Hyperfine Interact (2012) 208:1–6
DOI 10.1007/s10751-011-0458-6

Atomic short-range order in iron based Fe-Mo alloys studied by ^{57}Fe Mössbauer spectroscopy

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Abstract The room temperature Mössbauer spectra of ^{57}Fe were measured for iron-based solid solutions $Fe_{1-x}Mo_x$ with x in the range $0.01 \leq x \leq 0.05$. The obtained spectra gave clear evidence that after annealing process the distribution of impurity atoms in the first and the second coordination spheres of ^{57}Fe nuclei is not random and it cannot be described by the binomial distribution. Quantitatively, the findings are presented with the short-range order parameters.

Keywords Mössbauer spectroscopy · Short-range order · Iron alloys · International conference · Applications · Mössbauer effect

1 Introduction

Magnetic and thermodynamic properties of alloys depend, in general, on local fluctuations in composition. These fluctuations can be quantitatively described in terms of atomic short-range order (SRO) parameters α_i, introduced by Cowley [1].

$$\alpha_i = 1 - \frac{P_i\,(BA)}{x_B} \tag{1}$$

where P_i (BA) denotes the probability of finding an atom of type B in the ith nearest neighbour shell when centred on an atom of type A and x_B is a fraction of atoms B in the alloy. It is clear that the SRO parameter yields the same result when evaluated on a representative A or B atom. Physically, the parameter measures the deviation at short range from the random state, with values from 1-1/x_B to 1; 0 corresponds to the random state.

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In the last years, there was much interest of theoretical [2, 3] and experimental [4–8] determination of SRO parameters in Fe-based binary alloys. Our work concerns determination of such parameters in $Fe_{1-x}Mo_x$ alloys, with x in the range $0.01 \leq x \leq 0.05$, using ^{57}Fe Mössbauer spectroscopy. We performed three series of measurements. The first for samples just after preparation by melting and being frozen-in high temperature state, second for samples after annealing at 1270 K for 2 h and third for samples after additional annealing at 1270 K for the next 2 h. Differences of SRO parameters derived from these three different series of data should show how the annealing process of $Fe_{1-x}Mo_x$ alloys influences, the distribution of Mo atoms in the nearest neighbour spheres of the ^{57}Fe Mössbauer probe and what is the type of interaction between Mo and Fe atoms (predominance of Fe-Fe and Mo-Mo or Fe-Mo bonds).

2 Experimental and results

The samples of iron-molybdenum alloys containing 1, 2, 3, 4 and 5 at. % of Mo, were prepared by melting appropriate amounts of the Aldrich 99.999% pure iron and 99.97% pure molybdenum in an arc furnace filled with argon. The ingots were cold-rolled to the final thickness of about 0.05 mm and then the room temperature ^{57}Fe Mössbauer spectra were measured for the foils by means a constant-acceleration POLON spectrometer of standard design. In the next step the samples were annealed in vacuum at 1270 K for 2h. After that they were slowly cooled to room temperature during 6h. Under these conditions, diffusion effectively stops at about 700 K [9], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to 700 K. In the last step we repeated the annealing process at 1270 K for the next 2 h. The final concentrations of elements in the $Fe_{1-x}Mo_x$ specimens were estimated taking into account the weight losses during the melting process and assuming that they were due to evaporation of molybdenum only. The values of x estimated this way are: 0.00970(40), 0.01989(15), 0.02965(42), 0.0389(12) and 0.0491(11), where in brackets the maximal uncertainty of x is given.

Spectra for samples as-obtained and after the second annealing process are presented in Figs. 1 and 2. They were analysed in terms of six six-line patterns corresponding to different hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Mo atoms located in the first two coordination shells of the probing nuclei. It was done under assumption that the influence of Mo atoms on B as well as the corresponding isomer shift IS of a subspectrum, is additive and independent of the atom positions in the given coordination shell of the nuclear probe although it can be different for atoms located in unlike shells. In other words it was accepted that for each subspectrum the quantities B and IS are linear functions of the numbers n_1 and n_2 of Mo atoms located, respectively, in the first and the second coordination shells of ^{57}Fe and the functions can be written as follows:

$$\begin{aligned} B\,(n_1, n_2) &= B_0 + n_1 \Delta B_1 + n_2 \Delta B_2, \\ IS\,(n_1, n_2) &= IS_0 + n_1 \Delta IS_1 + n_2 \Delta IS_2, \end{aligned} \tag{2}$$

where ΔB_1 (ΔIS_1) and ΔB_2 (ΔIS_2) stand for the changes of B (IS) with one Mo atom located in the first and the second coordination shells of the Mössbauer probe. At the same time the quadruple splitting QS of a subspectrum is a free parameter

