Hyperfine Interact
DOI 10.1007/s10751-011-0480-8

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

Robert Konieczny · Rafał Idczak · Jakub Elsner · Jan Chojcan

Abstract The room temperature Mössbauer spectra of ^{57}Fe were measured for iron-based solid solutions $Fe_{1-x}Pt_x$ 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 platinum atoms in the studied materials using the extended Hrynkiewicz–Królas idea. It was found that for $x < 0.05$ the energy is positive or Pt atoms interact repulsively. The extrapolated value of E_b for $x = 0$ was used for computation of the enthalpy H_{Fe-Pt} of solution of platinum in iron. The result $H_{Fe-Pt} = -0.62(16)$ eV/atom was compared with the corresponding values resulting from the semi-empirical Miedema's model of alloys and the proper data obtained with Calphad's calculations as well as theoretical computations on the basis of the modified embedded-atom model. The comparison shows that all mentioned values of H_{Fe-Pt} are in a qualitative agreement i.e. they are negative, and moreover our findings agree also quantitatively with the Miedema's model predictions.

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

1 Introduction

It has been proved that the ^{57}Fe Mössbauer spectroscopy is a useful tool for the study of interactions of impurity atoms dissolved in iron [1–5]. The 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. Nevertheless, our present studies [6] show that the technique can

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

Published online: 29 November 2011

be also successfully applied to binary iron systems for which one observes unresolved Mössbauer spectra. The facts are worth noticing as the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [7] and the enthalpy is widely used in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [8–12]. 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 [13, 14]. 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 γ (fcc) phases whereas the Mössbauer studies provide information about enthalpy of solution in low-temperature α (bcc) phase. All the above encouraged us to use the ^{57}Fe Mössbauer spectroscopy for supplying the experimental enthalpy of solution of different elements in α-Fe.

In this paper we present results of the enthalpy investigations of the Fe-Pt system. For the system the shape of a spectrum is directly affected by atoms located in the first two coordination shells of the probing nuclei, but the Pt atoms have relatively small effect on the hyperfine field generated at the probe ^{57}Fe [15] and the spectrum measured is unresolved so simple study of annealed samples only does not give satisfied results. That is why to obtained proper data we performed the present studies such as previously for the Fe-Ni and Fe-Co systems [6].

2 Experimental and results

The samples of $Fe_{1-x}Pt_x$ alloys with x equal to 0.01, 0.02, 0.03, 0.04 and 0.05 were prepared by melting the Aldrich 99.999% pure iron and 99.9% pure platinum in an arc furnace filled with argon. The ingots were cold-rolled to the final thickness of about 0.02 mm and then the room temperature ^{57}Fe Mössbauer spectra were measured for the foils by means of a constant-acceleration POLON spectrometer of standard design. In the next step the samples 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 [16], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to 700 K (the 'freezing' temperature T_d). Spectra for these samples are presented in Fig. 1

All the obtained spectra were analysed in terms of three six-line patterns corresponding to different hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Pt atoms located in the first two coordination shells of the probing nuclei. It was done under assumption that the influence of n Pt atoms on B as well as the corresponding isomer shift (IS) is additive and independent of the atom positions in the neighbourhood of the nuclear probe so the relationship between B, IS and n can be written as follows:

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

where $\Delta B_{1,2}$ ($\Delta IS_{1,2}$) stand for the changes of B (IS) with one Pt atom in the first or second coordination shell of the Mössbauer probe. At the same time the quadruple splitting (QS) of a subspectrum is a free parameter [17]. In most cases the above assumptions are enough to obtain reasonable results. However, platinum neighbours

