

An enthalpy of solution of rhenium in iron studied by ^{57}Fe Mössbauer spectroscopy

Robert Konieczny · Rafał Idczak · Weronika Szarypo · Jan Chojcan

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Abstract The room temperature Mössbauer spectra of ^{57}Fe were measured for iron-based solid solutions $\text{Fe}_{1-x}\text{Re}_x$, with x in the range $0.01 \leq x \leq 0.05$. The obtained data were analysed in terms of the binding energy E_b between two rhenium atoms in the Fe-Re system. The extrapolated value of E_b for $x = 0$ was used for computation of enthalpy of solution of rhenium in iron. The result was compared with that resulting from the cellular atomic model of alloys by Miedema. The comparison shows that our findings are in a qualitative agreement with the Miedema's model predictions.

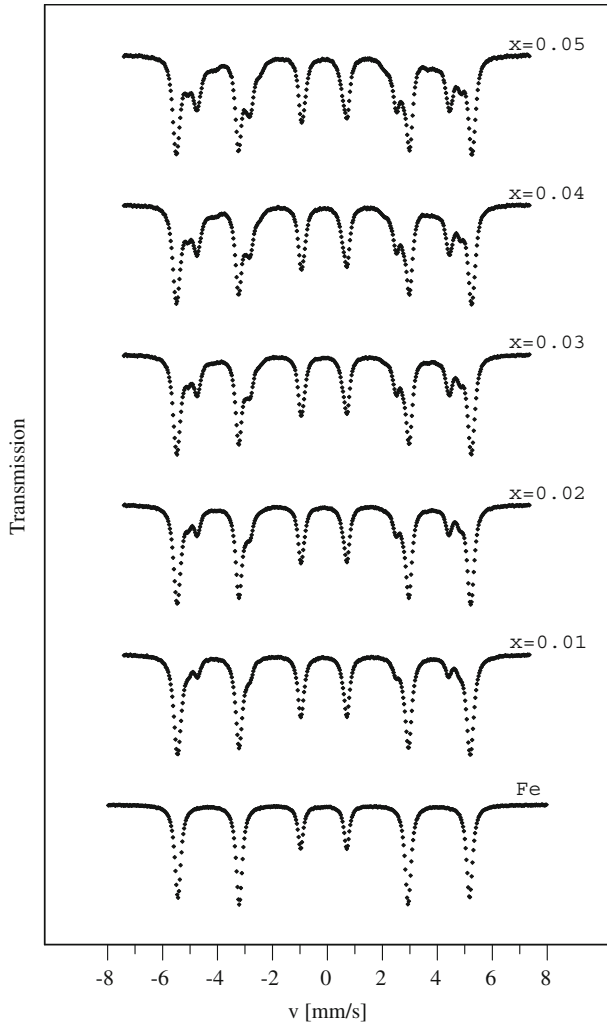
Keywords Mössbauer spectroscopy · Binding energy · Enthalpy of solution · Iron alloys

1 Introduction

The ^{57}Fe Mössbauer spectroscopy is a useful tool for the study of interactions of impurity atoms dissolved in iron [1–8]. At the same time from the findings concerning the impurity interactions one can easily derive the enthalpy of solution of the impurity elements in iron [9]. This considerably increases importance of the studies as the experimental values of the enthalpy play an essential role in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [10–16]. The main source of such experimental data is calorimetric study of the enthalpy of formation of binary systems [17]. Unfortunately, sometimes there are significant discrepancies in the data obtained by different authors. This is observed e.g. for the Fe-V alloys [18, 19]. Moreover, the calorimetric investigations are

R. Konieczny (✉) · R. Idczak · W. Szarypo · J. Chojcan
Institute of Experimental Physics, University of Wrocław,
pl. M. Borna 9, 50-204 Wrocław, Poland
e-mail: robi@ifd.uni.wroc.pl

Fig. 1 The ^{57}Fe Mössbauer spectra for the $\text{Fe}_{1-x}\text{Re}_x$ alloys measured at room temperature after the annealing process at 1270 K



performed in relatively high temperatures at which some of iron systems are in their high-temperature γ (fcc) phases. Such situation exists for instance in the case of the Fe-Mn system. Consequently, there is no calorimetric data concerning the enthalpy of solution of Mn in the low-temperature α (bcc) phase of Fe. All the above encouraged us to use the ^{57}Fe Mossbauer spectroscopy for supplying the experimental enthalpy of solution of different elements in α -Fe. In our previous studies we collected the proper spectra for the Fe-V [1], Fe-Cr [2], Fe-Mn [3], Fe-Al [4], Fe-Ni [5], Fe-Co [5], and Fe-Mo [6] alloys.

In this work we have extended the investigations to the Fe-Re system. According to our knowledge there is no experimental data concerning the enthalpy of solution of Re in Fe. The value of the enthalpy can be simply predicted only on the basis of the semi-empirical cellular atomic model of alloys developed by Miedema [10].

