

Behaviour of vacancies in dilute Fe–Re alloys: a positron annihilation study

R. Idczak · R. Konieczny

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Abstract Positron annihilation lifetime spectroscopy was used in a room temperature study of the influence of heat treatment on behaviour of vacancies in $\text{Fe}_{0.97}\text{Re}_{0.03}$ and $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloys. In this experiment, the vacancies were created during the formation and further mechanical processing of the iron systems under consideration so the lifetime spectra of positrons were collected at least twice. The first samples were taken just after the melting process in an arc furnace, and the second ones were taken for the specimens annealed at 1,270 K and then cold-rolled at room temperature. After that, the spectra were measured for all studied samples after annealing at some temperatures gradually increasing from 300 to 1,270 K. It was found that vacancy-Re pairs are the dominant type of structural defects in alloys just after the melting process. In the case of alloys after a cold rolling process, the dominant type of structural defects is vacancies associated with edge dislocations. Moreover, for cold-rolled samples annealed at 473–573 K, the growth of the vacancy clusters associated with edge dislocations is observed by an increase in the mean positron lifetime. Finally, at temperatures above 573 K, vacancy clusters associated with edge dislocations as well as vacancy-Re pairs become unstable, and freely migrating vacancies sink at grain boundaries.

1 Introduction

Iron alloys including steels have been intensively studied for years because of their importance as construction

materials for the modern industry. One of the most important parts of these studies is dedicated to expanding the knowledge about behaviour of structural defects such as vacancies, impurities, or dislocations existing or created in the materials during their utilization [1–9]. This behaviour is crucial for better understanding diffusion and alloying processes as well as mechanical, thermodynamic, and magnetic properties of the alloys under consideration. A phenomenon which should be taken under consideration in this type of study is the interaction between impurity atoms and vacancies. In two recent papers [10, 11], the authors present theoretical calculations based on density functional theory (DFT), which suggests that the interaction between vacancies and transition-metal impurities dissolved in iron-based alloys is attractive. These results lead to the conclusion that in the iron-based alloy which contains vacancies and transition-metal impurities, an energetically favourable pairing process should generate vacancy–impurity pairs in large numbers. The existence of vacancy-Re (v-Re) pairs in Fe–Re alloys at room temperature has been recently observed experimentally [12, 13]. The positron annihilation lifetime spectroscopy detects vacancies in samples which contain Re impurities, and Mössbauer spectroscopy localizes the vacancies mainly in the vicinity of non-iron atoms. These results speak in favour of the suggestion that in an iron matrix, the solute Re atoms interact attractively with vacancies (as it is predicted by theoretical computations) and the energy of the interaction is large enough for the paired vacancy–solute atom exists at room temperature.

It is worth noting that positron annihilation lifetime spectroscopy (PALS) is a non-destructive, highly sensitive method for detection of defects in metals. That is because an energetic positron injected into the studied material is quickly slowing down to the thermal energies and after

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

that, during its diffusion movement, can be trapped by low-electron density regions of the material which are lattice defects, for example. A trapped positron is easily seen by PALS, as it lives longer than that being in the bulk and encounters bigger electron density. For example, the estimated experimental lifetime τ_b of a positron in a defect-free α -Fe crystal is not greater than about 110 ps (106 ps [14], 110 ps [15]), while the annihilation lifetime τ_v of positron in a vacancy in α -Fe is 175 ps [15].

In this work the PALS technique was used to study vacancies in $\text{Fe}_{0.97}\text{Re}_{0.03}$ and $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloys. The vacancies were created during the formation and further mechanical processing of the iron systems under consideration, so the PALS spectra were collected for each sample at least twice. The first one for the samples was obtained just after the melting process in an arc furnace and the second one for the alloys after a cold-rolling process. Moreover, the spectra for all samples were measured after subsequent annealing at temperatures in the range between 300 and 1,270 K to determine the dependence of the positron lifetimes on annealing temperature. Worth noting is the fact that iron alloys belong to the most important engineering materials, and it seems appropriate to investigate polycrystalline samples of the alloys after such processes as melting and cold-rolling, which are widely used by modern industry.

