An Enthalpy of Solution of Cobalt and Nickel in Iron Studied with ^{57}Fe Mössbauer Spectroscopy

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The room temperature Mössbauer spectra of ^{57}Fe were measured for iron-based solid solutions $Fe_{1-x}Co_x$ and $Fe_{1-x}Ni_x$ 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 Co or Ni atoms in the studied materials using the extended Hrynkiewicz–Królas idea. It was found that the energy is positive or the non-iron atoms interact repulsively. The extrapolated value of E_b for $x = 0$ was used for computation of the enthalpy of solution of cobalt and nickel in iron. The results were compared with our previous Mössbauer spectroscopy findings, the values resulting from the Miedema's model of alloys and the data derived from the enthalpy of formation of the Fe-Co and Fe-Ni systems, obtained with calorimetric methods. The comparison shows that the present results are in a qualitative agreement with the Miedema's model predictions and calorimetric measurements but they are at variance with the previous Mössbauer spectroscopy findings.

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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 [1–6]. 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. 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. The fact is worth noticing as the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [8] and the enthalpy is widely used in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [9–14]. 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 [15, 16]. 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.

The data concerning enthalpy of solution of Ni and Co in iron, previously derived by us from the proper ^{57}Fe Mössbauer spectra [2, 4], are at variance with both Miedema's model predictions and calorimetric data. It seems that such situation exists because the Co and Ni neighbours of the Mössbauer probe in iron crystal have too small effect on the hyperfine field generated at the probe, to yield distinguishable components in the Mössbauer spectrum attributed to unlike configurations of the probe neighbours. Taking the above into account we decided to repeat the Mössbauer study of the Fe-Co and Fe-Ni systems and use a different method for analysis of the obtained spectra.

2. Experimental and results

The samples of $Fe_{1-x}Co_x$ and $Fe_{1-x}Ni_x$ 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, 99.98% pure nickel and 99.995% pure cobalt 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. The ingots were cold-rolled to the final thickness of about 0.05 mm and then the room temperature ^{57}Fe Mössbauer spectra were measured for the foils by means a constant-acceleration POLON spectrometer of standard design. In the next step the samples were annealed in vacuum at 1270 K for 4 h. After that they were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at about 700 K [17], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to 700 K. Spectra for these samples are presented in Fig. 1 and Fig. 2.

All the measured 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 non-iron atoms located in the first two coordination shells of the probing nuclei. It was done under assumption that the influence of the n non-iron atoms on B as well as the corresponding isomer shift (IS) is additive and independent of the atom positions in the

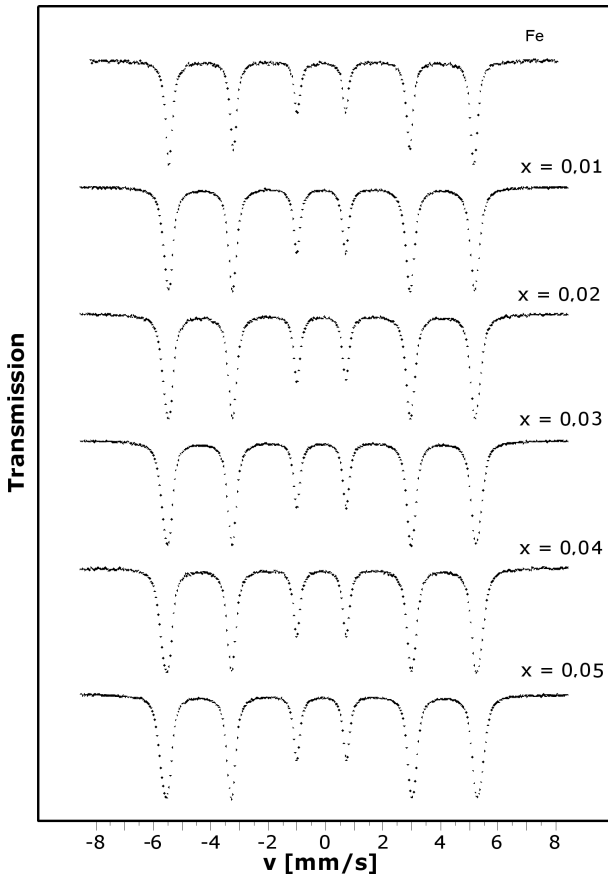* corresponding author; e-mail: `ridczak@ifd.uni.wroc.pl`

Fig. 1. The ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Co_x$ alloys measured at room temperature after the annealing process at 1270 K.

