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Point defect study in $Fe_{75}Al_{25}$ and $Fe_{70}Al_{25}X_5$ X=(Cr, Ni) alloys as a function of thermal treatment by Positron Lifetime Spectroscopy

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Abstract

Positron lifetime spectroscopy (PALS) is employed to study retained vacancies in $Fe_{75}Al_{25}$ and $Fe_{70}Al_{25}X_5$ X= (Cr, Ni) after various thermal treatments. The PALS spectra were analyzed with the two states trapping model. The positron lifetime in defects suggests that they are Fe-monovacancies. The vacancy concentration, determined by the rates of trapping positrons to vacancies, strongly depends on the cooling rate of the sample and the ternary addition. An addition of Cr lowers, whereas an addition of Ni increases the concentration of the retained vacancies in relation to $Fe_{75}Al_{25}$ samples after the same heat treatment.

Keywords: point defects; Positron Lifetime Spectroscopy; Fe-Al; Fe-Al-Cr; Fe-Al-Ni;

1. Introduction

Iron aluminides are materials known for their high-temperature corrosion resistance, mechanical strength, and relatively low density. Such properties are mainly determined by defect structure present in these materials and strongly depend on this structure. In spite of this, however, technical application of these alloys is still limited due to their poor ductility and fracture toughness at room temperatures. It is believed then that modifying the structure of intermetallic alloys with the proper heat treatment combined with doping with transition metals, may enhance their mechanical properties enough to make them more

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workable. For example, it is known that quenching from elevated temperatures, retains a high concentration of thermal vacancies in iron aluminides, which increases their yield strength and hardness at room temperature. Fe–(25–28) at.% Al alloys are often alloyed with 3–5% Cr to increase their ductility [1]. Our studies focus on the influence of Cr and Ni additions on defect structure in $Fe_{75}Al_{25}$ (Fe25Al), $Fe_{70}Al_{25}X_5$ (Fe25Al5X, X=Cr, Ni) systems. In the studies, PALS technique was used. The results were analyzed by a special procedure offered by new software – LT10 [2].

2. Material

The materials investigated were Fe25Al and Fe25Al5X where X= (Cr, Ni) alloys obtained from Fe of 99.99% purity, Al of 99.999% purity and chromium and nickel of 99.99% purity. The alloys were produced by vacuum induction melting. The samples were examined in seven different states (Table 1).

Table 1. The heat treatments of the investigated samples

Abbreviation	Heat treatment
A	annealed for 20h at 1000°C and slowly cooled with furnace
SC	A + annealed for 4h at 1000°C and slowly cooled with furnace
Q	A + annealed for 4h at 1000°C and quenched to oil
SC5	A + annealed for 4h at 540°C and slowly cooled with furnace
Q5	A + annealed for 4h at 540°C and quenched to oil
SC4	A + annealed for 700 h(month) at 420°C and slowly cooled with furnace
Q4	A + annealed for 700 h(month) at 420°C and quenched to oil

3. Measurement and data analysis

The positron lifetime measurements were carried out at room temperature with a conventional fast-fast spectrometer of resolution width (FWHM) equal to 246 ps and scale of 6.4 ps per channel. The positron source (POSK [3]) with the activity of about 100 kBq, covered with 25 μm kapton foils was used. For each sample, a series of spectra was collected. Then, the spectra were added together by means of a special procedure accounting the drift of the zero-time channel. In this way, each resultant spectrum had the statistics of about $5 \cdot 10^6$ counts.

The data were analyzed with the LT10 computer program using a least-square fitting procedure [4, 5], which allows to analyze spectra with different theoretical models (multiexponential as well as the 2,3,4-state simple trapping models) directly implemented into the code. The program allows to fit a chosen model to a series of spectra simultaneously. Each parameter of the model can be constrained. It is accomplished due to a feature called the *status of parameter*. The following statuses are available:

local free – a value of a particular parameter of the theoretical model is individual and variable,

local fixed – a chosen parameter's value is constant for a single spectrum but it may be different for different spectra,

common free (group-common free) – all (or a chosen group of) spectra share a common but variable value for a particular parameter of the theoretical model,

common fixed (group-common fixed) – all (or a chosen group of) spectra share a common but constant value of a particular parameter.

