

Mössbauer studies of interactions between titanium atoms dissolved in iron

Robert Konieczny · Rafał Idczak · Jan Chojcan

© Springer Science+Business Media Dordrecht 2012

Abstract The room temperature ^{57}Fe Mössbauer spectra for binary iron-based solid solutions $\text{Fe}_{1-x}\text{Ti}_x$, with x in the range $0.010 \leq x \leq 0.045$, were analysed in terms of binding energy E_b between two Ti atoms in the Fe-Ti system. The extrapolated values of E_b for $x = 0$ were used for computation of enthalpy of solution of titanium in iron. The results were compared with that resulting from the Miedema's model of alloys as well as those derived from the heat of formation of the system, obtained with both calorimetric measurements and theoretical calculations. The comparison shows that our Mössbauer spectroscopy findings are in a quite good agreement with all the other results mentioned above.

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

1 Introduction

Properties of the Fe-Ti system are fundamentally important for the description of several higher-order systems of considerable technical interest. It is therefore important to establish the properties of the Fe-Ti system. Several attempts have been made using the calorimetric measurements [1–3] and theoretical calculations [4, 5], but the results differ considerably. When analyzing the properties of higher-order systems, various authors have chosen different descriptions of the Fe-Ti system. Thus, it seems urgent to compare the various available assessments.

The ^{57}Fe Mössbauer spectroscopy is a useful tool for the study of interactions of impurity atoms dissolved in iron [6–13]. In general, an appearance of impurity atoms in the vicinity of the Mössbauer probe leads to a change of the Mössbauer spectrum

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

hyperfine parameters such as isomer shift IS , quadruple splitting QS and hyperfine magnetic field B . The impurity interaction study is especially credible 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 [14] for example) it follows that there are many binary iron systems suitable for the studies mentioned above. The fact is worth noticing as the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [15] and the enthalpy is widely used in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [16–20]. Moreover, the Mössbauer spectroscopy findings concerning the enthalpy in some cases can be useful to verify the corresponding experimental data derived from the calorimetric studies [21, 22]. The possibility is limited because the calorimetric investigations are performed in relatively high temperatures at which most of iron systems are in their high-temperature paramagnetic phases, mainly γ (fcc) whereas the Mössbauer studies provide information about enthalpy of solution in low-temperature ferromagnetic phase α (bcc). In other words, in comparison with calorimetric data, the Mössbauer values concern materials being at temperature closer to that at which they are normally used - the room temperature for example.

All the above encouraged us to use the ^{57}Fe Mössbauer spectroscopy to supply the “low-temperature” thermodynamic parameters of different iron systems. In this paper we present the results obtained for the Fe-Ti system.

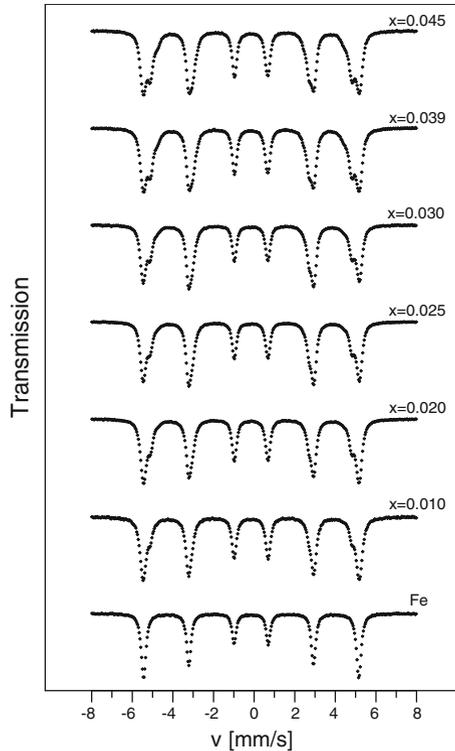
2 Experimental and results

The samples of $\text{Fe}_{1-x}\text{Ti}_x$ alloys with $x = 0.010, 0.025, 0.030, 0.039$ and 0.045 , were prepared by melting appropriate amounts of the Aldrich 99,98 % pure iron and 99,99 % pure titanium in an arc furnace filled with argon. The weight losses during the melting process were below 1 % so the compositions of the obtained ingots were close to nominal ones. Resulting ingots were cold-rolled to the final thickness of about 0.05 mm. In the next step 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 [12, 23], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to 700 K.

The room temperature measurements of the ^{57}Fe Mössbauer spectra for each sample were performed twice – before and after the annealing process mentioned above. The spectra were taken in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 60 mCi ^{57}Co -in-Rh standard source with a full width at half maximum (FWHM) of 0.24 mm/s. Some of the spectra are presented in Fig. 1.