2 Experimental details

The samples of $\text{Fe}_{0.97}\text{Re}_{0.03}$ and $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloys were prepared in two steps. The first one was arc melting of appropriate amounts of Sigma-Aldrich 99.98 % pure iron and 99.995 % pure rhenium in an argon atmosphere followed by quick cooling to about 300 K. The weight losses during the melting process were below 1 %, so the compositions of the obtained ingots were close to nominal ones. In the second step the resulting ingots were cold-rolled to final thickness of about 0.04 mm. To ensure that alloys were homogenous and defect-free before cold-rolling, they were annealed in a vacuum at 1,270 K for 2 h and slowly cooled to room temperature over 6 h. Each step was followed by subsequent annealing at several temperatures in the range between 300 and 1,270 K for 15 min or 24 h and slowly cooling to room temperature over several hours.

Positron lifetimes were measured at room temperature (300 K) with a conventional fast–fast coincidence system having a resolution of about 300 ps. The source of positrons consisted of 1 MBq of $^{22}\text{NaCl}$ evaporated on a thin Kapton–Hostaphan foil. In case of cold-rolled alloys, the positron source was sandwiched between two stacks of identical 0.04 mm plates. To prevent positrons from annihilation outside the studied samples, each stack consisted

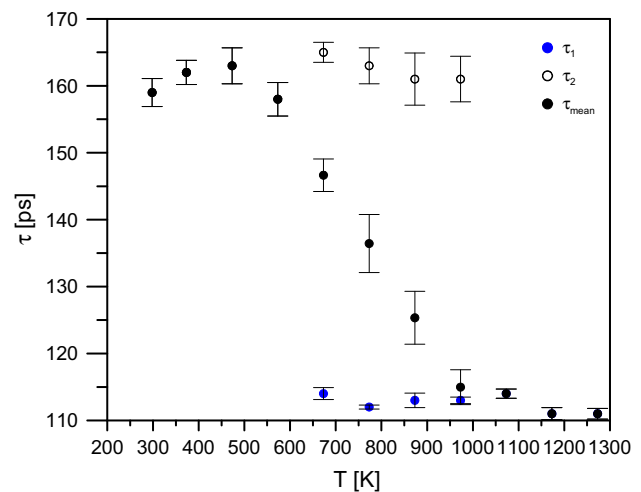


Fig. 1 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy after the melting process, annealed at temperatures in the range between 300 and 1,270 K for 15 min

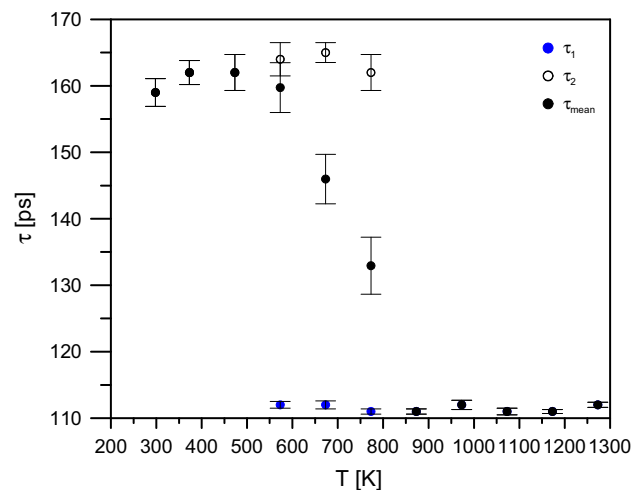


Fig. 2 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy after the melting process, annealed at temperatures in the range between 300 and 1,270 K for 24 h

of three plates. The obtained spectra containing 3×10^6 counts were analysed using the LT-9.0 program of Kansy [16], taking into account the correction for the annihilation of positrons in the source setting. All PALS spectra were described by three or four exponential components, characterized by mean lifetimes τ_1 , τ_2 , τ_{s1} , and τ_{s2} , where the components with shorter mean lifetimes τ_1 (τ_2) and intensities I_1 (I_2) may be considered as related to positron annihilation in studied alloys. At the same time, the two components with longer mean lifetimes $\tau_{s1} = 0.370$ (35) ns and $\tau_{s2} = 1.71$ (19) ns correspond to the positron annihilation in the Kapton–Hostaphan foil.