At the beginning, an extra measurement and its analysis were performed to determine the apparatus parameters, i.e. the contribution of self-annihilations in the positron source and the spectrometer resolution. The parameters were estimated by means of several reference samples (well annealed Si, Ni,

Cu, In and Sn) [6] of well known positron bulk lifetimes [7]. In our case, precise determination of the source contribution was necessary due to its high value expected. Indeed, the estimated level of the contribution for Fe-Al samples was 41%.

During the main analysis, the spectra of samples of different compositions and various heat treatments were analyzed together as one series. The parameters related to the source and the resolution were fixed and constant for all the spectra (*common fixed* parameters). The fitted model was the 2-state simple trapping model [5] in which we assumed two channels of positron annihilation, i.e. in the bulk material – with lifetime τ_f, and in one type of defects – with lifetime τ_v. To avoid too large scattering of fitted values of τ_f's and τ_v's, we postulated that the parameters depend exclusively on the sample composition but not on its heat treatment, so we searched for three different values of τ_f and τ_v related to Fe25Al, Fe25Al5Cr and Fe25Al5Ni, respectively. This way, the lifetimes were treated as the *group-common free* parameters while the values of the rate of positron trapping to defects (κ) were fitted individually to each spectrum of the series of spectra (a *local free parameter*).

4. Results and discussion

The resulting values of τ_f and τ_v for samples of different compositions are shown in Fig.1. Both lifetimes depend slightly on chemical composition of the samples showing a week increase with the atomic number of the ternary addition. The $Fe_{75}Al_{25}$ alloy was formally considered as $Fe_{70}Al_{25}Fe_5$. The bulk lifetime in Fe25Al of 122.1 ± 0.5 ps is close to the recently measured values of 118 ± 5 ps [8] and 117 ps (for Fe28Al) [9] and a bit higher than 112 ps reported in [10, 11]. Theoretical values of τ_f are calculated as 112 ps [11], 108 ps [12] or 110 ps [13]. The theoretical values are somewhat lower than the experimental ones. The discrepancy may results from a mixture of τ_f with a slightly higher positron lifetime (e.g. in dislocations) or from inaccuracy of the theoretical model used in calculations (in [13], the authors published, besides τ_f =112 ps, another theoretical value, 118 ps, obtained with another theoretical approach).
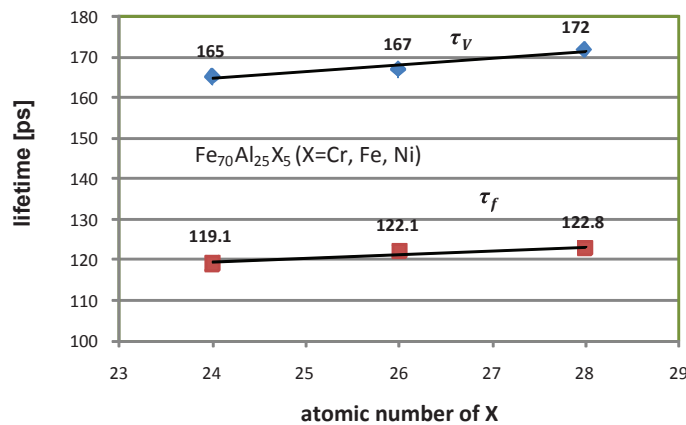

Fig. 1. Positron lifetimes in bulk (τ_f) and in defects (τ_v) versus atomic number of the ternary addition. Numerical values of lifetimes are indicated above the points. Deviation bars are included within the symbols of points.

The determined value of τ_v for Fe25Al equal to 167±1.5 ps is lower than usually measured positron lifetimes in an iron vacancy: 190.8±0.4 ps for $Fe_{75.99}Al_{24.01}$ [13], about 182 for Fe_3Al [8, 12, 14], 178 ps [12] or 170±2 ps (in $Fe_{72}Al_{28}$) [15]. However, it is higher than the value measured in an in-situ

experiment, i.e. 160 ps [16]. Therefore, it seems reasonable to assign τ_v, determined in this work, to positron annihilation in mono-vacancy.