Each measured spectrum was fitted with a sum of certain number of different six-line patterns corresponding to unlike hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Ti atoms located in the first two coordination shells of the probing nuclei. The number of fitted patterns increased with concentration of Ti in the samples and in the case of $x > 0.020$ it was three. The fitting procedure was done under assumption that the influence of Ti atoms on B as well as the

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



corresponding isomer shift IS of a six-line subspectrum, is additive and independent of the atom positions in the first two coordination shells of the nuclear probe [14]. In other words it was accepted that for each subspectrum the quantities B and IS are linear functions of the number n of Ti atoms located in the first two coordination shells of ^{57}Fe and the functions can be written as follows:

$$\begin{aligned} B(n) &= B + n\Delta B_{1,2} \\ IS(n) &= IS + n\Delta IS_{1,2} \end{aligned} \quad (1)$$

where $\Delta B_{1,2}$ ($\Delta IS_{1,2}$) stands for the change of B (IS) with one Ti atom in the first or second coordination shell of the Mössbauer probe. At the same time the quadruple splitting QS was accepted to be zero. Moreover, it was assumed that the shape of each line is lorentzian and the three linewidths Γ_{16} , Γ_{25} and Γ_{34} as well as the two line area ratios I_{16}/I_{34} and I_{25}/I_{34} are the same for all six-line components of the given spectrum. It is worth noticing that the fits obtained under these assumptions are quite good – see Fig. 2. 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. [14] one can find that for the $\text{Fe}_{0.97}\text{Ti}_{0.03}$ alloy $\Delta B_{1,2} = -1.91(3)$ T and $\Delta IS_{1,2} = -0.013(2)$ mm/s.

As the main result of the analysis the values of parameters c_1 and c_2 of the second and third components of each spectrum were determined. The components are related to the existence of one Ti atom and two Ti atoms in the neighbourhood of

Fig. 2 The ^{57}Fe Mössbauer spectrum for the $\text{Fe}_{0.955}\text{Ti}_{0.045}$ alloy measured at room temperature after the annealing process at 1270 K, fitted with three six-line subspectra

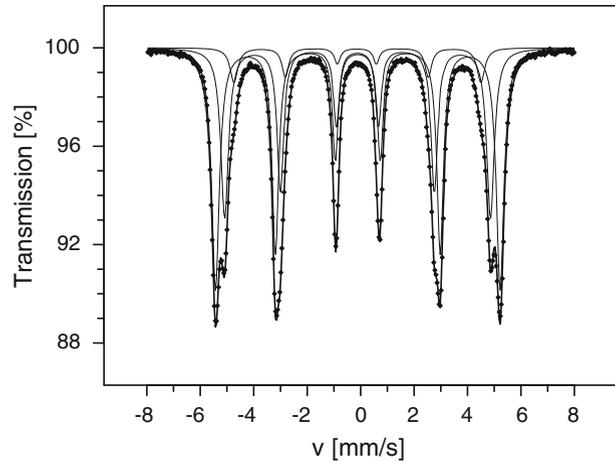


Table 1 Some of the best-fit parameters of the assumed model of the ^{57}Fe Mössbauer spectrum measured for annealed samples of $\text{Fe}_{1-x}\text{Ti}_x$ alloys

x	$B_0[\text{T}]$	$\Delta B_{1,2}[\text{T}]$	IS_0 [mm/s] (relative to $\alpha\text{-Fe}$)	$\Delta IS_{1,2}$ [mm/s]
0.010	33.184(35)	-2.144(12)	0.00078(33)	-0.012(13)
0.020	33.089(20)	-2.184(51)	0.00263(20)	-0.0139(53)
0.025	33.184(16)	-2.181(40)	0.00332(16)	-0.0145(40)
0.030	33.190(22)	-2.198(46)	0.00390(22)	-0.0156(46)
0.039	33.121(27)	-2.197(45)	0.00389(27)	-0.0127(44)
0.045	33.165(26)	-2.194(41)	0.00494(25)	-0.0133(40)

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

^{57}Fe , respectively. Assuming that the Lamb-Mössbauer factor is independent of the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the c_1 and c_2 values describe intensities of the components mentioned above. 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 Ti atoms in the studied materials. The computations were performed, on the basis of the modified Hryniewicz-Królas formula [6] for E_b :

$$E_b = -kT_d \ln((1 + 2c_2/c_1)(c_2/c_1)(1 + 2p(2)/p(1))^{-1}(p(2)/p(1))^{-1}). \quad (2)$$

In Eq. 2, k is the Boltzmann constant, T_d denotes the “freezing” temperature for the atomic distribution in the sample ($T_d = 700(50)$ K) whereas $p(1)$ and $p(2)$ are probabilities for the existence of one and two Ti atoms among all N atoms located in the first two coordination spheres of the ^{57}Fe probe in corresponding random alloy (for b.c.c lattice $N = 6 + 8 = 14$). The values of p are computed with the binomial function $p(n) = [N!/((N - n)!n!)]x^n(1-x)^{N-n}$ where $n = 1$ or 2 and x stands for a concentration of titanium atoms in the alloy. The obtained E_b values are collected in Table 2.

