Thermal defects in iron-based Fe-V solid solutions

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Abstract Room temperature [57]Fe Mössbauer spectra, positron annihilation lifetime data, X-ray diffraction patterns, and energy distributions of X-rays induced by an electron beam were measured for samples of the $Fe_{0.947}V_{0.053}$ solid solution quenched from different temperatures not exceeding 1250 K, into water being at about 295 K. The data were analysed in terms of concentration of unoccupied sites in the 14-site neighbourhood of the [57]Fe Mössbauer probe in the specimens. It was found that the vacancy formation enthalpy amounts to 0.8 ± 0.2 eV in the materials studied.

Key words dilute Fe-based alloys • Mössbauer spectroscopy • thermal point defects • vacancy formation enthalpy

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Introduction

Nuclear methods are widely used for the investigation of point defects in crystals as they are relatively highly sensitive to different kinds of defects, in particular vacancies and antistructure atoms existing in ordered systems, see [2, 3, 7]. Among various nuclear probes the most sensitive ones to the presence of vacancies are positive muons (μ^+) and positrons (e^+). They can detect vacancy concentrations as low as 10^{-8} and 10^{-7}, respectively, in pure α-Fe [14]. At the same time, methods based on using e^+ (and μ^+ as well) do not give information concerning the real concentration of vacancies without earlier calibration (performed with the help of differential dilatometry, for example [3]). Fortunately, lack of this calibration does not influence determination of the vacancy formation enthalpy H_V in the material studied with positron annihilation, where H_V is the fundamental input parameter for some theoretical models of alloys (see e.g. [1]). However, in the case of iron-based solid solutions in the low-temperature α (bcc) phase, the quantitative analysis of positron annihilation data is handicapped by the $\alpha\gamma$ structural phase transition at about 1100–1200 K (1184 K for pure Fe) [13]. The latter means that the analysis has to be simplified (being less precise) by decreasing the number of the derived parameters. All the above encouraged us to seek a more suitable tool for the investigation of the vacancy formation in iron solid solutions. Based on the results obtained for the Fe-Cr system [6], it seems that [57]Fe Mössbauer spectroscopy can be the proper candidate. In this paper, we test this suggestion using Fe-V samples containing about 5 at.% of vanadium and frozen-in thermal vacancies produced at different temperatures.

Experimental and results

The iron-vanadium alloy was prepared by melting the Johnson-Matthey vanadium of spectral purity and Aldrich 99.999% pure iron in an arc furnace filled with argon. Resulting ingot was cold-rolled to the final thickness of about 0.07 mm and then the foil was cut into several similar pieces. Next, the samples were gradually annealed in vacuum in three steps: 1) at 1170 K for 0.25 h, 2) at 1270 K for 0.25 h and 3) at 1370 K for 0.25 h. After each step, the specimens were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at about 700 K [8], so the observed distributions of atoms in the annealed samples should be the frozen-in state corresponding to 700 K, whereas the concentration of vacancies should approach null (the equilibrium concentration of vacancies at room temperature). The annealed samples were heated in an argon atmosphere at different temperatures ranging from 600 to 1250 K, and quenched in water being at about 295 K in order to freeze the high temperature vacancies as well as distribution of atoms in the specimens. After the quenching process, each sample was chemically polished to remove possible surface contaminants.

The atomic compositions of all the specimens were checked by an analysis of the energy distribution of X-rays (EDX) induced by the 20 keV electron beam. The EDX data showed that the samples under investigation contain 5.3 ± 0.2 at.% of vanadium and composition of bulk parts of the samples does not depend on the quenching process. Moreover, the data proved that the chemical polishing causes a certain increase in the surface concentration of vanadium, i.e., the applied etching agent reacts more strongly with iron. At the same time, the phase composition of the specimens was investigated with a DRON-3 diffractometer using CoK_α radiation. According to the X-ray diffraction results, all the samples were single-phase systems with bcc structure. Moreover, the effectiveness of the quenching process (in freezing the high temperature vacancies) was observed with positron annihilation lifetime spectroscopy. Data show that the positron lifetime increases with increasing temperature T from which samples are being quenched. Hence, the quenching process really increases the number of low-electron-density regions like vacancies in the sample and the number of the regions is greater for higher T.

The measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design. Some spectra are presented in Fig. 1. All the spectra were analysed, as in our previous papers [4, 5], in terms of four six-line patterns corresponding to different hyperfine fields (HF) at ^{57}Fe nuclei generated by different numbers of Fe and V atoms located in the first and second coordination shells of the probing nuclei – compare Ref. [15]. The analysis was performed under the assumption that the effect of a V atom on HF is independent of its position in the neighbour shells. As a result of the analysis the relative areas c_B and c_{BB} of the second and third components of each spectrum were determined. The components are related to the existence of one V atom and two V atoms in the mentioned above neighbourhood of the Mössbauer probe, respectively. Assuming that the Lamb-Mössbauer factor is independent of the configuration of atoms in the
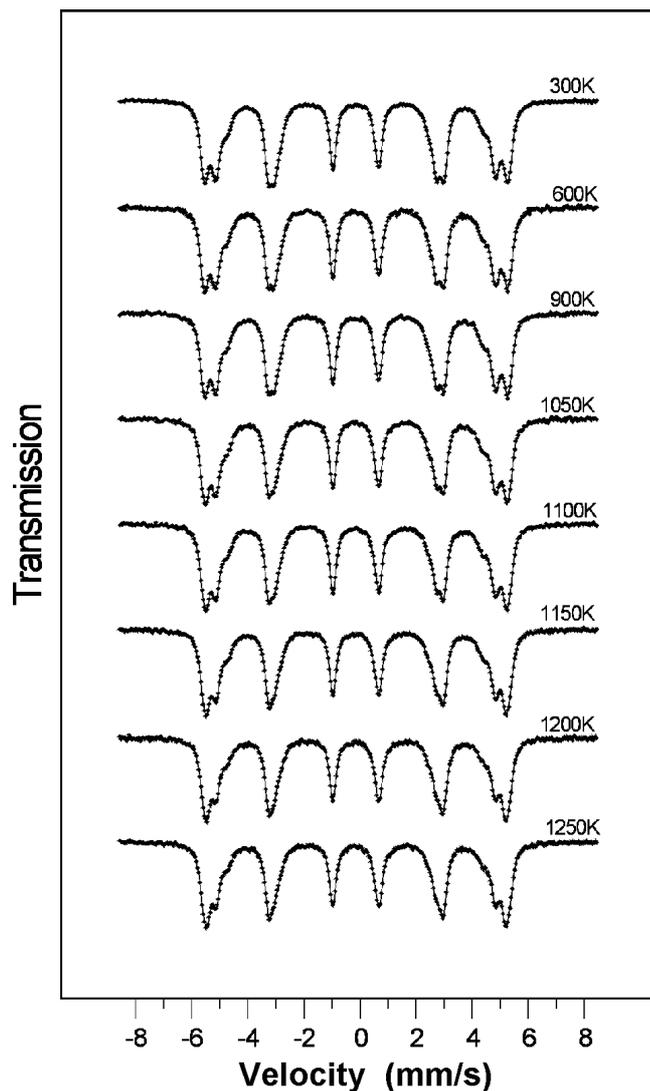
Fig. 1. ^{57}Fe Mössbauer spectra for the $Fe_{0.947}V_{0.053}$ alloys annealed and quenched from different temperatures. The spectrum of an annealed and slowly cooled sample from 1370 K to room temperature is marked with 300 K.

neighbourhood of the ^{57}Fe nucleus (quite reasonable for a metal [2]), the c_B and c_{BB} values describe intensities of the second and third components of a spectrum. The results are listed in Table 1.

The c_B and c_{BB} values for the annealed samples were used to calculate the binding energy E_b for pairs of V atoms in the studied materials. The computations were performed, as in Ref. [5], on the basis of the modified Hrynkiewicz-Królas formula [4, 9], assuming that the ratio of the concentrations of the individual pairs of V atoms and isolated V atoms in the specimen is equal to the quotient of the intensities c_{BB} and c_B mentioned above.

$$(1) \quad E_b = -kT_d \cdot \ln[(1 + 2 \cdot c_{BB}/c_B) \cdot (c_{BB}/c_B) \cdot \\ \cdot (1 + 2 \cdot p(2)/p(1))^{-1} \cdot (p(2)/p(1))^{-1}],$$

where k is the Boltzmann constant, T_d denotes the "freezing" temperature for the atomic distribution in the sample (due to the slow cooling of the annealed samples $T_d = 700$ K), $p(n) = [N!/((N-n)! \, n!)] \, x^n (1-x)^{N-n}$ is the

probability for the existence of n V atoms among all N atoms located in the first and second coordination shells of the Fe atom (the binomial expression results from statistical considerations for random distributions of two kinds of non-interacting atoms in a given lattice), and thus $p(2)/p(1) = 0.5\,x(N-1)/(1-x)$, finally x stands for the concentration of V atoms and N, in the case of annealed samples being at the room temperature, is practically $8 + 6 = 14$ (the total number of the lattice sites in the first and second coordination shells of an atom in the bcc lattice). The E_b values obtained for the annealed samples are collected in Table 1.

The mean value of E_b, i.e. 5 ± 1 meV, was used to estimate the concentration of vacancies in the quenched specimens according to the idea given in Ref. [6]. The idea is based on the assumption that a creation of vacancies in iron-based solid solutions goes together with a certain decrease in the number N of nearest and next-nearest neighbours of iron atoms and the decrease of N is responsible for a change in relative intensities of the ^{57}Fe Mössbauer spectrum components observed when going from a well annealed sample (no vacancies) to a quenched sample (vacancies) of the same material. The change in intensities of spectrum components on quenching is easily visible in Fig. 1 – compare, for example, the spectra marked with 300 and 1250 K. The number N for the quenched materials was determined assuming that the value of E_b is temperature independent and applying the equation (1) in a more convenient form:

$$(2) \quad N = 0.5 \cdot \{3x - 1 + (1-x)\,[1 + 8 \cdot (1 + 2 \cdot c_{BB}/c_B) \cdot \\ \cdot (c_{BB}/c_B) \cdot \exp(+E_b/(kT_d))]^{0.5}\,\}/x.$$

Having known the value for N one can calculate the concentration $c_V = (14-N)/14$ of vacancies or the number of unoccupied sites in the 14-site neighbourhood of the ^{57}Fe probe atom. The results of such calculations are presented in Table 1 and in Fig. 2.