The fitting of the two-state-trapping model allows to determine changes in κ after various heat treatments. These values of κ were used for estimation of retained vacancy concentrations (c_v) after various heat treatments of the samples.

$$c_v = \kappa/\mu \qquad\qquad\qquad (1)$$

We assumed that the trapping constant μ does not depend on the local environment of vacancy and is equal to 4×10^{14} s^{-1} [10]. The estimated values of c_v are shown in Fig. 2.
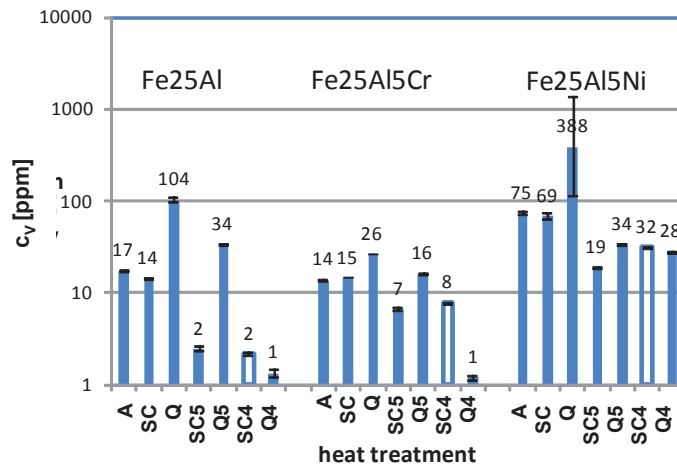

Fig. 2. Vacancy concentration in Fe25Al, Fe25Al5Cr and Fe25Al5Ni samples after various heat treatments. Numerical values of c_v in ppm are indicated above the bars. The heat treatments abbreviations are explained in Table 1.

The most striking feature is the dependence of c_v on the ternary addition. Comparing c_v for the samples of analogical heat treatment but different chemical composition, it can be seen that, in general, Cr lowers, whereas Ni elevates the respective concentrations of vacancies. In the case of samples quenched from 1000°C, the differences are particularly large. The concentration of quenched vacancies in Fe25Al5Ni sample exceeds c_v in Fe25Al several times and is even higher by an order than c_v in Fe25Al5Cr.

According to expectations, c_v depends on the cooling rate of the sample and the temperature at which the sample was annealed before cooling. Generally, c_v increases distinctly with the rate of cooling but an "abnormal" behavior is observed for the samples annealed for a month at 420°C. The vacancy concentration in quenched samples is lower than in the respective samples which were slowly cooled from annealing temperature. This suggests some structural processes occurring during the slow cooling at temperatures below 420°C. The effect is especially pronounced for Fe25Al5Cr. Hamana [17] observed that microhardness of Fe28Al2Cr and Fe28Al5Cr samples annealed at 300°C increases with annealing time and achieves a maximal value after about 30 minutes. The author attributes the increase to the intense formation of the D0$_3$ antiphase domain. Taking into account the vacancy hardening mechanism, one can conclude that short annealing of samples at temperatures below 400°C generates a certain amount of vacancies of the concentration higher than the equilibrium vacancy concentration at the temperature slightly over 400°C. We suppose that a similar process takes place also in our samples. From the results

shown in Fig. 2, we can estimate the vacancy concentration induced by slow cooling from 420°C. It is about 7 ppm for Fe25Al5Cr and about 1-2 ppm for Fe25Al and Fe25Al5Ni. The result seems to confirm the conclusion of Diego et al. [12] that a noticeable concentration of vacancy-type defects is always present in the Fe-Al samples even after long annealing at intermediate temperatures.

5. Conclusions

Lifetime spectra of the investigated alloys could be well described with two state trapping model. LT10 allowed to determine that model parameters in a single fitting procedure which greatly reduced number of free parameters and made the results more consistent and reliable.

The determined positron lifetimes in defects allowed to identify them as Fe-monovacancies. Both positron lifetimes in bulk and defects seems to depend linearly on atomic number of the ternary addition to Fe25Al alloy. Moreover, the addition modifies defect concentration. In general, Cr addition lowers, whereas Ni increases vacancy concentrations in samples of the same heat treatment.

According to expectation, the quenched samples contained heightened defect concentration comparing to slow cooled ones. However, an "abnormal behavior" is observed for samples annealed for a month at 420°C.

Acknowledgements

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