3 Results and discussion

Figures 1 and 2 show the positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy, which after the melting process was annealed at temperatures in the range between 300 and 1,270 K for 15 min or 24 h, respectively. The shortest lifetime $\tau_1 = 112(2)$ ps was assigned to positrons annihilating in an almost perfect Fe–Re alloy [12, 13], $\tau_2 = 161(5)$ ps was assigned to positrons annihilating in vacancies of the v–Re pairs [12, 13], and the positron mean lifetime τ_{mean} was calculated using the formula: $\tau_{\text{mean}} = \tau_1 I_1 + \tau_2 I_2$. The rapid decrease of τ_{mean} values at annealing temperatures exceeding 573 K could be explained by detrapping of vacancies associated with Re atoms following their free migration to reach grain boundaries. Moreover, as it could be expected, the decrease of τ_{mean} is greater for the sample which was annealed for 24 h.

The dependence of τ_{mean} on annealing temperature T is quite different for the alloy after the cold-rolling process (Figs. 3, 4). At low temperatures, the obtained τ_{mean} values suggest that positrons “see” mainly vacancies associated with edge dislocations [13]. The expected mean lifetime of a positron trapped in the vacancy associated with edge dislocation is about 140–150 ps [15]. Taking the above into account, one can say that during the cold-rolling process of previously annealed samples, a large number of vacancies and dislocations are generated. Moreover, the majority of vacancies are located on the dislocation lines. An increase of τ_{mean} values observed for the alloys annealed at 573 K (15 min) and 473 K (24 h) could be explained on the basis of two models. According to the first one, the vacancies are released from the edge dislocations and form v–Re pairs [17]. The expected lifetime of a positron trapped in a vacancy formed by a v–Re pair is much higher than for a positron trapped in a vacancy associated with edge dislocations [13, 15]. The second model is based upon possible diffusion of vacancies along edge dislocations, which could lead to forming vacancy clusters associated with edge dislocations. The calculated lifetimes, using Finnis–Sinclair N-body potential, of a positron trapped in vacancy clusters consisting of two and three vacancies associated with edge dislocations are 157 and 167 ps, respectively [18]. Taking into account that attractive interaction energy between vacancy and edge dislocation is much greater than between vacancy and Re impurity [11, 15], the first explanation seems rather unlikely. Moreover, a more detailed spectra analysis using two-state trapping model reveals that the longer positron annihilation lifetime τ_2 increases with T . This result also favours creation of vacancy clusters associated with edge dislocations over formation of v–Re pairs. Finally, the decrease of τ_{mean} values at temperatures

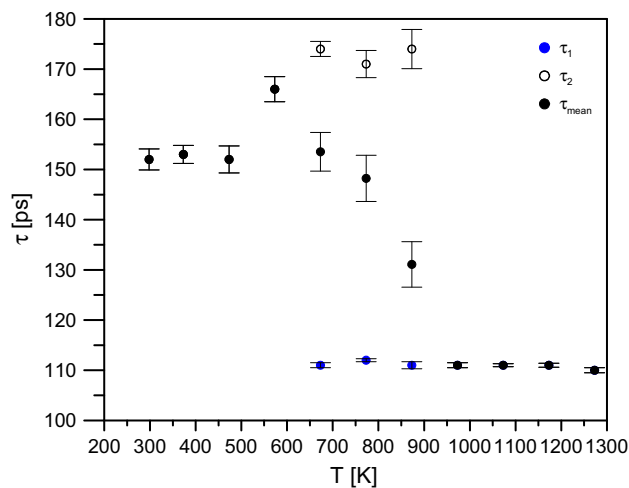


Fig. 3 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy after the cold-rolling process annealed at temperatures in the range between 300 and 1,270 K for 15 min