Fig. 2. The ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Ni_x$ alloys measured at room temperature after the annealing process at 1270 K.

neighbourhood of the nuclear probe so the relationship between B, IS and n can be written as follows:

$$B(n) = B_0 + n\Delta B,$$

$$IS(n) = IS_0 + n\Delta IS, \tag{1}$$

where ΔB (ΔIS) stand for the changes of B (IS) with one non-iron 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 [18]. 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.

In most cases the above assumptions are enough to obtain reasonable results. However, cobalt and nickel neighbours of the Mössbauer probe have a very small effect on the hyperfine field generated at the probe — see Fig. 1 and Fig. 2, so proper decomposition of the Mössbauer spectra to several components is impossible without additional assumptions on parameters of the components. For successful analysis of these spectra we suggest to use two series of measurements. The first for samples just after melting being frozen-in high temperature state and second for samples after annealing at 1270 K.
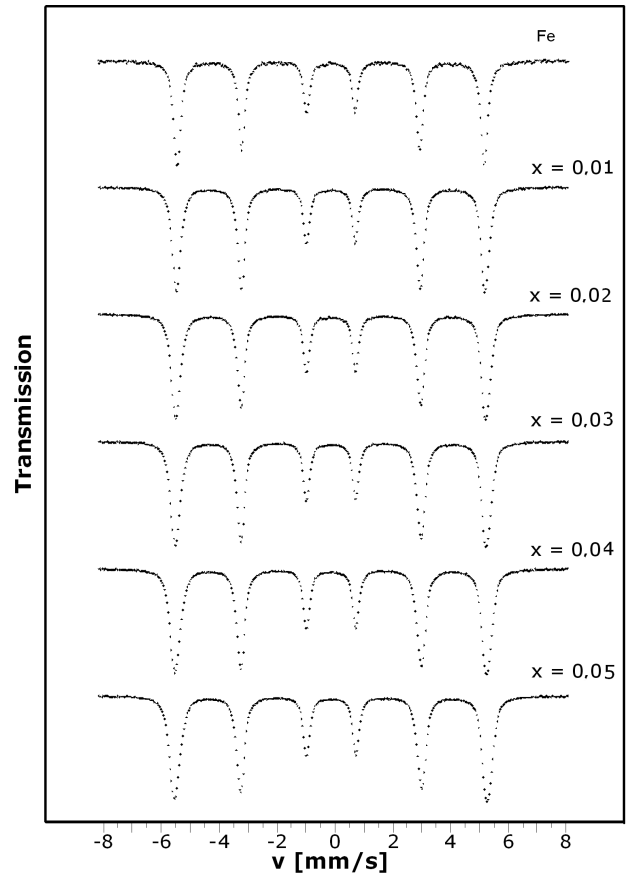
TABLE I

Some of the best-fit parameters of the assumed model of the ^{57}Fe Mössbauer spectrum measured for as-obtained alloys $Fe_{1-x}Co_x$ and $Fe_{1-x}Ni_x$. The standard uncertainties for the parameters result from the variance of the fit.

	Fe-Ni		Fe-Co	
x	B_0 [T]	ΔB [T]	B_0 [T]	ΔB [T]
0.01	33.0138(30)	7.55(26)	32.9730(30)	9.40(27)
0.02	33.0769(40)	7.26(17)	33.0214(36)	9.40(16)
0.03	33.0576(50)	7.25(14)	33.1097(46)	9.61(13)
0.04	33.0563(61)	7.27(12)	33.1491(45)	9.662(95)
0.05	33.0668(73)	7.45(12)	33.1581(41)	9.820(67)