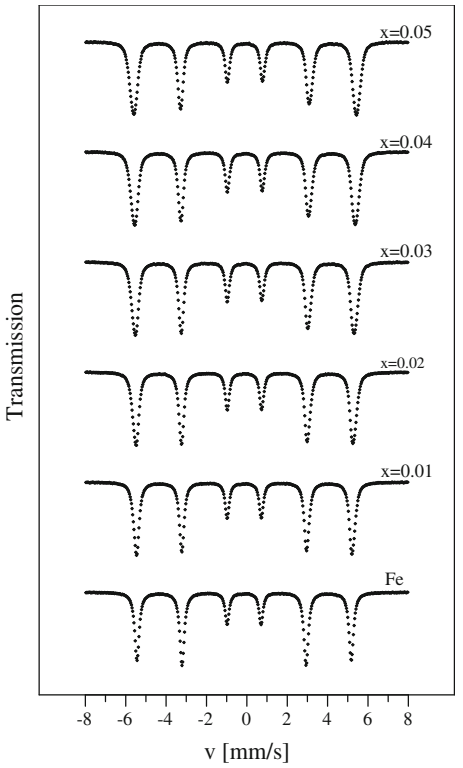

Fig. 1 The room temperature ^{57}Fe Mössbauer spectra for $Fe_{1-x}Pt_x$ alloys annealed in vacuum at 1,270 K for 2 h and slowly cooled to room temperature

Table 1 Some of the best-fit parameters of the assumed model of the ^{57}Fe Mössbauer spectrum measured for as-obtained samples of $Fe_{1-x}Pt_x$ alloys

x	B_0 [T]	$\Delta B_{1,2}$[T]	IS_0[mm/s] (relative to α-Fe)	$\Delta IS_{1,2}$[mm/s]
0.01	33.217(10)	0.9535(87)	0.0057(25)	0.0149(82)
0.02	33.346(11)	1.0220(52)	0.0130(26)	0.0146(49)
0.03	33.435(14)	0.9235(45)	0.0195(29)	0.0131(39)
0.04	33.579(19)	0.9500(45)	0.0291(32)	0.0110(36)
0.05	33.686(22)	0.9525(41)	0.0383(36)	0.0079(34)

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

of the Mössbauer probe have a very small effect on the hyperfine field generated at the probe—see Fig. 1, so proper decomposition of the Mössbauer spectra to several components is impossible without additional assumptions on parameters of the components. The successful analysis of the experimental data was performed by taking into account two series of the spectra, measured for samples as-obtained in an arc furnace and after a certain heat treatment—see [6] for details. 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 quantitative agreement with corresponding data given in the literature; e.g. in Ref. [15]. The results were

Table 2 The binding energy E_b between a pair of Pt atoms in $Fe_{1-x}Pt_x$ alloys deduced from the ^{57}Fe Mössbauer spectra

x	c_1	c_2	$p(1)$	$p(2)$	E_b(eV)
0.01	0.1449(10)	–	0.1229	0.0081	–
0.02	0.2647(11)	0.01282(27)	0.2153	0.0286	0.069(13)
0.03	0.3715(17)	0.0521(14)	0.2827	0.0568	0.0272(77)
0.04	0.4155(18)	0.0944(14)	0.3294	0.0892	0.0141(49)
0.05	0.4434(20)	0.1683(15)	0.3593	0.1229	−0.0089(19)

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_{Fe-Pt} [eV/atom] of solution of platinum in iron

Miedema's model [11]	MEAM (γ-Fe) [18]	CALPHAD (γ-Fe) [19]	This work (α-Fe)
−0.585	−1.14	−1.18	−0.62(16)

used to determine parameters c_1 and c_2 for annealed samples (Table 2). Assuming that the Lamb-Mössbauer factor is independent of the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the c parameters describe intensities of the components of a spectrum which are related to the existence of one and two Pt atoms in the two first coordination shells of ^{57}Fe.

Using the c_1 and c_2 values we calculated the binding energy E_b for pairs of Pt atoms in the studied materials (Table 2). The computations were performed, as in Refs. [1–6], on the basis of the modified Hrynkiewicz-Królas formula [1] for a $Fe_{1-x}D_x$ system

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

The E_b values are presented in Table 2.

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 enthalpy H_{Fe-Pt} of solution of platinum in iron. The calculations were performed on the basis of the Królas model [7] for the binding energy according to which:

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

where z is the coordination number of the crystalline lattice ($z = 8$ for α-Fe). The result is displayed in Table 3 together with proper value resulting from the Miedema's model of alloys [11] as well as with corresponding findings obtained with the modified embedded-atom model (MEAM) [18] and CALPHAD calculation [19] for γ (fcc) iron.

