Journal of Alloys and Compounds 317–318 (2001) 423–427

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Low temperature formation of nanocrystalline Fe–W and Fe–Mo compounds

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Abstract

Nanocrystalline Fe–W and Fe–Mo compounds obtained by coupled reduction of fine dispersed FeOOH with H_2WO_4 (or with H_2MoO_4) in continuous H_2 flow at the temperature range 700–740°C were studied by means of Mössbauer spectroscopy and X-ray diffraction. The formation of partially disordered and even amorphous intermetallic phases and solid solutions with extended concentrations was observed. Hydrogen incorporation in the structure of disordered intermetallic phases during the reduction process was revealed.

Keywords: Nanocrystalline compounds; Intermetallic and amorphous phases; Mössbauer spectroscopy

1. Introduction

Comparative structural analysis of nanocrystalline compounds Fe–W and Fe–Mo prepared by the same method: coupled reduction of dispersed oxygen containing compounds in continuous H_2 flow at the temperature range 700–740°C is interesting for the understanding of low temperature alloying processes. The equilibrium phase diagrams of these two systems are very similar. They have very narrow (near 1%) regions of b.c.c. solid solutions Fe and W (or Mo) for both end members and several intermetallic compounds. Among them λ-Fe_2W (or Fe_2Mo) and μ-Fe_7W_6 (or Fe_7Mo_6) are stable at room temperature. The interfacial enthalpies in kJ per mole for solved W (or Mo) in Fe [1] estimated by Miedema are small and different: $\Delta H=0$ for Fe–W and $\Delta H=-7$ for Fe–Mo. But for both Fe–W and Fe–Mo nanocrystalline powder compounds obtained by ball milling or by vapour quenching the different concentration ranges of amorphous phases formation were established experimentally [2–5].

The purpose of the present paper is to analyse the nonequilibrium phase formation process during the coupled reduction in Fe–W and Fe–Mo by means of X-ray diffraction and Mössbauer spectroscopy.

2. Experimental

Chemically dispersed nanocrystalline Fe–W and Fe–Mo compounds with different W (or Mo) concentrations were obtained by means of a coupled reduction of fine dispersed FeOOH and H_2WO_4 (or H_2MoO_4) in continuous H_2 flow at the temperature range 700–740°C [6,7].

X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were used for the structural characteristics study of the samples (grain size, phase composition, concentrations of diluted elements in solid solutions). XRD was performed at Rigaku-DX/Max θ–2θ diffractometer with Cu Kα radiation. The Mössbauer spectra were obtained at room temperature using constant acceleration spectrometer with Co^{57} (Rh) source. The spectra were fitted by means of the UNIVEM and MSTools programs. As usual, all the isomer shift values are given with respect to metallic Fe at room temperature.

3. Results and discussion

XRD patterns of the Fe–W nanocrystalline compositions with W concentrations of 9–55 at% are shown in Fig. 1. Judging from the picture, besides the peaks from b.c.c. crystalline solid solutions Fe and W, a diffusive halo appears in the range of angles 35–50°. This halo is most

