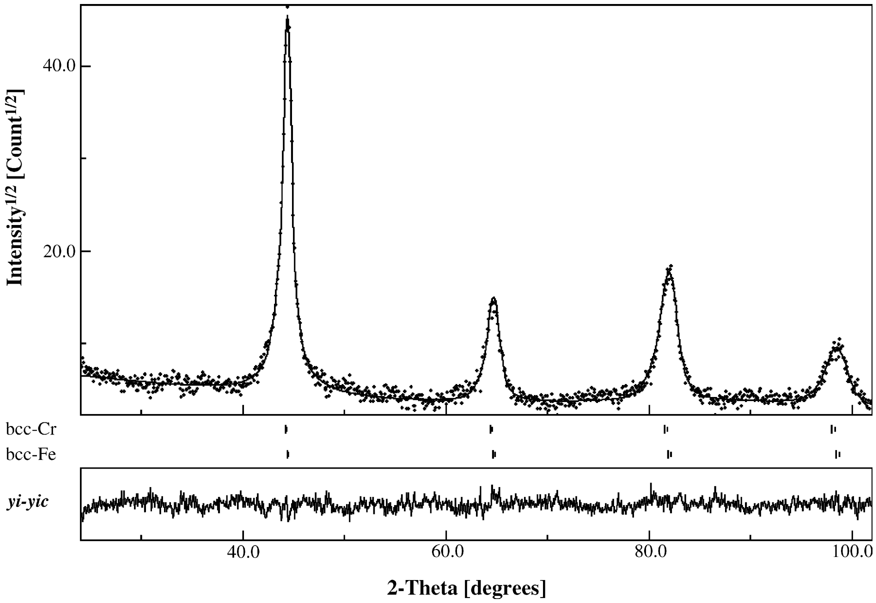

Fig. 3. Rietveld refinement for XRD pattern of Fe–31Cr–12Co mixture milled for 6 h.

is found to decrease gradually between 12 and 24 h of milling then drastically for further milling time (Fig. 6a), while along the [2 0 0] and [3 1 0] directions, $\langle L\rangle$ decreases linearly with milling time. The final value reached after 48 h of milling, $\langle L\rangle = 5 \pm 1$ nm, is approximately the same for the all directions. This can be explained by the fact that the coherent diffraction domains become equiaxial with further milling time. However, the lattice microstrains are found to exhibit significantly anisotropy behaviour (Fig. 6b). In effect, the lattice microstrains increase with milling time with a value much larger along [2 0 0] direction than those along other directions [1 1 0] and [3 1 0]. This may be due to the elastic moduli of Fe which is equal to 219 and 153 GPa along the [1 1 0] and [3 1 0] directions, respectively, while it is smaller (about 130 GPa) along the [2 0 0] direction [6]. This leads thus to preferential distortions along [2 0 0] direction which needs less energy to introduce defects in the crystallite lattice.

From the results obtained by a careful analysis of Bragg peaks of X-ray patterns, it can be thus concluded that the complete dissolution of Cr and Co atoms into Fe matrix within 12 h of milling gives rise to the formation of a BCC Fe(Cr, Co) SS. Because of the anisotropic elastic moduli of Fe, the excessive milling leads to anisotropic internal strains as clearly revealed by the *h k l*-dependent X-rays profiles.

