Temperature dependence of the short-range order parameter for Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys

Rafał Idczak, Robert Konieczny

Abstract. The $^{57}$Fe Mössbauer spectra for the iron-based solid solutions Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ were measured at different temperatures ranging from 300 K to 900 K. Analysis of the obtained spectra shows that the distribution of impurity atoms in the two first coordination shells of $^{57}$Fe nuclei is not random and it cannot be described by the binomial distribution. Quantitatively, the effects were described in terms of the atomic short-range order (SRO) parameters and the pair-wise interaction energy with the help of a quasi-chemical type formulation introduced by Cohen and Fine. The obtained results reveal strong clustering-type correlations in the studied samples (a predominance of Fe-Fe and Cr-Cr bonds). Moreover, the changes in SRO values observed during thermal processing suggest that the distribution of Cr atoms in an α-iron matrix is strongly temperature dependent.

Key words: iron alloys • Mössbauer spectroscopy • nuclear materials • short-range order

Introduction

In the last few years, there has been much interest shown in theoretical [1–3] and experimental [4–7] determination of atomic short-range order (SRO) parameters in Fe-Cr alloys. The motivation for these studies is the fact that high-chromium ferritic/martensitic steels, containing up to 15 at.% of Cr, are candidate materials for advanced fission reactors (Generation IV), accelerator-driven systems using spallation neutron sources and fusion reactors [8, 9]. These types of steels are capable of performing reliably for a long time under high irradiation levels (total dose of 50 to 200 displacements per atom (dpa)) and at high temperatures (up to 900 K). A quantitative understanding of the mechanisms leading to the change of the properties of these steels after a long-term exposure to irradiation is, therefore, recognized to be of high importance in the safe design and operation of innovative nuclear systems. A great deal of understanding can be achieved by studying simpler model systems, such as Fe-Cr alloys in this case.

Taking the above discussion into account we decided to examine the influence of temperature on structural properties of iron-based Fe-Cr alloys. A proper investigation was performed with $^{57}$Fe Mössbauer spectroscopy. This spectroscopy is a very useful tool for such studies as it can give information on the distribution of Cr atoms in the vicinity of the $^{57}$Fe Mössbauer probe and then on atomic short-range order and the type of interactions between Cr and Fe atoms in the materials under consideration.
Experimental details and results

The samples of Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys were prepared in an arc furnace. Appropriate amounts of the components of the alloys were melted in an argon atmosphere. The weight losses during the melting process were below 1%; hence, the compositions of the obtained ingots were close to the nominal ones. The resulting ingots were cold-rolled to the final thickness of about 0.03 mm. The $^{57}$Fe Mössbauer spectra for the Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys measured at different temperatures ranging from 300 K to 900 K were recorded in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 60-mCi $^{57}$Co-in-Rh standard source. The full width at half maximum (FWHM) of the spectral lines for the source was 0.24 mm/s. Some of the obtained spectra are presented in Figs. 1 and 2.

Each measured spectrum was fitted with a transmission integral for a sum of different six-line patterns corresponding to various hyperfine fields $B$ at $^{57}$Fe nuclei generated by different numbers of Fe and Cr atoms located in the first two coordination shells of the probing nuclei. The number of fitted six-line patterns depends on the concentration of Cr in the samples, and the values were ten for Fe$_{0.90}$Cr$_{0.10}$ and twelve for Fe$_{0.88}$Cr$_{0.12}$. The fitting procedure was carried out under the assumption that the influence of Cr 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 various shells. In other words, it was accepted that for each subspectrum,

$$B(n_1, n_2) = B_0 + n_1\Delta B_1 + n_2\Delta B_2$$

$$\text{IS}(n_1, n_2) = \text{IS}_0 + n_1\Delta\text{IS}_1 + n_2\Delta\text{IS}_2$$

where $\Delta B_1(\Delta\text{IS}_1)$ and $\Delta B_2(\Delta\text{IS}_2)$ stand for the changes of $B$ (IS) with one Cr atom in the first and the second coordination shells of the Mössbauer probe. At the same time, we assume that the quadrupole splitting $QS$ in a cubic lattice is equal to zero. Some results of the spectrum analysis are displayed in Tables 1 and 2.