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01420-1

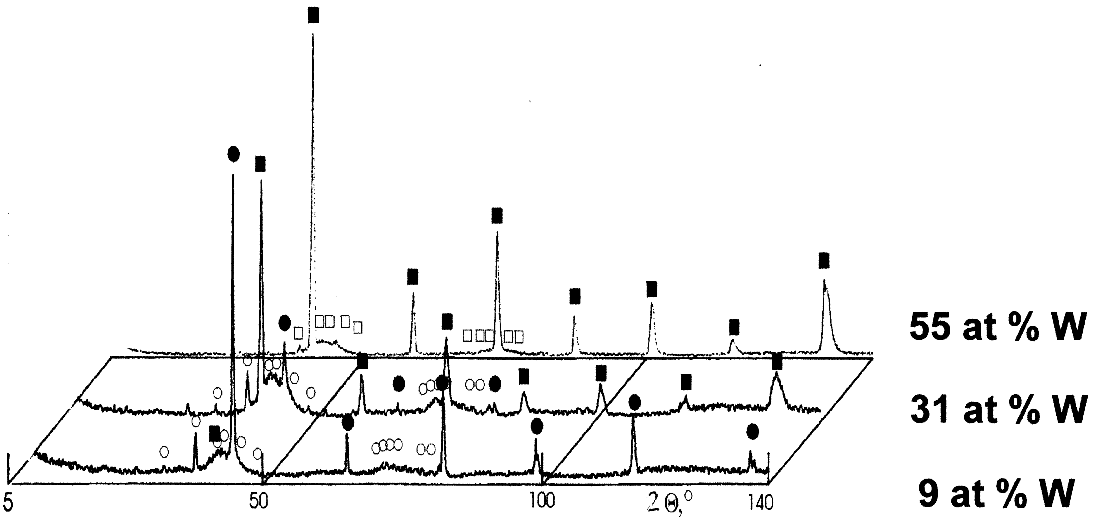

Fig. 1. X-Ray diffraction patterns of the nanocrystalline Fe–W compositions (α-Fe (●), W (■), Fe_2W (○), Fe_7W_6 (□)).

intense in the XRD pattern of the sample with 31 at% W and may be taken as indication of the amorphous phase formation. The peaks also seen in those angle regions can be considered as forming intermetallic λ- and μ-phases contributions. In any case we have here the coexistence of several phases. The same situation was observed in XRD patterns of the Fe–Mo system.

In Fig. 2a and b, the grain sizes of the b.c.c. solid solutions derived from X-ray lines broadening are plotted versus concentration. It is noted that the grain sizes