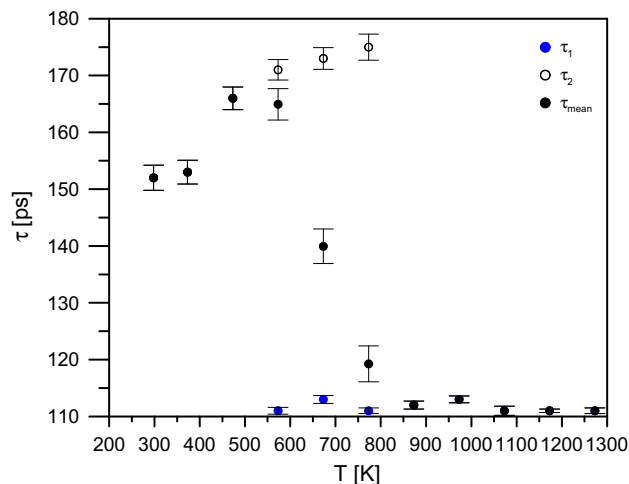


Fig. 4 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ alloy after the cold-rolling process annealed at temperatures in the range between 300 and 1,270 K for 24 h

above 573 K suggests that vacancy clusters associated with edge dislocations become thermally unstable, and detrapped, freely migrating vacancies sink at grain boundaries.

The positron annihilation lifetimes obtained for the $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy after the melting and cold-rolling processes (annealed at temperatures in the range between 300 and 1,270 K for 15 min and 24 h) are presented in Figs. 5, 6, 7 and 8. As one can notice, the behaviour of vacancies in this alloy is quite similar to $\text{Fe}_{0.97}\text{Re}_{0.03}$. The small differences between observed τ_{mean} for studied samples obtained after the melting process could be connected with larger vacancy concentration c_v in an $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy.

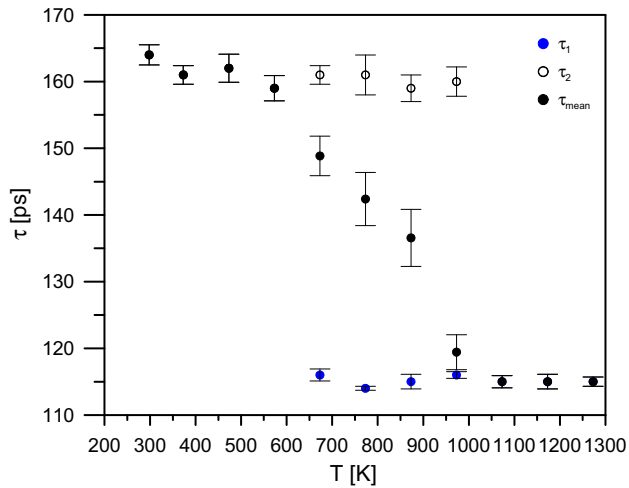


Fig. 5 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy after the melting process, annealed at temperatures in the range between 300 and 1,270 K for 15 min

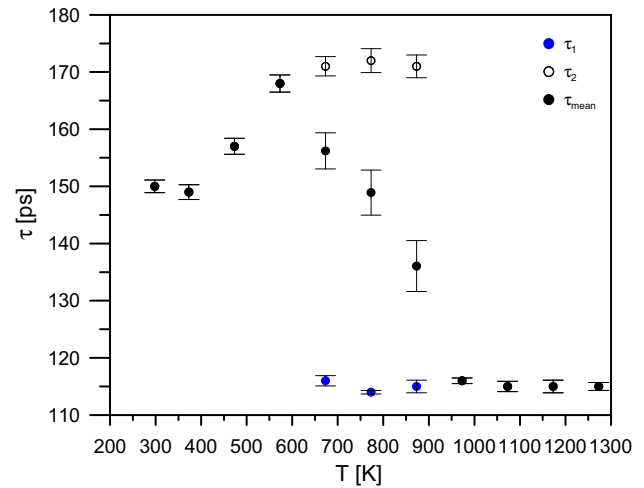


Fig. 7 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy after the cold-rolling process annealed at temperatures in the range between 300 and 1,270 K for 15 min

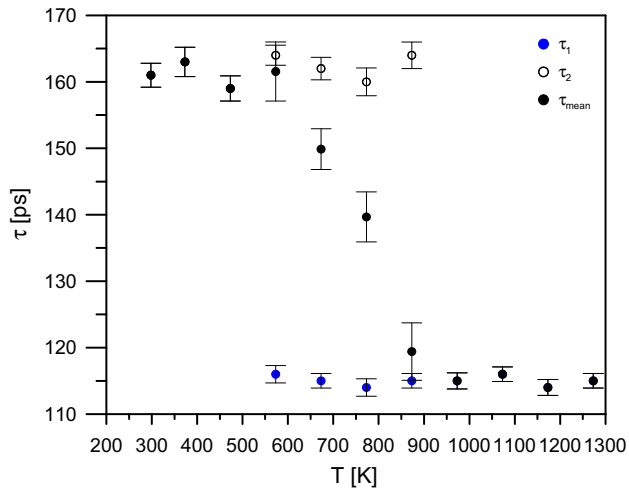


Fig. 6 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy after the melting process, annealed at temperatures in the range between 300 and 1,270 K for 24 h