In the next step we found the extrapolated value of binding energy E_b for $x = 0$, using the E_b values derived from data for samples with the smallest content of Ti,

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

x	c_1	c_2	$p(1)$	$p(2)$	E_b (eV)
0.010	0.2062(21)	–	0.1229	0.0081	–
0.020	0.2821(12)	–	0.2153	0.0286	–
0.025	0.2970(11)	0.02020(82)	0.2518	0.0420	0.0637(53)
0.030	0.3259(14)	0.0334(10)	0.2827	0.0568	0.0499(42)
0.039	0.3755(14)	0.0695(11)	0.3294	0.0892	0.0279(24)
0.045	0.3809(13)	0.0778(10)	0.3462	0.1060	0.0326(26)

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 $H_{\text{Fe-Ti}}$ [eV/atom] of solution of titanium in iron

Paramagnetic phase		Ferromagnetic phase	
Calorimetric data *[21],** [2],*** [3]	Miedema’s model [16]	#LDA [4] #MEAM [5]	This work
–0.42*		–1.04 [#]	
–0.64**	–0.791	–0.52 ^{##}	–0.53(15)
–1.14***			

i.e. with $x = 0.025$ and 0.030 . Such procedure was determined by the fact that the applied Hryniewicz-Królas method of the E_b estimation was developed for very dilute alloys-with x close to zero. Finally, the found value of $E_b(0)$ equal to $0.133(38)$ eV, was used for computation of the enthalpy $H_{\text{Fe-Ti}}$ of solution of titanium in iron. The calculations were performed on the basis of the Królas model [15] for the binding energy according to which

$$H_{\text{Fe-Ti}} = -z \cdot E_b(0)/2, \quad (3)$$

where z is the coordination number of the crystalline lattice ($z = 8$ for $\alpha\text{-Fe}$). The result is displayed in Table 3 together with the findings based on calorimetric measurements [2, 3, 21] and theoretical calculation [4, 5] of the enthalpy of formation H^{for} of the Fe-Ti alloys as well as the value resulting from the cellular atomic model of alloys developed by Miedema [16]. The enthalpy of formation is related to the enthalpy of solution in the following way:

$$H_{\text{Fe-Ti}} = [dH^{\text{for}}/dx]_{x=0}. \quad (4)$$

3 Conclusions

Positive values of binding energy between two Ti atoms in the studied $\text{Fe}_{1-x}\text{Ti}_x$ alloys suggest that interaction between titanium atoms in ferromagnetic iron matrix is repulsive when concentration of the atoms is relatively small - not exceeding about 4.5 at. % in our case.

An enthalpy $H_{\text{Fe-Ti}}$ of solution of titanium in iron obtained with the ^{57}Fe Mössbauer spectroscopy is of negative value equal to $-0.53(15)$ eV/atom. The value agrees quite good with corresponding value resulting from the Miedema’s model of alloys

[16] as well as those derived from the heat H^{for} of formation of the Fe-Ti systems, obtained with both calorimetric methods [2, 3, 21] and theoretical calculations: LDA and MEAM [4, 5].

The result is interesting because the Mössbauer spectroscopy delivers information on the dilute-limit enthalpy of solution of titanium in the α (bcc) phase of Fe, being at about 700 K or in the ferromagnetic state whereas the calorimetric data concern iron systems at relatively high temperatures at which they are paramagnetic phases γ (fcc). It may suggest that for the Fe-Ti system the determined $H_{\text{Fe-Ti}}$ value hardly depends on structural and magnetic properties of the system, which are influenced by its temperature.

Acknowledgements This work was supported by the University of Wrocław under the grant 2282/M/IFD/12.