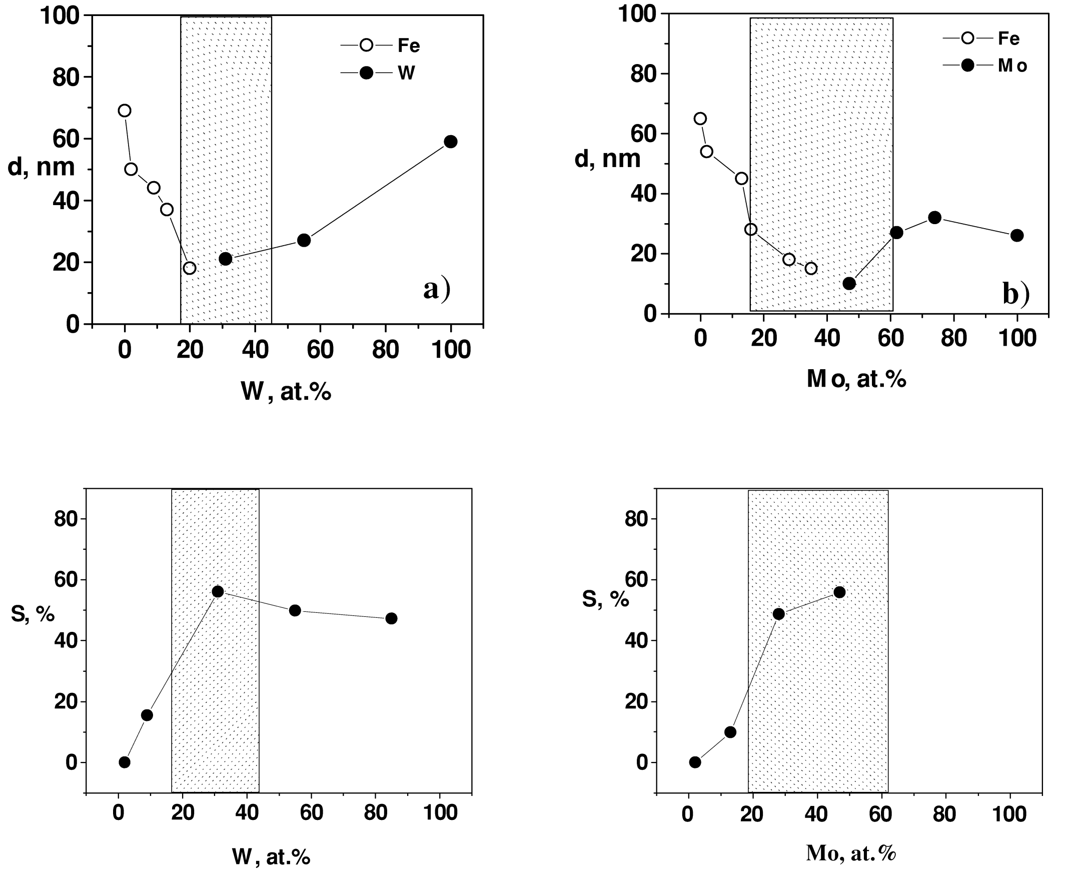

Fig. 2. Concentration dependencies of the grain sizes (*d*, nm) of the b.c.c. solid solutions for Fe–W (a) and Fe–Mo (b) compounds and total quantity (as subspectra area *S*, %) of intermetallic phases in these compounds (c,d).

decrease from the pure constituent components to the multiphase regions and especially to the shaded regions of amorphous phases formation [2,5]. Thus, a strong influence of the initial elements concentration on the grain size is observed.

MS was used to analyse phase compositions in the samples under study. MS is sensitive to the chemical and structural environment of iron atoms on a nearest-neighbour length scale and therefore allows the solid solutions to be detected at very low concentrations. Such a parameter as hyperfine magnetic field value (H), is very sensitive to replacement Fe by W (or Mo). Furthermore, the nonmagnetic phases in Fe–W and Fe–Mo systems such as Fe_2W, Fe_7W_6, Fe_2Mo and Fe_7Mo_6 are readily distinguished in the Mössbauer spectra because they have their own parameters, such as quadrupole splitting and isomer shift [2,3,8]. MS also gives the opportunity to estimate the relative quantity of phases present in the sample by measurements of their subspectra intensities, and the degree of structure disordering by measurement of line width.

Fig. 3 shows Mössbauer spectra obtained from nanocrystalline compounds Fe–W (a) and Fe–Mo (b) with various W and Mo atomic concentrations. Two main components are clearly visible in these spectra. The first component, due to b.c.c. Fe solid solution, is magnetically ordered in a six-line pattern. The second central nonmagnetic pattern appears gradually in the spectra with an