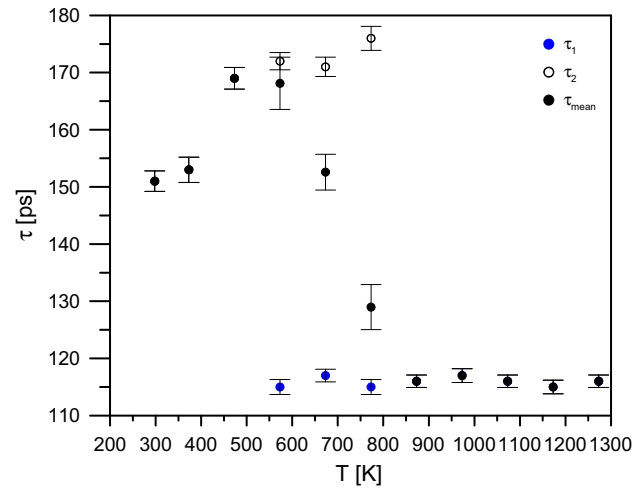


Fig. 8 The positron annihilation lifetimes obtained for the $\text{Fe}_{0.94}\text{Re}_{0.06}$ alloy after the cold-rolling process annealed at temperatures in the range between 300 and 1,270 K for 24 h

This also confirms the v-Re pairing process due to fact that an increased number of Re atoms dissolved in an iron matrix can trap a larger number of vacancies generated during thermal treating. The vacancy concentration c_v calculated for the samples obtained after the melting process uses formula [2]:

$$c_v = \frac{1}{\mu_v} \cdot \frac{I_2}{I_1} (\tau_1^{-1} - \tau_2^{-1}), \quad (1)$$

where $\mu_v = 1.1 \times 10^{15} \text{ s}^{-1}$ is the value of the trapping coefficient for a single vacancy in pure Fe (Table 1).

4 Conclusions

The positron annihilation lifetimes obtained for the $\text{Fe}_{0.97}\text{Re}_{0.03}$ and $\text{Fe}_{0.94}\text{Re}_{0.06}$ samples just after the melting process as well as after a cold-rolling process depends strongly on the annealing temperature. It was found that v-Re pairs are a dominant type of structural defect in alloys just after the melting process. In the case of alloys after the cold rolling process, the dominant type of structural defect is vacancies associated with edge dislocations. As it was

Table 1 The vacancy concentration c_v calculated for the alloys obtained after melting process

Annealing temperature T (K)	Vacancy concentration c_v (at. ppm)			
	Fe _{0.97} Re _{0.03}		Fe _{0.94} Re _{0.06}	
	Annealing time 15 min	Annealing time 24 h	Annealing time 15 min	Annealing time 24 h
473	Saturation	Saturation	Saturation	Saturation
573	Saturation	30	Saturation	49
673	4.8	4.8	6.1	7.4
773	2.4	1.9	3.4	3.2
873	0.88	<0.02	2.1	0.26
973	0.11	<0.02	0.19	<0.02
1,073	<0.02	<0.02	<0.02	<0.02

shown, for cold-rolled samples, an increase of the mean positron lifetime at 473–573 K could be explained by two models. In the first one, the vacancies are released from the edge dislocations and form v-Re pairs. The second is based upon the effect of vacancy diffusion along edge dislocations, which could lead to forming vacancy clusters associated with edge dislocations. Taking into account all data presented in this paper, one can conclude that the second one is much more probable. At temperatures above 573 K, vacancy clusters associated with edge dislocations, as well as v-Re pairs, become unstable and detrapped, and freely migrating vacancies sink at grain boundaries. Finally, it is worth noting that the possibility of Re segregation to dislocations (for cold-rolled samples) and to grain boundaries (for both types of samples) as well as a possible influence of this effect on the concentration of vacancy-Re pairs is still unknown.