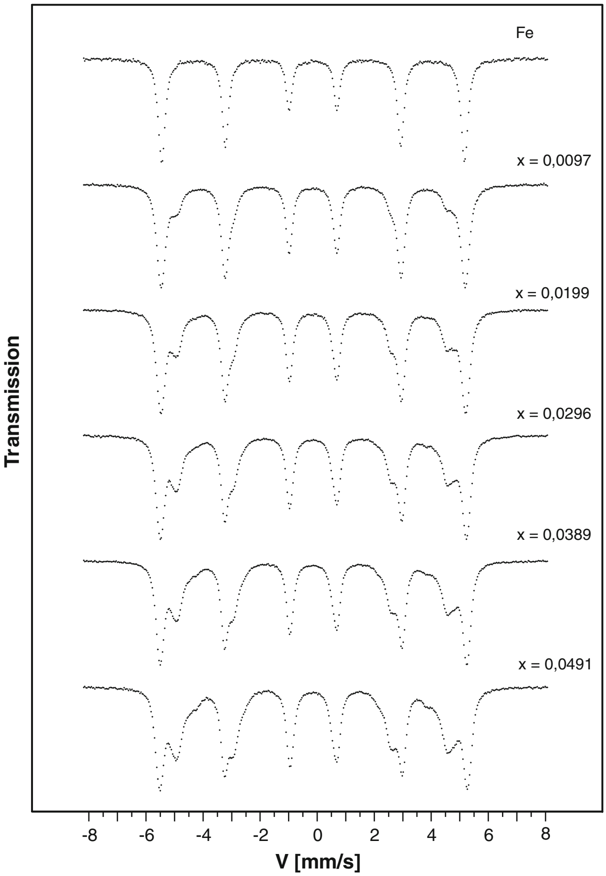


Fig. 1 The ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Mo_x$ alloys measured at room temperature after melting process in an arc furnace

[10]. More details concerning sample preparations and method of analysing of the obtained spectra, including the values of B and IS parameters, can be found in our previous paper [11].

In disordered iron-based alloys, the probability $P(n_1, n_2)$ of local configuration of impurity atoms in the first and the second coordination spheres of ^{57}Fe nucleus is described by the binomial distribution:

$$P(n_1, n_2) = \frac{N_1!}{n_1!\,(N_1 - n_1)!}\frac{N_2!}{n_2!\,(N_2 - n_2)!}x^{n_1+n_2}\,(1 - x)^{N_1+N_2-n_1-n_2} \tag{3}$$

where N_1 and N_2 denotes the coordination numbers of the first and the second sphere, x is the concentration of impurity atoms and n_1, n_2 stands for the numbers of impurity atoms in the first and the second coordination spheres. In the case of $Fe_{1-x}Mo_x$ alloys with the x range $0.01 \leq x \leq 0.05$ where atoms are distributed in the b.c.c. lattice, so $N_1 = 8$ and $N_2 = 6$. In the real alloys the distribution of impurity atoms is generally different than statistically predicted by (3). This deviation from the random state can be quantitatively described by SRO parameters. The Mössbauer spectroscopy is a very useful tool for determination of the parameters because the hyperfine field B and isomer shift IS depend on the number of impurity atoms in the

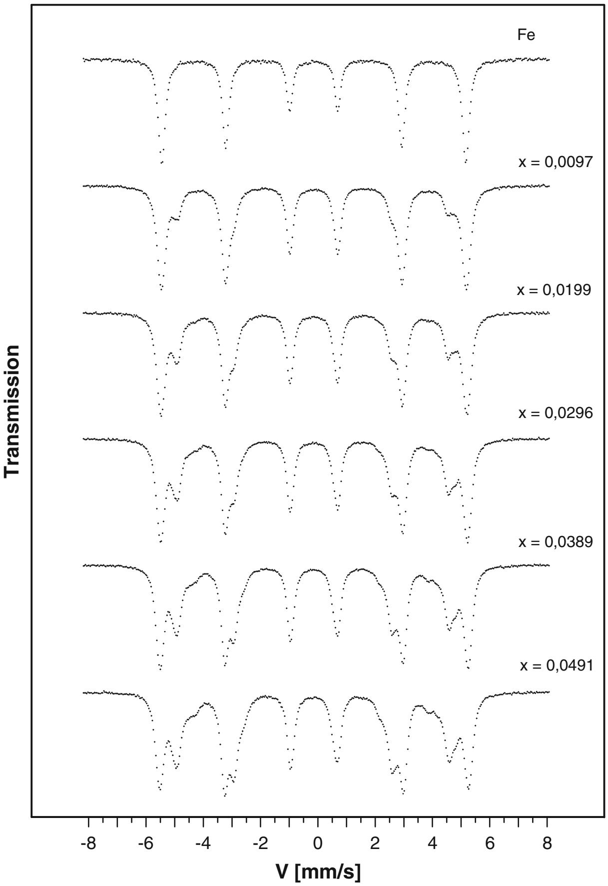


Fig. 2 The ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Mo_x$ alloys measured at room temperature after the second the annealing process at 1270 K

vicinity of ^{57}Fe probe. The SRO parameters for systems with b.c.c. lattice have the following form:

$$\alpha_1 = 1 - \frac{\langle n_1 \rangle}{8x}, \alpha_2 = 1 - \frac{\langle n_2 \rangle}{6x} \tag{4}$$

where:

$$\langle n_1 \rangle = \sum\nolimits_{n_1=1}^{8} n_1 P_{\exp}(n_1, n_2), \langle n_2 \rangle = \sum\nolimits_{n_2=1}^{6} n_2 P_{\exp}(n_1, n_2) \tag{5}$$

$< n_1 >$ and $< n_2 >$ are the average numbers of non-iron Mo atoms in the first and the second coordination spheres of an iron atom and $P_{\exp}(n_1, n_2)$ denotes the probability of the configuration (n_1, n_2) of non-iron Mo atoms obtained from the analysis of the experimental Mössbauer spectra.