Table 1 Some of the best-fit parameters of the assumed model of the ^{57}Fe Mössbauer spectrum measured for $\text{Fe}_{1-x}\text{Re}_x$ alloys

x	B_0 [T]	ΔB_1 [T]	ΔB_2 [T]	ΔIS_1 [mm/s]	ΔIS_2 [mm/s]
0.01	33.197(15)	-4.710(10)	-2.396(28)	-0.0348(10)	0.0104(10)
0.02	33.296(16)	-4.7524(63)	-2.502(13)	-0.0344(10)	0.0119(11)
0.03	33.396(14)	-4.8039(58)	-2.561(11)	-0.0320(10)	0.0154(11)
0.04	33.474(17)	-4.8152(63)	-2.609(10)	-0.0318(12)	0.0170(14)
0.05	33.523(19)	-4.8260(64)	-2.6490(98)	-0.0328(11)	0.0222(27)

The standard uncertainties for the parameters result from the variance of the fit

2 Experimental and results

The samples of iron-rhenium alloys containing 1, 2, 3, 4 and 5 at. % of Re, were prepared by melting appropriate amounts of the Aldrich 99.999% pure iron and 99.99% pure rhenium in an arc furnace filled with argon. Resulting ingots were cold-rolled to the final thickness of about 0.05 mm and then the foils were annealed in vacuum at 1270 K for 2 h. After that they were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at about 700 K [20], so the observed distributions of atoms in the annealed samples should be the frozen-in state corresponding to 700 K (the ‘freezing’ temperature T_d). The room temperature measurements of the ^{57}Fe Mössbauer spectra for Fe-Re alloys were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design. The spectra measured are presented in Fig. 1.

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 Re atoms located in the first two coordination shells of the probing nuclei. It was done under assumption that the influence of Re 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 Re atoms located, respectively, in the first and second coordination shells of ^{57}Fe and the functions can be written as follows:

$$\begin{aligned}
 B(n_1, n_2) &= B_0 + n_1 \Delta B_1 + n_2 \Delta B_2, \\
 IS(n_1, n_2) &= IS_0 + n_1 \Delta IS_1 + n_2 \Delta IS_2,
 \end{aligned}
 \tag{1}$$

where ΔB_1 (ΔIS_1) and ΔB_2 (ΔIS_2) stand for the changes of B (IS) with one Re atom in the first and second coordination shell of the Mössbauer probe. At the same time the quadruple splitting QS of a subspectrum is a free parameter [21]. It is worth noticing that the fits obtained under these assumptions are quite good and the found values of the best-fit parameters (displayed in Table 1) are in a good agreement with corresponding data given in the literature; e.g. in Ref. [22] one can find that for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy $\Delta B_1 = -4.72(3)$ T, $\Delta B_2 = -2.25(7)$ T, $\Delta IS_1 = -0.035(5)$ mm/s.

As the main result of the analysis the values of parameters c_1 and c_2 of each spectrum were determined. Assuming that the Lamb-Mössbauer factor is independent of the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the parameters are total intensities of those components of a spectrum which are related to the

Table 2 The binding energy E_b between a pair of Re atoms in $\text{Fe}_{1-x}\text{Re}_x$ alloys deduced from the ^{57}Fe Mössbauer spectra

x	c_1	c_2	p_1	p_2	E_b (eV)
0.01	0.1758(15)	–	0.1229	0.0081	–
0.02	0.2472(25)	0.0206(30)	0.2153	0.0286	0.033(10)
0.03	0.3084(27)	0.0464(33)	0.2827	0.0568	0.0219(55)
0.04	0.3329(28)	0.0898(33)	0.3294	0.0892	0.0003(31)
0.05	0.3417(25)	0.1246(31)	0.3593	0.1229	–0.0054

The standard uncertainties for c_1 and c_2 result from the variance of the fit of the assumed model to the spectrum measured. The values of uncertainty for E_b were computed assuming that the uncertainty for the ‘freezing’ temperature T_d is 50 K

Table 3 The enthalpy $H_{\text{Fe-Re}}$ [eV/atom] of solution of rhenium in iron

Miedema’s model [10]	This work (α -Fe)
–0.015	–0.22(13)

existence of one and two Re atoms in the two first coordination shells of nuclear probes ^{57}Fe , respectively.

$$\begin{aligned}c_1 &= c(1, 0) + c(0, 1), \\c_2 &= c(2, 0) + c(1, 1) + c(0, 2).\end{aligned}\quad (2)$$

The results are listed in Table 2.

The c_1 and c_2 values were used to calculate the binding energy E_b for pairs of Re atoms in the studied materials (Table 2). The computations were performed on the basis of the modified Hryniewicz-Królas formula [7, 23]

$$E_b = -kT_d \cdot \ln \left[(1 + 2 \cdot c_2/c_1) \cdot (c_2/c_1) \cdot (1 + 2 \cdot p(2)/p(1))^{-1} \cdot (p(2)/p(1))^{-1} \right]. \quad (3)$$

In the next step we found the extrapolated value of E_b for $x = 0$ using $E_b(0.02)$ and $E_b(0.03)$. Finally, the $E_b(0)$ value was used for computation of the enthalpy of solution $H_{\text{Fe-Re}}$ of Re in iron. The calculations were performed on the basis of the Królas model [9] for the binding energy according to which

$$H_{\text{Fe-Re}} = -z \cdot E_b(0) / 2 \quad (4)$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α -Fe). The result is displayed in Table 3 together with the value resulting from Miedema’s model of alloys [10].

3 Conclusions

The positive value of the binding energy E_b between two rhenium atoms in the $\text{Fe}_{1-x}\text{Re}_x$ alloys with $x \leq 0.03$, speaks in favour of the suggestion that Re atoms interact repulsively in iron matrix. The value $-0.22(13)$ eV/atom for the enthalpy of solution $H_{\text{Fe-Re}}$ of rhenium in α -iron, determined from the ^{57}Fe Mössbauer spectra are in a qualitative agreement with that -0.015 eV/atom, resulting from the semi-empirical Miedema’s model of alloys [10] which is based on hundreds calorimetric data

concerning the heat of formation for different binary systems. Both $H_{\text{Fe-Re}}$ values mentioned above are negative but absolute values of them are essentially different.

Although till now, in the available literature, one cannot find proper theoretical calculations of $H_{\text{Fe-Re}}$, we hope that our experimental findings presented in this paper will stimulate such computations in future, just as it happened in the case of the Fe-Mo system [16].

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