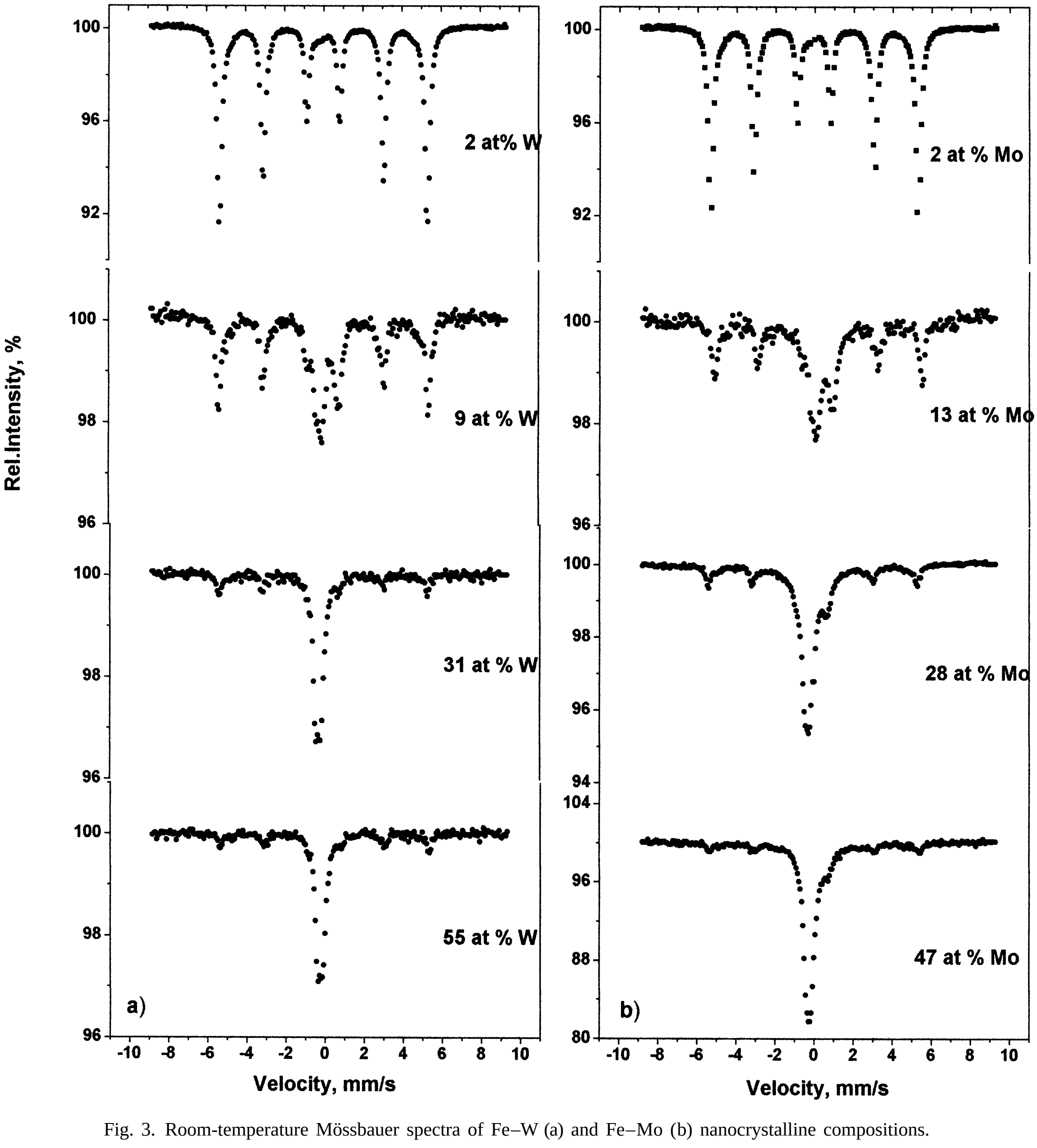

Fig. 3. Room-temperature Mössbauer spectra of Fe–W (a) and Fe–Mo (b) nanocrystalline compositions.

increase of W (or Mo) concentration in the mixture and consists of several subspectra with parameters of quadrupole splitting (Q) and isomer shifts (δ) corresponding to intermetallic and even amorphous phases known in these systems and to b.c.c. W (or Mo) solid solutions. All these intermetallic phases may be considered as disordered because their subspectra have line widths extended from experimental value 0.28 up to 0.36 mm/s. In Fig. 2c and d, the total intermetallic phases intensities (without solid solutions components) obtained from the Mössbauer spectra fitting are plotted versus concentration.

To separate the spectral contributions of formed intermetallic phases we performed the analysis of distribution functions $P(\delta)$ and $P(Q)$ for the paramagnetic pattern of the spectra: the hyperfine parameters of the magnetic components were calculated separately and kept constant in this fitting procedure. Normalised distribution functions $P(\delta)$ for both Fe–W and Fe–Mo systems are shown in Fig. 4a and b. The isomer shift parameters of well crystallised λ- and μ-phases, amorphous phases and W (or Mo) solid solutions are indicated in these pictures too. The three $P(\delta)$ for the samples with similar atomic concentration may be explained in the following way.

A broad (especially for Fe–Mo system) single peak covers all the δ region of both intermetallic and amorphous phases for the samples with low second element concentration (9 and 13 at%). The most likely phases to be formed at these concentrations are λ- and amorphous ones. Considerable shift of this peak to the negative isomer shift values as well as an increase of its intensity could be observed in the pictures for the samples with middle concentrations (31 and 28 at%). This shift may be explained by hydrogen incorporation in the disordered structure of forming intermetallic μ- and λ-phases during the coupled reduction process. The hydrogen atoms incorporated in the structure add their electrons to the electron density near iron atoms and correspondingly the isomer shift parameter decreases up to values $\delta=-0.4$–0.45 mm/s. The distribution functions for the samples with high concentration of a second element (55 and 47 at%) have a different form. A narrow single peak with a maximum corresponding to μ-phase isomer shift can be observed for Fe–W compound. Apart from the peak we mentioned before, the second small peak corresponding to amorphous phase δ value appears in the picture of Fe–Mo compound.

As was reported in our paper [7] the analysis of hyperfine magnetic field distribution functions for Fe(W) and Fe(Mo) solid solutions showed an extention of up to 4–5 at% concentration of diluted elements in them.