The first series of samples one can treat as disorder alloys where the probability for the existence of n non-iron atoms among all N atoms located in the two first coordination shells of the Fe atom is given by binomial distribution $p(n) = \left[N!/\left((N-n)!n!\right)\right]x^n(1-x)^{N-n}$. The B values obtained under this assumption are presented in Table I. They were used to determine parameters c_1 and c_2 for annealed samples — Table II. The parameters are intensities of the components of a spectrum which are

related to the existence of one or two non-iron 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 Co and Ni atoms in the studied materials (Table II). The computations were performed on the basis of the modified Hrynkiewicz–Królas formula [2, 19] for a $Fe_{1-x}D_x$ system:

$$E_b = -kT_d ln\Big((1 + 2c_2/c_1)(c_2/c_1)$$
$$\times \big(1 + 2p(2)/p(1)\big)^{-1}\big(p(2)/p(1)\big)^{-1}\Big), \qquad (2)$$

where k is the Boltzmann constant, T_d denotes the "freezing" temperature for the atomic distribution in the annealed sample ($T_d = 700$ K). The E_b values are presented in Table II.

In the next step we found the extrapolated value of E_b for $x = 0$ using $E_b(0.03)$ and $E_b(0.04)$ for Fe-Ni; $E_b(0.02)$ and $E_b(0.03)$ for Fe-Co systems. Finally, the $E_b(0)$ value was used for computation of enthalpy of solution H^{sol} of cobalt and nickel in iron. The calculations were performed on the basis of the Królas model [8] for the binding energy according to which:

$$H^{sol} = -zE_b(0)/2, \qquad (3)$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α-Fe). The results are displayed in Table III together with previous Mössbauer spectroscopy findings [2, 4], values resulting from the Miedema's model of alloys [9] and corresponding data derived from the enthalpy of formation of the system, obtained with calorimetric measurements [16, 20].

TABLE III

Enthalpy of solution H^{sol} [eV/atom] of nickel and cobalt in iron.

	Miedema model	Calorimetric data (γ-Fe)	Previous Mössbauer data (α-Fe)	This work (α-Fe)
FeNi	–0.062 [9]	–0.034 [16]	+0.432(40) [2]	–0.338(93)
FeCo	–0.023 [9]	–0.030 [20]	+0.73(14) [4]	–0.505(80)

TABLE II

The binding energy E_b between a pair of Co and Ni atoms in the annealed alloys $Fe_{1-x}Co_x$ and $Fe_{1-x}Ni_x$, deduced from the ^{57}Fe Mössbauer spectra. 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.

	FeNi			FeCo		
x	c_1	c_2	E_b [eV]	c_1	c_2	E_b [eV]
0.01	0.14047(24)	0	—	0.17375(22)	0	—
0.02	0.26539(27)	0	—	0.28579(50)	0.01239(40)	0.0766(59)
0.03	0.37585(57)	0.03083(41)	0.0653(47)	0.30140(44)	0.03002(34)	0.0518(38)
0.04	0.42451(71)	0.05335(49)	0.0589(43)	0.33906(44)	0.08486(31)	0.0064(55)
0.05	0.45000(70)	0.09467(45)	0.0396(28)	0.37855(31)	0.12458(21)	0.0038(28)

3. Conclusions

The positive values of the binding energy E_b between a pair of Co or Ni atoms in the Fe-Co and Fe-Ni alloys respectively, speaks in favor of the suggestion that cobalt and nickel atoms interact repulsively in iron matrix.

The enthalpies of solution H^{sol} in α-iron for nickel –0.338(93) eV/atom, and cobalt –0.505(80) eV/atom, determined from the ^{57}Fe Mössbauer spectra in the way proposed in this paper, are at variance with the corresponding values 0.432 eV/atom and 0.73 eV/atom obtained previously on the basis of standard analysis of the Mössbauer spectra for annealed samples. Simultaneously the present results on enthalpies of solution H^{sol} of Ni and Co in Fe are in a qualitative agreement with the values –0.062 eV/atom and –0.023 eV/atom resulting from the Miedema's model of alloys as well as the data –0.030 eV/atom and –0.034 eV/atom derived from calorimetric measurements. It may suggest that the method presented in this paper can be successfully applied for the systems where impurity neighbours of the Mössbauer probe have a small effect on the hyperfine field generated at the probe and simple study of annealed samples only does not give satisfied results.

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