As the main result of the analysis, effective thicknesses $T_A(n_1, n_2)$ related to the components of each spectrum were determined.

$$T_A(n_1, n_2) = \sigma_0 t_A N c(n_1, n_2)$$

where $\sigma_0$ is the maximal cross-section for nuclear $\gamma$ resonance absorption, $t_A$ denotes the thickness of the absorber, $N$ stands for the total number of resonant absorbing atoms of $^{57}$Fe per unit volume, $c(n_1, n_2)$ describes the fraction of absorbing atoms corresponding to the component under consideration and $f$ is the Lamb–Mössbauer factor. Assuming that the Lamb–Mössbauer factor does not depend on the configuration of atoms in the surroundings of the $^{57}$Fe nucleus, the fraction $c(n_1, n_2)$ can be easily calculated using the $T_A(n_1, n_2)$ values as in such cases:

$$c(n_1, n_2) = \frac{T_A(n_1, n_2)}{\sum T_A(n_1, n_2)}$$

![Fig. 1. The $^{57}$Fe Mössbauer spectra for the Fe$_{0.90}$Cr$_{0.10}$ alloy at different temperatures ranging from 300 K to 900 K.](image1)

![Fig. 2. The $^{57}$Fe Mössbauer spectra for the Fe$_{0.88}$Cr$_{0.12}$ alloy at different temperatures ranging from 300 K to 900 K.](image2)
Temperature dependence of the short-range order parameter for Fe_{0.90}Cr_{0.10} and Fe_{0.88}Cr_{0.12} alloys

The computed \( c(n_1, n_2) \) values were used to find other parameters:

\[
\langle n_1 \rangle = \sum_{n_1=1}^{86} n_1 c(n_1, n_2)
\]
\[
\langle n_2 \rangle = \sum_{n_1=1}^{86} n_2 c(n_1, n_2)
\]
\[
\langle n_{12} \rangle = \langle n_1 \rangle + \langle n_2 \rangle
\]

where \( <n_1> \), \( <n_2> \) and \( <n_{12}> \) are the average numbers of Cr atoms in the first, the second and two first coordination shells of the \( ^{57}\text{Fe} \) Mössbauer probe, respectively.

The average value of the short-range order (SRO) parameter for the first two coordination shells in a bcc lattice has the following form [6, 10]:

\[
\alpha_{12} = 1 - \frac{\langle n_{12} \rangle}{14x}
\]

where \( x \) is the atomic concentration of Cr. This averaging procedure is usually employed for bcc alloys, in which the first and the second neighbor distances are very close to each other [4, 6, 11].

The values of the SRO parameter \( \alpha_{12} \) in Fe_{0.90}Cr_{0.10} and Fe_{0.88}Cr_{0.12} alloys calculated from Eq. (5) are presented in Figs. 3 and 4. As one can see, the positive values of the SRO parameter gave a clear evidence of clustering tendencies in studied alloys. The Cr atoms dissolved in the Fe matrix cluster into a separate Cr-rich phase. In terms of interactions, it means that the interaction between Fe and Cr atoms is repulsive (predominance of Fe-Fe and Cr-Cr bonds). Moreover, the changes of SRO values observed during thermal processing suggest that the distribution of Cr atoms in the Fe matrix is strongly temperature dependent. In particular, the significant decrease of SRO parameter values during the heating process indicates that at elevated temperatures, the Cr clusters disappear and the studied alloys become more homogeneous. In the case of the cold-rolled Fe_{0.88}Cr_{0.12} alloy annealed below 700 K, the determined relatively small and constant SRO values could be associated with the frozen high-temperature state obtained just after the melting.