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References

1. G. Vogl, A. Schaefer, W. Mansel, J. Prechtel, W. Vogl, Mössbauer studies of low-temperature radiation damage in α -iron. *Phys. Stat. Sol.* **59**, 107–120 (1973)

2. A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kauppila, P. Moser, Vacancies and carbon impurities in α -iron: electron irradiation. *Phys. Rev. B* **25**, 762–780 (1982)
3. P. Hautojärvi, L. Pollanen, A. Vehanen, J. Yli-Kauppila, Vacancies and carbon impurities in α -iron: neutron irradiation. *J. Nucl. Mater.* **114**, 250–259 (1983)
4. Y.-K. Park, J.T. Waber, M. Meshii, C.L. Snead Jr, C.G. Park, Dislocation studies on deformed single crystals of high-purity iron using positron annihilation: determination of dislocation densities. *Phys. Rev. B* **34**, 823–836 (1986)
5. U. Holzwarth, A. Barbieri, S. Hansen-Ilzhöfer, P. Schaaff, M. Haaks, Positron annihilation studies on the migration of deformation induced vacancies in stainless steel AISI 316 L. *Appl. Phys. A* **73**, 467–475 (2001)
6. M.K. Roy, V.S. Subrahmanyam, H.C. Verma, Defect studies in Fe–Cu alloys prepared by electrodeposition. *Phys. Lett. A* **328**, 375–379 (2004)
7. K. Sato, T. Yoshiie, T. Ishizaki, Q. Xu, Behavior of vacancies near edge dislocations in Ni and α -Fe: positron annihilation experiments and rate theory calculations. *Phys. Rev. B* **75**, 094109 (2007)
8. H.F.M. Mohamed, J. Kwon, Y.-M. Kim, W. Kim, Vacancy-type defects in cold-worked iron studied using positron annihilation techniques. *Nucl. Instrum. Methods Phys. Res. B* **258**, 429–434 (2007)
9. K.M. Mostafa, J. De Baerdemaeker, P.R. Calvillo, N. Van Caenegem, Y. Houbaert, D. Segers, A study of defects in iron based alloys by positron annihilation techniques. *Acta Phys. Pol. A* **113**, 1471–1478 (2008)
10. P. Olsson, T.P.C. Klaver, C. Domain, *Ab initio* study of solute transition-metal interactions with point defects in bcc Fe. *Phys. Rev. B* **81**, 054102 (2010)
11. O.I. Gorbатов, P.A. Korzhavyi, A.V. Ruban, B. Johansson, YuN Gornostyrev, Vacancy–solute interactions in ferromagnetic and paramagnetic bcc iron: *Ab initio* calculations. *J. Nucl. Mater.* **419**, 248–255 (2011)
12. R. Idczak, R. Konieczny, J. Chojcan, Study of defects in Fe–Re and Fe–Mo alloys by the Mössbauer and positron annihilation spectroscopies. *Solid State Commun.* **152**, 1924–1928 (2012)
13. R. Idczak, R. Konieczny, J. Chojcan, A study of defects in iron-based binary alloys by the Mössbauer and positron annihilation spectroscopies. *J. Appl. Phys.* **115**, 103513 (2014)
14. H.-E. Schaefer, Investigation of thermal equilibrium vacancies in metals by positron annihilation. *Phys. Status Solidi (a)* **102**, 47–65 (1987)
15. Y. Kamimura, T. Tsutsumi, E. Kuramoto, Calculations of positron lifetimes in a jog and vacancies on an edge-dislocation line in Fe. *Phys. Rev. B* **52**, 879–885 (1995)
16. J. Kansy, Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl. Instrum. Methods Phys. Res. A* **374**, 235–244 (1996)
17. K. Sato, T. Yoshiie, T. Ishizaki, Q. Xu, Behavior of vacancies near edge dislocations in Ni and α -Fe: positron annihilation experiments and rate theory calculations. *Phys. Rev. B* **75**, 094109 (2007)
18. L. Petrov, T. Troev, N. Nankov, E. Popov, Model calculations of edge dislocation defects and vacancies in α -iron lattice. *J. Phys.: Conf. Ser.* **207**, 012037 (2010)