4. Conclusions

The coupled reduction of fine dispersed oxygen containing compounds Fe–W and Fe–Mo in continuous H_2 flow at the temperature range 700–740°C results in different partially disordered and even amorphous intermetallic compounds and solid solutions with extended concentration formation. This phenomenon is due to the energetic contribution of the high density of interfaces formed upon

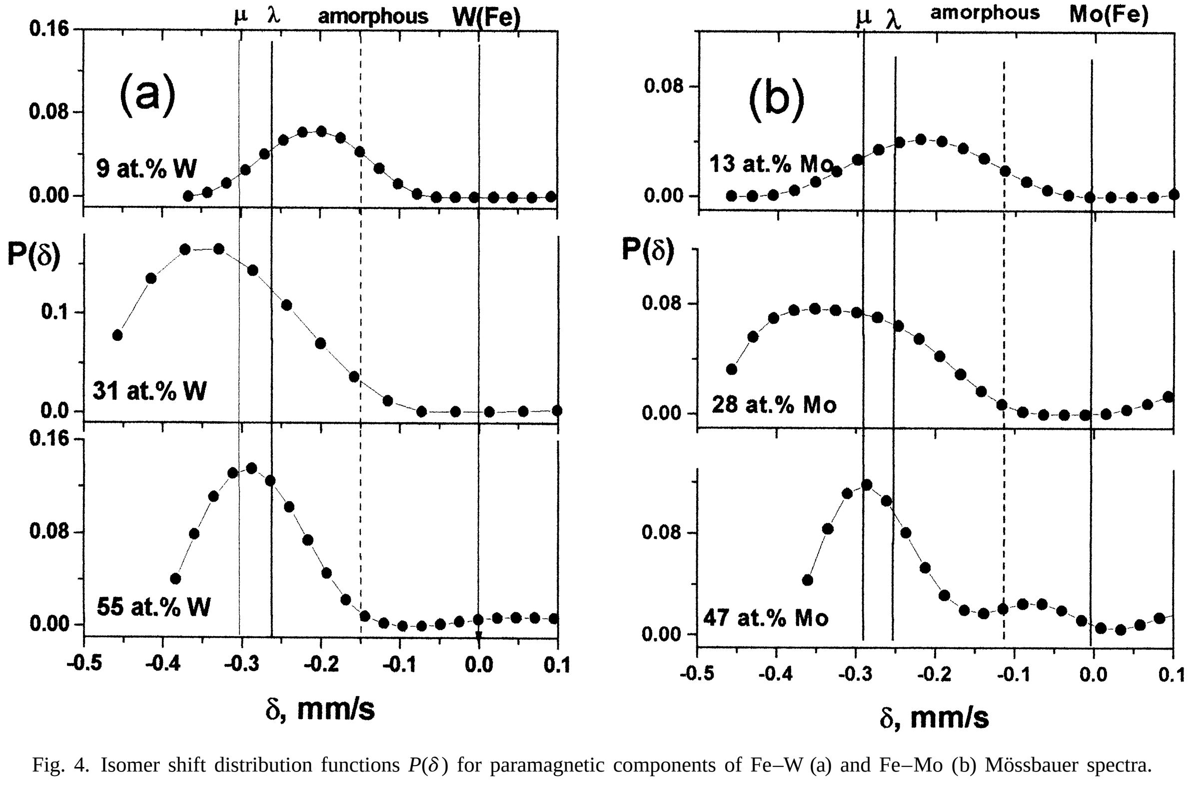

Fig. 4. Isomer shift distribution functions $P(\delta)$ for paramagnetic components of Fe–W (a) and Fe–Mo (b) Mössbauer spectra.

the reduction process. The grain sizes, type and quantities of forming phases depend on the initial concentration of constituent elements in obtained compositions, but we observed the coexistence of several phases in all of them. It must be mentioned, that the concentration region of amorphous phase formation is wider for the Fe–Mo system. Hydrogen incorporation in the disordered intermetallic phases was revealed for concentrations near 30 at% of W (or Mo) in both systems.

Acknowledgements

This work was supported by the Russian Scientific Foundation (Grant No 00-02-16603).

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