Table 1. Some of the best-fit parameters of the assumed model of the \( ^{57}\text{Fe} \) Mössbauer spectrum measured for an Fe_{0.90}Cr_{0.10} alloy

<table>
<thead>
<tr>
<th>( T [\text{K}] )</th>
<th>( B_0 [\text{T}] )</th>
<th>( \Delta B_1 [\text{T}] )</th>
<th>( \Delta B_2 [\text{T}] )</th>
<th>( \Delta IS_0 ) (relative to ( \alpha-\text{Fe} )) [\text{[mm/s]}]</th>
<th>( \Delta IS_1 ) [\text{[mm/s]}]</th>
<th>( \Delta IS_2 ) [\text{[mm/s]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>33.97(1)</td>
<td>-3.12(2)</td>
<td>-2.05(2)</td>
<td>0.006(7)</td>
<td>-0.024(2)</td>
<td>-0.010(2)</td>
</tr>
<tr>
<td>400</td>
<td>33.20(1)</td>
<td>-2.99(2)</td>
<td>-1.93(2)</td>
<td>-0.064(8)</td>
<td>-0.024(2)</td>
<td>-0.012(2)</td>
</tr>
<tr>
<td>500</td>
<td>32.21(1)</td>
<td>-2.99(3)</td>
<td>-1.94(3)</td>
<td>-0.137(8)</td>
<td>-0.024(2)</td>
<td>-0.012(2)</td>
</tr>
<tr>
<td>600</td>
<td>31.00(1)</td>
<td>-2.90(2)</td>
<td>-1.86(2)</td>
<td>-0.206(8)</td>
<td>-0.024(2)</td>
<td>-0.012(2)</td>
</tr>
<tr>
<td>700</td>
<td>29.49(1)</td>
<td>-2.85(2)</td>
<td>-1.81(2)</td>
<td>-0.276(8)</td>
<td>-0.023(2)</td>
<td>-0.011(2)</td>
</tr>
<tr>
<td>800</td>
<td>27.43(1)</td>
<td>-2.80(2)</td>
<td>-1.78(2)</td>
<td>-0.339(9)</td>
<td>-0.024(2)</td>
<td>-0.011(2)</td>
</tr>
<tr>
<td>900</td>
<td>24.76(2)</td>
<td>-2.77(3)</td>
<td>-1.75(2)</td>
<td>-0.397(9)</td>
<td>-0.029(3)</td>
<td>-0.011(2)</td>
</tr>
</tbody>
</table>

Table 2. Some of the best-fit parameters of the assumed model of the \( ^{57}\text{Fe} \) Mössbauer spectrum measured for an Fe_{0.88}Cr_{0.12} alloy

<table>
<thead>
<tr>
<th>( T [\text{K}] )</th>
<th>( B_0 [\text{T}] )</th>
<th>( \Delta B_1 [\text{T}] )</th>
<th>( \Delta B_2 [\text{T}] )</th>
<th>( \Delta IS_0 ) (relative to ( \alpha-\text{Fe} )) [\text{[mm/s]}]</th>
<th>( \Delta IS_1 ) [\text{[mm/s]}]</th>
<th>( \Delta IS_2 ) [\text{[mm/s]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>33.98(1)</td>
<td>-3.14(2)</td>
<td>-2.05(2)</td>
<td>0.009(8)</td>
<td>-0.022(2)</td>
<td>-0.010(2)</td>
</tr>
<tr>
<td>400</td>
<td>33.21(1)</td>
<td>-3.05(2)</td>
<td>-1.99(2)</td>
<td>-0.066(8)</td>
<td>-0.021(2)</td>
<td>-0.011(2)</td>
</tr>
<tr>
<td>500</td>
<td>32.21(1)</td>
<td>-3.04(2)</td>
<td>-1.98(2)</td>
<td>-0.140(8)</td>
<td>-0.020(2)</td>
<td>-0.011(2)</td>
</tr>
<tr>
<td>600</td>
<td>30.99(1)</td>
<td>-3.00(2)</td>
<td>-1.95(2)</td>
<td>-0.209(8)</td>
<td>-0.022(2)</td>
<td>-0.011(2)</td>
</tr>
<tr>
<td>700</td>
<td>29.50(1)</td>
<td>-2.97(2)</td>
<td>-1.92(2)</td>
<td>-0.279(9)</td>
<td>-0.020(2)</td>
<td>-0.010(2)</td>
</tr>
<tr>
<td>800</td>
<td>27.42(1)</td>
<td>-2.87(2)</td>
<td>-1.89(2)</td>
<td>-0.342(9)</td>
<td>-0.020(2)</td>
<td>-0.010(1)</td>
</tr>
<tr>
<td>900</td>
<td>24.84(2)</td>
<td>-2.82(3)</td>
<td>-1.81(3)</td>
<td>-0.396(9)</td>
<td>-0.019(1)</td>
<td>-0.015(3)</td>
</tr>
</tbody>
</table>