3 Conclusions

The positive values of the binding energy E_b between a pair of platinum atoms in the dilute iron-based Fe-Pt alloys speaks in favor of the suggestion that Pt atoms interact repulsively in iron matrix.

The enthalpy H_{Fe-Pt} of solution of platinum in iron determined from the ^{57}Fe Mössbauer spectra, −0.62(16) eV/atom, and the corresponding value of H_{Fe-Pt} resulting from the Miedema's model of alloys, −0.585 eV/atom, are practically the same or they are in a very good quantitative agreement. The result is interesting because the Mössbauer spectroscopy delivers information on the enthalpy of solution of platinum in the α (bcc) phase of Fe, being at about 700 K or in the ferromagnetic state whereas the semiempirical Miedema's model is based on calorimetric data which concern iron systems at relatively high temperatures at which they are paramagnetic. In other words the findings suggest that the experimental H_{Fe-Pt} value is practically independent of the magnetic order of iron and its temperature when the temperature exceeds 700 K.

The absolute values of H_{Fe-Pt} for γ (fcc) iron, resulting from the modified embedded-atom model (MEAM) [18] as well as calculations with the CALPHAD method [19] are about twice the value obtained by us for α-Fe. The difference is large enough to think that the unlike structure of the considered systems is not the only reason for that.

Acknowledgements This work was supported by the University of Wrocław under the grant 1466/M/IFD/11.

References

1. Chojcan, J.: Interaction between impurity atoms of 3d transition metals dissolved in iron. J. Alloys Compd. **264**, 50 (1998)
2. 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)
3. Chojcan, J.: Interactions between V atoms in iron-based Fe-V solid solutions. J. Alloys Comp. **350**, 62 (2003)
4. Chojcan, J., Ostrasz, A.: A dilute-limit heat of solution of aluminium in iron studied with ^{57}Fe Mössbauer spectroscopy. Acta Phys. Pol. A **114**, 1573 (2008)
5. 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)
6. Idczak, R., Konieczny, R., Konieczna, Ż, Chojcan, J.: An enthalpy of solution of cobalt and nickel in iron studiem with ^{57}Fe Mössbauer spectroscopy. Acta Phys. Polon. A **119**, 37 (2011)
7. Królas, K.: Correlation between impurity binding energies and heat of formation of alloys. Phys. Lett. A **85**, 107 (1981)
8. Bonny, G., Pasianot, R.C., Malerba, L., Caro, A., Olsson, P., Lavrentiev, M.Yu.: 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)
9. 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. Physica **115B**, 285 (1983)
10. Dursun, I.H., Güvenç, Z.B., Kasap, E.: A simple analytical EAM model for some bcc metals. Commun. Nonlinear Sci. Numer. Simulat. **15**, 1259 (2010)
11. Miedema, A.R.: Energy effects and charge transfer in metal physics, modeling in real space. Physica B **182**, 1 (1992)
12. Lejaeghere, K., Cottenier, S., Claessens, S., Waroquier, M., Van Speybroeck, V.: Assessment of a low-cost protocol for an ab inito based prediction of the mixing enthalpy at elevated temperatures: the Fe-Mo system. Phys. Rev. B **83**, 184201 (2011)
13. 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)
14. Swartzendruber, L.J., Itkin, V.P., Alcock, C.B.: In: Okamoto, H. (ed.) Phase diagrams of binary iron alloys. Materials Information Society, Materials Park, Ohio (1993)
15. Vincze, I., Campbell, I.A.: Mössbauer measurements in iron based alloys with transition metals. J. Phys. F **3**, 647 (1973)

16. 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.: Condens. Matter **1**, 829 (1989)
17. Falepin, A., Cottenier, S., Comrie, C.M., Vantomme, A.: Interpreting Mössbauer spectra reflecting an infinite number of sites: an application to $Fe_{1-x}Si$ synthesized by pulsed laser annealing. Phys. Rev. B **74**, 184108 (2006)
18. Kim, J., Koo, Y., Lee, B.-J.: Modified embedded-atom method interatomic potential for the Fe–Pt alloy system. J. Mater. Res. **21**, 199 (2006)
19. Fredriksson, P., Sundman, B.: A thermodynamic assessment of the Fe–Pt system. Calphad **25**, 535 (2001)