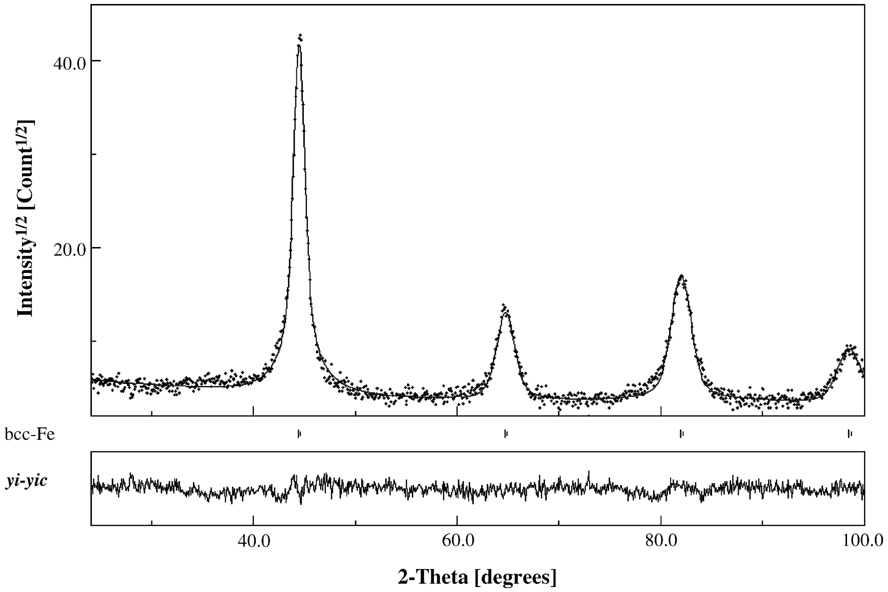

Fig. 4. Rietveld refinement for XRD pattern of Fe–31Cr–12Co mixture after 12 h of milling.

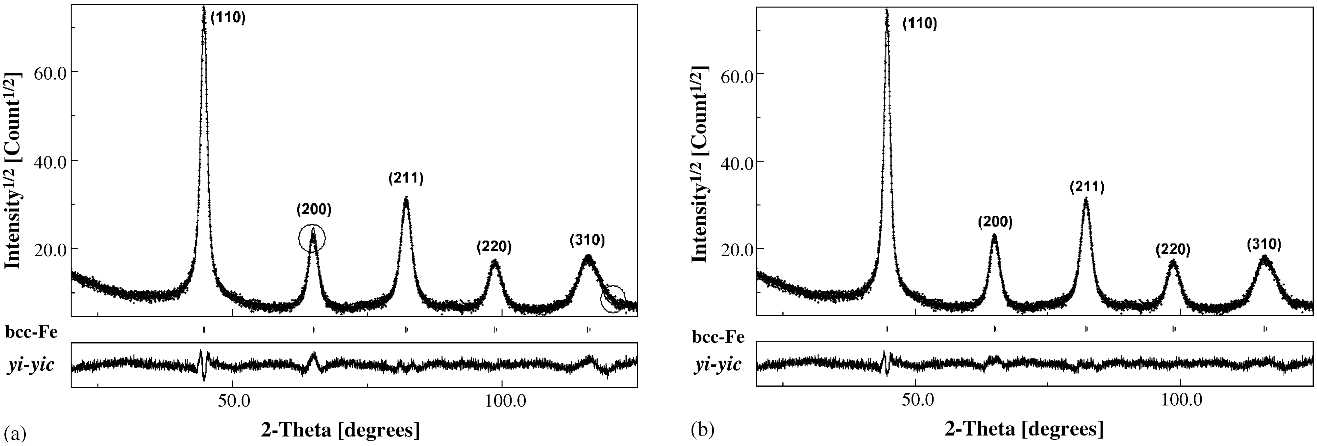

Fig. 5. Rietveld refinement for XRD pattern of Fe–31Cr–12Co mixture milled for 24 h using isotropic (a) and anisotropic (b) models.

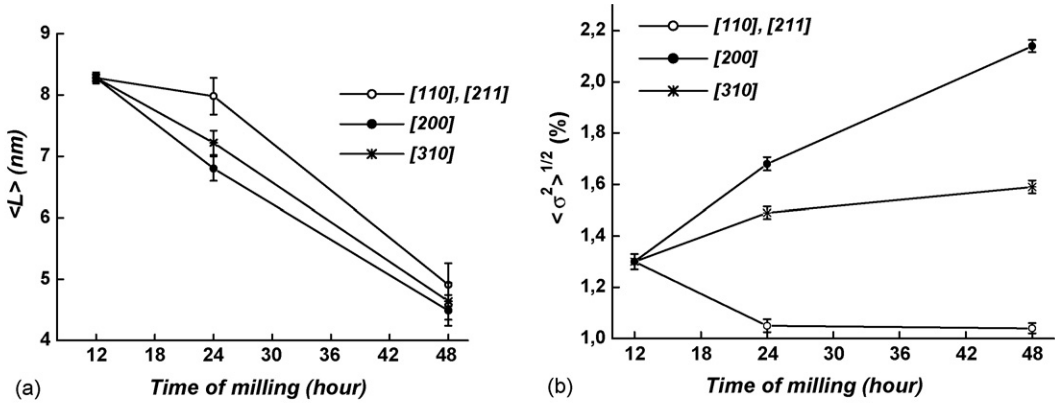

Fig. 6. Milling time dependence of the mean crystallite size (a) and microstrain (b) for different [*h k l*] directions.

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