An Enthalpy of Solution of Silicon in Iron Studied by ^{57}Fe Mössbauer Spectroscopy

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The room temperature Mössbauer spectra of ^{57}Fe were measured for Fe$_{1-x}$Si$_x$ solid solutions 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 silicon atoms in the studied materials using the extended Hrynkiewicz–Królas idea. The extrapolated value of E_b for $x = 0$ was used to computation of an enthalpy of solution H_{FeSi} of Si in α-Fe matrix. It was found that the H_{FeSi} value is negative or Si atoms interact repulsively. The result was compared with corresponding values given in the literature which were derived from experimental calorimetric data as well as with the value resulting from the cellular atomic model of alloys by Miedema.

1. Introduction

It has been proved that the ^{57}Fe Mössbauer spectroscopy is a useful tool for the study interactions of impurity atoms in iron alloys [1–6]. This technique is especially powerful when the impurity neighbours of the Mössbauer probe have a sufficiently large effect on the hyperfine field generated at the probe, to yield distinguishable components in the Mössbauer spectrum attributed to different configurations of the probe neighbours. From the data given in the literature (see [7] for example) it follows that there are many binary iron systems suitable for the studies mentioned above. Worth noting is the fact that the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [8]. The enthalpy are widely used in developing and testing different models of binary alloys and methods for calculating the alloy parameters [9–11]. Moreover, the Mössbauer spectroscopy findings in some cases can be unique i.e. impossible to obtain with other methods, in particular the calorimetric ones. It can happen because the Mössbauer studies provide information about enthalpy of solution at relatively low temperature, below the Curie temperature whereas the calorimetric investigations are performed for samples at relatively high temperatures, above the Curie temperature, at which influence of magnetic interactions on thermodynamic properties of studied alloys cannot be observed. Additionally, the Mössbauer studies concern iron alloys in low-temperature α(bcc) phase in contrast to high-temperature calorimetry where most of iron systems under investigation are in γ(fcc) phase [1–6, 12].

In this paper the dilute Fe–Si iron based alloys were investigated by ^{57}Fe Mössbauer spectroscopy in order to determine an enthalpy of solution H_{FeSi} of Si in α-Fe

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matrix [8, 13]. According to our knowledge in the available literature the values of enthalpy of solution of Si in Fe were estimated experimentally only for liquid phase at temperatures above 1700 K [14].

2. Experimental details and results
2.1. Samples preparation and measurements

The samples of Fe$_{1-x}$Si$_x$ alloys with x in the range $0.01 \leq x \leq 0.05$ were melted in an arc furnace under an argon atmosphere and quickly cooled down to the room temperature. The weight losses during the melting process were below 0.2% so the compositions of the obtained ingots were close to nominal ones. In the next step ingots were cold-rolled to the final thickness of about 0.04 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.

The room temperature measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 50 mCi ^{57}Co-in-Rh standard source with a full width at half maximum (FWHM) of 0.24 mm/s.

2.2. Data analysis

Each measured spectrum was fitted with a transmission integral for a sum of different six-line patterns corresponding to various isomer shifts IS as well as hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Si atoms located in the first coordination shell of the probing nuclei. The number of fitted six-line patterns depends on concentration of Si in the samples and was two for $x = 0.01$ and three for $x = 0.05$. At the same time, we assume that the quadrupole splitting QS in a cubic lattice is equal to zero. The fits obtained under these assumptions are presented in Figs. 1 and 2. For most dilute iron alloys [1–7], the fitting procedure was done under the assumption that the influence of impurity atoms on B as well as the corresponding isomer shift IS on a subspectrum, is additive and independent
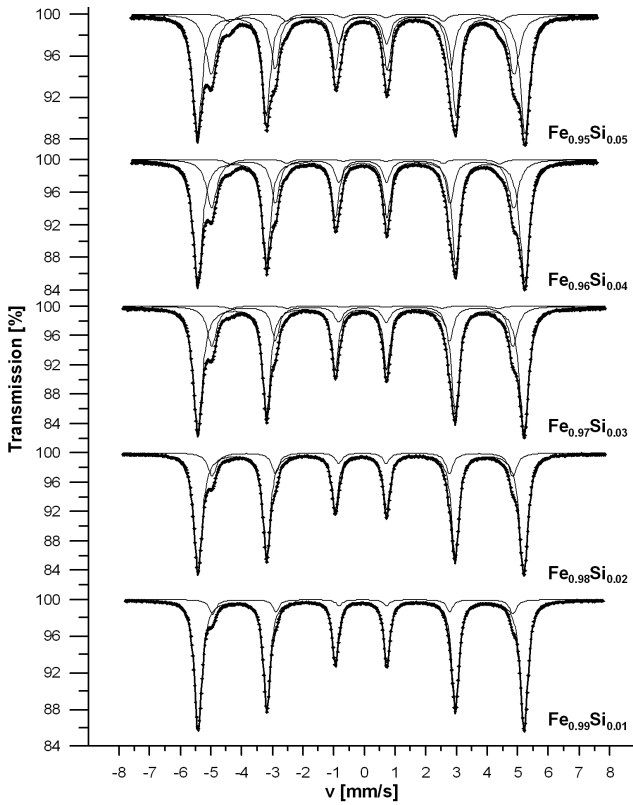
Fig. 1. The ^{57}Fe Mössbauer spectra for the Fe–Si alloys measured at room temperature before the annealing process at 1270 K, fitted with the Zeeman sextets.
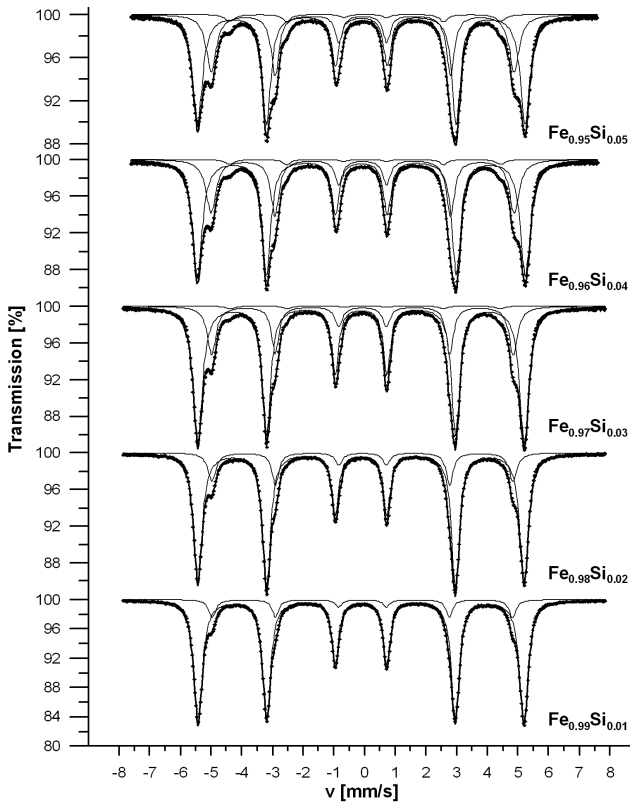

