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J. Mimault, O. Proux, R. Elkalkouli, T. Girardeau. On the Homogeneity of Single Phase Obtained in Metallic Systems with Positive Heat of Mixing. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-1025-C2-1026. 10.1051/jp4:19972127 . jpa-00255186

HAL Id: jpa-00255186

<https://hal.science/jpa-00255186>

Submitted on 1 Jan 1997

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On the Homogeneity of Single Phase Obtained in Metallic Systems with Positive Heat of Mixing

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Abstract. X-ray diffraction and absorption spectroscopy measurements have been performed in metastable solid materials obtained by mechanical attrition or codeposition process of immiscible systems in view to investigate the short and long range order obtained inside these solutions. Firstly, experiments show that $\text{Cu}_{80}\text{Fe}_{10}\text{Co}_{10}$ milled powders are in quasi perfect solid solution ; this result arouses interest because giant magnetoresistance is more readily controlled by decomposition of a supersaturated solid solution. Secondly, codeposition of $\text{Cu}_{50}\text{Mo}_{50}$ presents a long range order typical of a well-defined cristalline structure whereas the short range order appears very disordered.

1. Introduction

The present paper describes the structure (long and local range order) of some original materials generated from binary or ternary systems, chosen for their positive heat of mixing. Here, we focus attention on two examples where the microstructures were obtained by using two very different alloying techniques which have received a large development during the last decades : a mechanical alloying process applied to a mixed Cu/Fe/Co powder and attempted to synthesize a granular material, physically characterized by a giant magnetoresistance effect and a physical vapor deposition process used on a Cu/Mo mixed target with the aim to obtain a protective coating which improves the tribological performances.

2. Experimental

Using Cu $K\alpha$ radiation, long range order is revealed by X-ray diffraction patterns, obtained either by means of a Siemens θ -2 θ powder diffractometer in the case of the mechanically alloyed samples or with an home-made set-up X ray diffractometer used in a dispersed mode and asymmetric geometry [1] for thin deposited films ; a fixed and grazing incidence $\alpha=2^\circ$ improves the diffusion efficiency inside coatings. Short range order is evaluated by plotting the X-ray absorption spectra obtained around (from 200eV under the threshold to 800eV above) the different absorption K-edges which characterize each studied sample. These experiments were performed at LURE using synchrotron radiation from the DCI storage ring operating with an energy of 1.85 GeV. Measurements were carried out in a conversion electron mode on a system working at liquid nitrogen temperature [2]. Samples were orientated in such a way that the electric field was parallel to their surface.

3. Ball-milling in Cu/Fe/Co system

In recent years, the giant magnetoresistance effect has been extensively studied in Co/Cu and Fe/Cu magnetically coupled multilayers. More recently, a growing attention has been paid to granular materials usually obtained by codepositing two immiscible metallic components on a substrate. With Co/Cu and Fe/Cu systems [3] [4], the two metallic components tend to segregate, resulting in the formation of small magnetic precipitates embedded in a non magnetic matrix. The giant magnetoresistance effect can be emphasized or eroded, according to the temperature and time of a subsequent annealing.

The ball-milling process of multicomponent powders can be an alternative to obtain a similar effect in bulk compacted materials. A series of $\text{Cu}_{80}\text{Co}_{20}$, $\text{Cu}_{80}\text{Fe}_{20}$ [5] and $\text{Cu}_{80}\text{Fe}_{10}\text{Co}_{10}$ samples has been prepared by milling, at room temperature, a weighted and mixed powder in a Spex 8000 shaker mill. The total mass of powder was about 5g and the ratio of the ball to powder was 5 to 1 in weight. Balls and vial were both made of stainless steel and, after a milling time of 65 hours, samples were taken as metallic compacted plaques sticking to the inner walls. Then, they were thinned and polished.