References

1. Kostov, A., Friedrich, B., Živković, D.: Thermodynamic calculations in alloys Ti-Al, Ti-Fe, Al-Fe and Ti-Al-Fe. *J. Min. Metall.* **44B**, 49 (2008)
2. Gachon, J.C., Hertz, J.: Calphand: Comput. Coupling Phase Diagrams Thermochem. **7**, 1 (1983)
3. Dumitrescu, L.F.S., Hillert, M., Saunders, N.: Comparison of the Fe-Ti assessments. *J. Phase Equilibria* **19**, 441 (1998)
4. Watson, R.E., Weinert, W.: Transition-metal aluminide formation: Ti, V, Fe, and Ni aluminides. *Phys. Rev. B* **58**, 5981 (1998)
5. Inyoung, S., Byeong-Joo, L.: Modified embedded-atom method interatomic potentials for the Fe-Nb and Fe-Ti binary systems. *Scripta Materialia* **59**, 595 (2008)
6. Chojcan, J.: Interaction between impurity atoms of 3d transition metals dissolved in iron. *J. Alloys Compd.* **264**, 50 (1998)
7. Chojcan, J.: A dilute-limit heat of solution of 3d transition metals in iron studied with ^{57}Fe Mössbauer spectroscopy. *Hyperfine Interact.* **156/157**, 523 (2004)
8. Chojcan, J., Konieczny, R., Ostrasz, A., Idczak R.: A dilute-limit heat of solution of molybdenum in iron studied with ^{57}Fe Mössbauer spectroscopy. *Hyperfine Interact.* **196**, 377 (2010)
9. Idczak, R., Konieczny, R., Chojcan, J.: Thermodynamic properties of Fe-Ni solid solutions studied by ^{57}Fe Mössbauer spectroscopy. *Phys. B* **407**, 235 (2012)
10. Konieczny, R., Idczak, R., Elsner, J., Chojcan J.: An enthalpy of solution of platinum in iron studied by ^{57}Fe Mössbauer spectroscopy. *Hyperfine Interact.* **206**, 119 (2012)
11. Konieczny, R., Idczak, R., Szarypo, W., Chojcan, J.: An enthalpy of solution of rhenium in iron studied by ^{57}Fe Mössbauer spectroscopy. *Hyperfine Interact.* **206**, 135 (2012)
12. Idczak R., Konieczny R., Chojcan J.: An enthalpy of solution of chromium in iron studied with ^{57}Fe Mössbauer spectroscopy. *Phys. B* **407**, 2078 (2012)
13. Idczak, R., Konieczny, R., Konieczna, Ż., Chojcan, J.: An enthalpy of solution of cobalt and nickel in iron studied with ^{57}Fe Mössbauer spectroscopy. *Acta Phys. Polon. A* **119**, 37 (2011)
14. Vincze, I., Campbell, I.A.: Mössbauer measurements in iron based alloys with transition metals. *J. Phys. F* **3**, 647 (1973)
15. Królas, K.: Correlation between impurity binding energies and heat of formation of alloys. *Phys. Lett. A* **85**, 107 (1981)
16. Miedema, A.R.: Energy effects and charge transfer in metal physics, modeling in real space. *Phys. B* **182**, 1 (1992)
17. Bonny, G., Pasionot, R.C., Malerba, L., Caro, A., Olsson, P., Lavrentiev, M.Y.: Numerical predictions of thermodynamic properties of iron-chromium alloys using semi-empirical cohesive models: the state of the art. *J. Nucl. Mater.* **385**, 268 (2009)
18. Boom, R., De Boer, F.R., Niessen, A.K., Miedema, A.R.: Enthalpies of formation of liquid and solid binary alloys based on 3d metals. *Phys. B* **115**, 285 (1983)
19. Dursun, I.H., Güvenç, Z.B., Kasap, E.: A simple analytical EAM model for bcc metals. *Commun. Nonlinear Sci. Numer. Simul.* **15**, 1259 (2010)

20. Lejaeghere, K., Cottenier, S., Claessens, S., Waroquier, M., Van Speybroeck, V.: Assessment of a low-cost protocol for an ab initio based prediction of the mixing enthalpy at elevated temperatures: the Fe-Mo system. *Phys. Rev. B* **83**, 184201 (2011)
21. Hultgren, R., Desai, P.D., Hawkins, D.T., Gleiser, M., Kelley, K.K.: Selected values of thermodynamic properties of binary alloys. American Society for Metals. Metals Park, Ohio (1973)
22. Swartzendruber, L.J., Itkin, V.P., Alcock, C.B.: Phase diagrams of binary iron alloys. In: Okamoto, H. (ed.) Materials information society. Materials Park, Ohio (1993)
23. Cranshaw, T.E.: A Mössbauer study of ^{119}Sn in alloys of iron with Si, Al, and Rh: interaction potentials and phase diagrams. *J. Phys.: Condensed Matter* **1**, 829 (1989)