Fig. 2. As in Fig. 1, but after the annealing process.

of the atom positions in the first coordination shells of the nuclear probe (additive model). During analysis of measured spectra, it was found that that this assumption is not valid, in case of $Fe_{1-x}Si_x$ alloys. As one can notice in Table I, the $\Delta B2$ and $\Delta IS2$ values which are the changes of B and IS with two Si atoms in the first coordination shell of the Mössbauer probe are more than twice larger than $\Delta B1$ and $\Delta IS1$ (changes of B and IS with one Si atom). This fact suggests that influence of Si atoms on ^{57}Fe nuclei is much more complicated and it cannot be described by simple additive model. Finally, it is worth noting that the obtained values of $\Delta IS1$ are in quite good agreement with *ab initio* results presented by Błachowski et al. [15].

TABLE I

Some parameters of the assumed model fitted to the ^{57}Fe Mössbauer spectra measured for annealed $Fe_{1-x}Si_x$ alloys. The standard uncertainties for the parameters result from the variance of the fit. Values of the isomer shift IS_0 are reported relative to the corresponding value for α-Fe at room temperature.

x	B_0 [T]	$\Delta B1$ [T]	$\Delta B2$ [T]	IS_0 [mm/s]	$\Delta IS1$ [mm/s]	$\Delta IS2$ [mm/s]
0.01	32.909(3)	−2.57(2)	−	−0.0073(3)	0.0459(2)	−
0.02	32.948(4)	−2.55(2)	−	−0.0071(4)	0.0504(2)	−
0.03	32.964(6)	−2.50(1)	−5.71(9)	−0.0052(5)	0.0483(2)	0.139(3)
0.04	33.110(8)	−2.49(2)	−5.75(9)	0.0045(7)	0.0441(2)	0.124(2)
0.05	33.067(9)	−2.47(2)	−5.72(8)	0.0056(8)	0.0455(2)	0.124(1)

The effective thicknesses $T_A(n)$ related to components of each spectrum for studied samples could be expressed as follows:

$$T_A(n) = \sigma_0 t_A N f c(n), \tag{1}$$

where n stands for the number of Si atoms located, in the first coordination shell of ^{57}Fe, σ_0 is the maximal cross-section for nuclear γ resonance absorption, t_A denotes the thickness of the absorber, N stands for the total number of resonant absorbing atoms ^{57}Fe per unit volume, $c(n)$ 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 $c(n)$ can be easily calculated using the $T_A(n)$ values as in such case

$$c(n) = \frac{T_A(n)}{\sum T_A(n)}. \tag{2}$$

The computed $c(n)$ values were used to find parameters $c(0)$, $c(1)$ and $c(2)$ being the total intensities of those components of a spectrum which are related to the existence of zero, one, and two silicon atoms in the first coordination shell of nuclear probes ^{57}Fe. These parameters are presented in Fig. 3 together with calculated probabilities of finding zero $p(0)$, one $p(1)$ and two $p(2)$ Si atoms in the first coordination shell of an Fe atom in the random bcc $Fe_{1-x}Si_x$ alloy. In disordered (random) alloys, the probability $P(n)$ of local configuration of impurity