Fig. 3. The temperature dependence of the SRO parameter \( \alpha_{12} \) for the cold-rolled Fe_{0.90}Cr_{0.10} alloy.

Fig. 4. The temperature dependence of the SRO parameter \( \alpha_{12} \) for the cold-rolled Fe_{0.88}Cr_{0.12} alloy.

Fig. 5. The temperature dependence of the SRO parameter \( \alpha_{12} \) for the cold-rolled Fe_{0.90}Cr_{0.10} alloy.
process. As one can notice, this high-temperature state is thermally stable up to 600 K.

The interaction energy $V_i$ of an atom in the $i$th coordination shell with the central atom can be defined as follows [12]:

$$V_i = \frac{V_{AA}^{12} + V_{BB}^{12} - V_{AB}^{12}}{2}$$

(6)

where $V_{AA}^{12}$, $V_{BB}^{12}$ and $V_{AB}^{12}$ are the energies for the A-A, B-B and A-B bonds, respectively. The values of the average interaction energy $V_{12}$ of the central atom (an iron atom in our case) with atoms located in its first two coordination shells were computed using the obtained $\alpha_{12}$ values and the expression introduced by Cohen and Fine [12]:

$$V_{12} = -\frac{1}{2} kT \ln \left[ \frac{(\frac{\alpha_{12} + \frac{x}{1-x}}{1-x})^{\alpha_{12} + \frac{1}{x}}}{(1-\alpha_{12})^2} \right]$$

(7)

where $k$ is the Boltzmann constant and $T$ denotes the temperature characterizing the atomic distribution in the alloy under consideration. The $V_{12}$ values, calculated for the samples during the cooling stage, are presented in Fig. 5. Negative values of $V_{12}$ suggest that Fe-Fe and Cr-Cr bonds are more energetically favorable, thus confirming clustering tendencies. Moreover, the values of $V_{12}$ remain constant within the experimental error, and the estimated average interaction energy $V_{12}$ values for Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys are $V_{12} = -0.0148(11)$ eV and $V_{12} = -0.0135(11)$ eV, respectively.

**Conclusions**

The obtained positive values of the SRO parameter for Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys at different temperatures ranging from 300 K to 900 K gave a clear evidence of clustering tendencies in the studied materials. This result confirms previous theoretical predictions and experimental data. The changes in the SRO value observed during thermal processing suggest that the distribution of Cr atoms in the Fe matrix is strongly temperature dependent, and the significant decrease of the SRO parameter value during the heating process indicates that at elevated temperatures, the Cr clusters disappear and the studied alloys become more homogeneous. At the same time, the values of the average interaction energy $V_{12}$ of an Fe atom with atoms located in its first two coordination shells for Fe$_{0.90}$Cr$_{0.10}$ and Fe$_{0.88}$Cr$_{0.12}$ alloys are $V_{12} = -0.0148(11)$ eV and $V_{12} = -0.0135(11)$ eV, respectively. In the authors’ opinion, these unique experimental data could play an important role in developing and testing different models of the binary Fe-Cr alloys as well as methods for calculating the system parameters.

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**References**