The SRO parameters α_1 and α_2 for $Fe_{1-x}Mo_x$ alloys calculated from (4) are presented in Figs. 3 and 4. In the samples before annealing process parameters α_1 and α_2, on average, are close to 0 and this provides that the distribution of Mo atoms in these samples is almost random. Situation significantly changes for the annealed samples, i.e. α_1 essentially decreases and α_2 increases on annealing. This indicates

Fig. 3 The SRO parameter α_1 parameters as a function of fraction x of Mo atoms in the $Fe_{1-x}Mo_x$ alloys

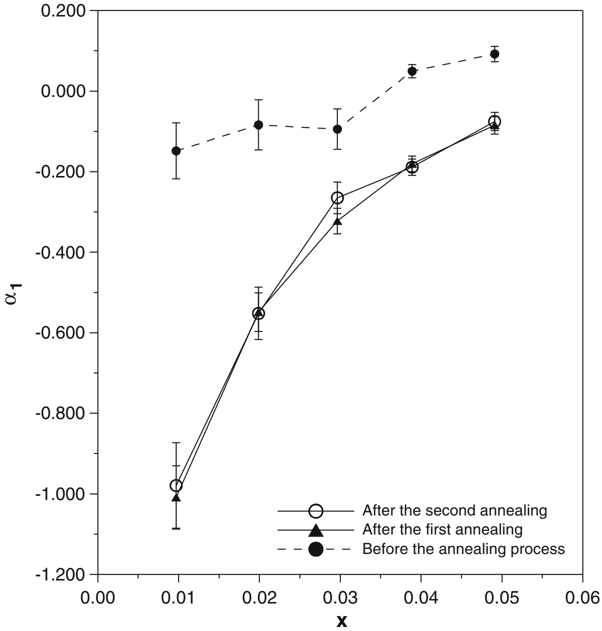
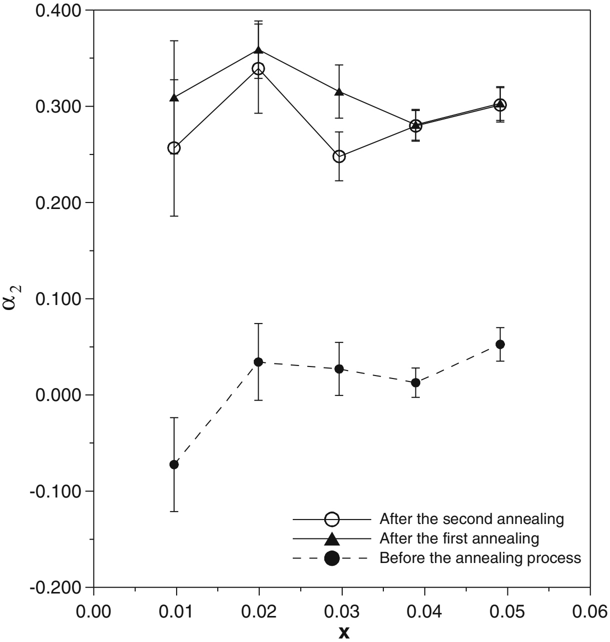


Fig. 4 The SRO parameter α_2 parameters as a function of fraction x of Mo atoms in the $Fe_{1-x}Mo_x$ alloys



that in the first coordination shell of ^{57}Fe probe, the Mo atoms are more abundant and in the second one they are rarer than it is expected for the random case. In terms of interactions it means that the interaction between Fe and Mo atoms is attractive (predominance of Fe-Mo bonds) and this is in agreement with findings of our previous work [11]. Worth mentioning is the fact, that the values of parameters α_1 and α_2 in samples after the first and the second annealing processes are practically the same. This may indicate that the first annealing process at 1270 K for 2 h was sufficient to obtain the equilibrium state of $Fe_{1-x}Mo_x$ alloys.

3 Conclusions

The Mössbauer study of SRO parameters for $Fe_{1-x}Mo_x$ alloys reveals that the parameters depend on the heat treatment of the investigated specimens. For the samples as-obtained i.e. before annealing process, the SRO parameters α_1 and α_2 are nearly equal to 0. This suggests that the distribution of Mo atoms in the first two coordination shells of ^{57}Fe probe is almost random in the as-obtained specimens. On the other hand for the samples after one and two annealing processes at 1270 K during 2 h, one observes ordering-type correlations (the predominance of Mo-Fe bonds) manifested as increasing of α_1 and decreasing of α_2 parameter, caused by attractive interaction between Fe and Mo atoms.

Acknowledgement This work was supported by the University of Wrocław under the grants 1463/M/IFD/11 and 1010/S/IFD.

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