atoms in the first coordination shell of ^{57}Fe nucleus is described by the binomial distribution

$$P(n) = \frac{N!}{n!(N-n)!}x^n(1-x)^{N-n}, \tag{3}$$

where N denotes the coordination number of the first shell. In the case of Fe$_{1-x}$Si$_x$ alloys with the x range of $0.01 \leq x \leq 0.05$ where atoms are distributed in the bcc lattice, $N = 8$. To be sure that considered above model of spectrum is correct, the experimental parameters $c(0)$, $c(1)$, and $c(2)$ were compared with those resulting from the second possible model of the spectrum which assumes that Si atoms located in the two first coordination shells of ^{57}Fe probes influence the values of B and IS almost in the same way ($N = 14$ in Eq. (4)). As one can see in Fig. 3, the second model is unlikely.
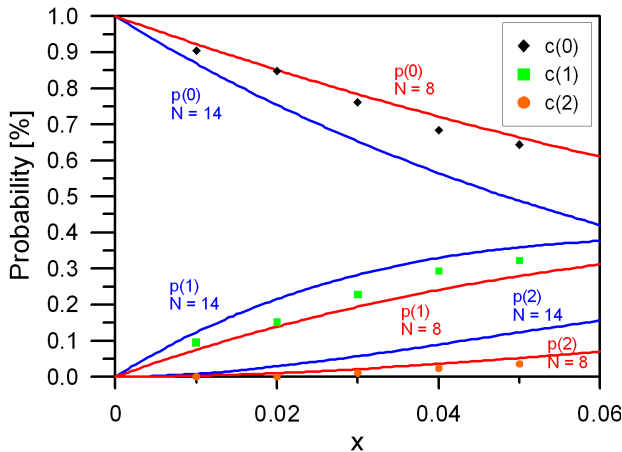

Fig. 3. Total intensities of those components of a spectrum which are related to the existence of zero $c(0)$, one $c(1)$ and two $c(2)$ Si atoms in the vicinity of nuclear probes ^{57}Fe in the Fe$_{1-x}$Si$_x$ alloys after the annealing process. The lines describe probabilities of finding zero $p(0)$, one $p(1)$ and two $p(2)$ Si atoms in the first ($N = 8$ red lines) and two first ($N = 14$ blue lines) coordination shells of an Fe atom in the random bcc Fe$_{1-x}$Si$_x$ alloy.

2.3. The binding energy of two Si atoms in Fe matrix

The binding energy E_b for pairs of Si atoms in the annealed materials was calculated using obtained $c(1)$ and $c(2)$ values. The calculations were performed on the basis of the modified Hrynkiewicz–Królas formula [1, 13], where E_b is expressed by

$$E_b = -kT_d \ln[(1 + 2c(2)/c(1))(c(2)/c(1))$$

$$\times(1 + 2p(2)/p(1))^{-1}(p(2)/p(1))^{-1}]. \tag{4}$$

In Eq. (4), k is the Boltzmann constant and T_d denotes the "freezing" temperature for the atomic distribution in a sample; $T_d = 700(50)$ K [3] in the case of the annealed sample. The estimated E_b values are 0.0559(55), 0.0432(32), and 0.0395(25) eV for Fe$_{0.97}$Si$_{0.03}$, Fe$_{0.96}$Si$_{0.04}$ and Fe$_{0.95}$Si$_{0.05}$, respectively. In the next step we found the extrapolated value of the binding energy E_b for $x = 0$.

The $E_b(0) = 0.095(31)$ eV. The obtained positive values of binding energy in Fe$_{1-x}$Si$_x$ alloys suggest that interaction between two Si atoms in iron matrix is repulsive.

2.4. An enthalpy of solution of silicon in iron

The $E_b(0)$ value was used to computation an enthalpy H_{FeSi} of solution of Si atoms in α-Fe matrix. The calculations were performed on the basis of the Królas model [8] for the binding energy according to which

$$H_{FeSi} = -zE_b(0)/2, \tag{5}$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α-Fe). The value of H_{FeSi} is presented in Table II together with corresponding values derived from calorimetric experiments [14] as well as calculated using the cellular atomic model of alloys developed by Miedema [9].

TABLE II

An enthalpy H_{FeSi} [eV/atom] of solution of silicon in iron.

Calorimetric data, liquid (1765 K) [14]	Miedema's model [9]	This work α−Fe (700 K)
–1.58	0.63	–0.38(13)

3. Conclusions

The results obtained in this study give rise to the following conclusions:

1. The obtained values of binding energy between two Si atoms in Fe–Si alloys suggest that interaction between Si atoms in the studied materials is repulsive.

2. The obtained value of enthalpy H_{FeSi} of solution of Si in α-Fe is –0.38(13) eV/atom. According to our knowledge, this thermodynamic parameter was estimated experimentally for the first time for Fe–Si system in α phase with atomic distributions corresponding to the temperature about 700 K (below the Curie temperature). Finally, it is worth noting that H_{FeSi} value calculated using Miedema's cellular atomic model of alloys is incorrect.

Acknowledgments

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