Table 1. The binding energy between a pair of V atoms (E_b) and concentration of vacancies (c_V) in the $Fe_{0.947}V_{0.053}$ alloy annealed ($T = 300$ K) and quenched from different temperatures T ($T \neq 300$ K). The standard deviations σ for c_B and c_{BB} result from the variance of the spectrum fit. The σ values for c_V were computed taking into account the c_B and c_{BB} errors only.

Sample	T (K)	c_B	c_{BB}	E_b (meV)	c_V
1	300	0.404(3)	0.141(2)	3.7(1.4)	0
	600	0.405(3)	0.136(3)		0.021(7)
2	300	0.406(3)	0.139(2)	5.3(1.4)	0
	900	0.399(3)	0.137(2)		0.013(5)
3	300	0.408(3)	0.135(2)	8.2(1.5)	0
	1050	0.380(3)	0.134(3)		–0.006(8)
4	300	0.405(3)	0.141(2)	3.9(1.4)	0
	1100	0.371(3)	0.121(2)		0.066(5)
5	300	0.407(3)	0.135(2)	8.0(1.5)	0
	1150	0.354(3)	0.117(2)		0.056(6)
6	300	0.405(3)	0.146(3)	1.0(1.9)	0
	1200	0.330(4)	0.103(3)		0.105(8)
7	300	0.404(3)	0.139(2)	4.9(1.4)	0
	1250	0.331(3)	0.100(3)		0.133(8)
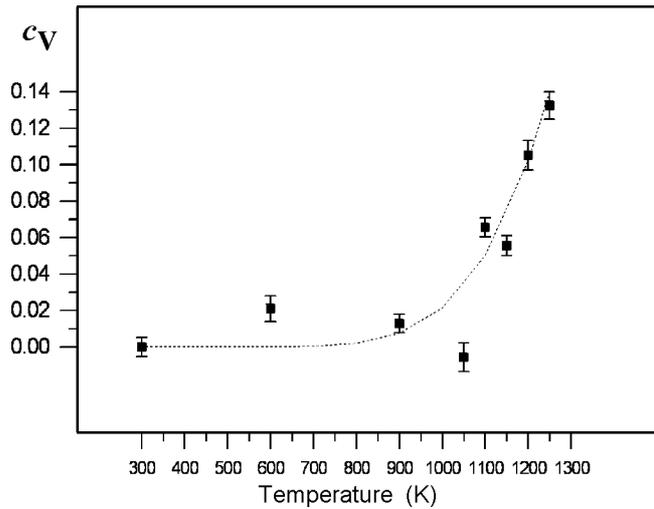
Fig. 2. Concentration c_V of vacancies in the bcc $Fe_{0.947}V_{0.053}$ samples as a function of the temperature from which the sample was quenched. The dashed line is a plot of the function $f(T) = C\,\exp(-H_V/(kT))$, fitted to the c_V values by the least-squares method; $H_V = 0.81 \pm 0.22$ eV.

Conclusions

The measured spectra suggest that the ^{57}Fe Mössbauer spectroscopy is sensitive enough to investigate thermal vacancies formed in the low-temperature α (bcc) phase of iron-based solid solutions – the influence of the V atoms and vacancies on the shape of the spectra is easily noticeable (see Fig. 1).

The data obtained for the annealed samples (Table 1) support our earlier findings [4] that the nature of the V pair interaction in the iron crystal is repulsive. The binding energy E_b between two V atoms in the Fe-V system containing about 5.3 at.% of vanadium is positive, close to 5 meV. At the same time, the obtained E_b value is small enough to fit well to that resulting from the semi-empirical Miedema-Królas model [10, 11] for Fe with trace concentrations of V; the latter being 78 meV.

The concentration c_V of quenched-in vacancies detected by the ^{57}Fe Mössbauer probe in its neighbourhood for the bcc $Fe_{0.947}V_{0.053}$ solid solution strongly depends on the quenching temperature T when the temperature exceeds 1000 K. The value of the vacancy formation enthalpy H_V in the sample, derived from the temperature dependence of c_V (see Fig. 2) amounts to 0.8 ± 0.2 eV and it is two times smaller than the corresponding value for Fe (1.74 ± 0.10 eV [13]). The result is in agreement with general regularity observed for the influence of impurities on the value of H_V – the value decreases with impurity concentration (see e.g. Ref. [12]).

The applied method of deriving the vacancy parameters from the Mössbauer spectrum is very recent [6] and it would be interesting to compare its findings with those obtained by other methods. However, currently we are unable to perform such a comparison. The successful analysis of our positron lifetime data, for example, needs an extra knowledge about the two unknown positron parameters – a mean lifetime in a vacancy and specific trapping rate by the vacancy.

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