Here, we report only the microstructural investigation obtained on the ternary sample, where annealing induces FeCo body-centered cubic precipitates. Figure 1 shows the θ -2 θ X-ray diffraction spectra obtained with this sample, compared to the mixed powder one. One can see that, after milling, all the diffraction peaks which indicate the presence of body-centered cubic iron or hexagonal cobalt have disappeared from the spectrum. On figure 2 the Fourier transforms of the Exafs spectra collected on Fe, Co and Cu absorption K-edge show three quasi identical signals. Nevertheless, a more precise analysis of the backtransformed Exafs signal of the first main peak shows some differences, especially for the Debye-Waller term : assuming that the environment of each atom species is quasi exclusively constituted by Cu atoms, very good fits are obtained, for the three signals, when first neighbours are located at a distance of 0.2535nm from the central excited atom. A mixed environment, in accordance with a perfect sursaturated solid solution, only slightly increases this parameter. Simulation also indicates that the

three spectra are well fitted when the coordination number is taken equal to 12, the differences being mainly provided by the Debye-Waller term which shows a relative topological disorder around a Fe atom ($\sigma = 0.0085\text{nm}$) in comparison with the Co one ($\sigma = 0.0077\text{nm}$) and the Cu one ($\sigma = 0.0069\text{nm}$), this former being typical of copper bulk at 80K.

Fig. 1 : X-ray diffraction patterns of the $\text{Cu}_{80}\text{Fe}_{10}\text{Co}_{10}$ samples before (b.m. 0h) and after (b.m. 65h) ball-milling.

Fig. 2 : Fourier Transform of the EXAFS signal of the $\text{Cu}_{80}\text{Fe}_{10}\text{Co}_{10}$ sample b.m. 65h at the 3 different K edges.

4. Co-deposited $\text{Cu}_x\text{Mo}_{1-x}$ thin films

Tribological properties of thin film coatings on a metal substrate are greatly influenced by their microstructures and composition. In particular, thin nanocrystalline films of copper and molybdenum co-deposited on steel substrates were found [6] to improve, sometimes drastically, the wear coefficient when composition is included within the domain $0.7 > x > 0.5$. The co-deposition is produced by ion beam sputtering technique and a split-target arrangement. A precise measurement of composition was achieved by energy x-ray dispersive spectrometry. Sample thickness was chosen about 300nm, because of the limited probing depth in conversion electron X-ray spectroscopy mode. Here, we report only results about the long and short range order encountered in the $\text{Cu}_{50}\text{Mo}_{50}$. Among the whole series of probed specimens, this composition presents the most typical short range deviations from a random distribution of atoms in a solid solution identified on the X-ray diffraction pattern reported on figure 3. This set of peaks is typical of a body cubic centered crystalline phase, which the dense plane family (110) displays a lattice spacing d_{111} in quasi complete accordance with the Vegard's law ; apart the (200) peak, partially truncated by the diffractometer geometry, positions of the (211) and (220) peaks are in coherence (see arrows) with this distance. Compared with that simple description of the matrix, the EXAFS results appears more complex ; the Fourier transforms (figure 4a and 4b) show environments typical of amorphous materials.

Fig. 3 : X-ray diffraction pattern of the $\text{Cu}_{50}\text{Mo}_{50}$ sample in asymmetric geometry (incidence : 2°)

Fig. 4 (a) : Fourier Transforms at the Cu K edge

Fig. 4 (b) : Fourier Transforms at the Mo K edge

Analysis of the backtransformed EXAFS signals can be resumed as follow : a) about the first coordination shell (8 atoms in BCC structure), the chemical distribution remains coherent with a random saturated solid solution ; but fits require several distances in this first shell : $d_{\text{Cu-Cu}} = 0.248\text{nm}$, $d_{\text{Cu-Mo}} = 0.267\text{nm}$ and $d_{\text{Mo-Mo}} = 0.271\text{nm}$ with an important disorder for the mixed pairs. b) the second shell appears so disordered that only some (3) Mo-Mo pairs ($d_{\text{Mo-Mo}} = 0.312\text{nm}$) can be extracted. The mean first shell distance value is nevertheless equal to the one deduced from XRD experiment.

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