Quenched-in vacancies in Fe-Al alloys

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Abstract. Quenched-in vacancies in Fe-Al alloys with Al content ranging from 24 to 49 at.% were investigated employing two complementary techniques of positron annihilation: slow positron implantation spectroscopy and positron lifetime measurements. It was found that quenched alloys exhibit a very high concentration of vacancies. Although the free positron component cannot be resolved in positron lifetime spectrum in majority of samples, the concentration of quenched-in vacancies can be still determined from the positron diffusion length measured by a variable energy positron beam. The lowest concentration of vacancies was found in a stoichiometric (SM) Fe3Al alloy. The concentration of defects increases with increasing degree of non-stoichiometry with respect to Fe3Al, i.e. in alloys with under-SM and over-SM Al concentration. However, the increase in concentration of quenched-in defects is more pronounced in Al-rich alloys, i.e. alloys containing more than 25 at.% of Al.

1. Introduction

Intermetallic Fe-Al alloys are prospective structure materials for high-temperature applications. A special feature of Fe-Al alloys is an extremely high concentration of vacancies (up to several at.%) which can be created at elevated temperatures and relatively easily quenched down to room temperature [1]. Vacancies play a very important role in Fe-Al alloys and cause, for example, a strong hardening [2]. Thus, it is obvious that a detailed investigation of vacancies and vacancy-related defects in Fe-Al alloys is necessary for understanding of physical properties of these materials. Positron lifetime (LT) spectroscopy has been employed [3,4] for investigations of vacancies in Fe-Al alloys with Al content ranging from 25 at.% (Fe3Al alloy with D03 structure) to 50 at.% (FeAl alloy with B2 structure). The lifetime of positrons trapped at defects varied in the range from 175 to 200 ps depending on Al content and thermal treatment [3,4]. This indicates that various configurations of vacancy-like defects are existing in Fe-Al alloys. There are still controversies among various authors in assignment of positron lifetimes to particular configurations of such defects.

The aim of this work is to characterise quenched-in defects in Fe-Al alloys with Al content (C(Al)) varying in the range from 24 to 49 at.%. Two complementary techniques of positron annihilation were employed: (i) LT spectroscopy which enables to identify defects and determine their concentrations and (ii) slow positron implantation spectroscopy (SPI) which allows for an estimation of defect concentration using the positron diffusion length even in materials with very high defect densities.
2. Experimental
In the present work we studied Fe-Al alloys with C(Al) = 24, 25, 28, 40, and 49 at.% prepared from pure Fe (99.99%) and Al (99.999%) by induction melting. The specimens were annealed at 1000°C for 1h in vacuum (10⁻³ mbar) encapsulated in silica glass ampoules. The annealing treatment was finished by quenching of the silica glass ampoules into water of room temperature.

A $^{22}$Na$_2$CO$_3$ positron source with an activity of 1.2 MBq deposited on a 2 µm thick Mylar foil was used for LT studies. The source contribution consists of two weak components with lifetimes $\tau_2 \approx 368$ ps and $\tau_3 \approx 1.5$ ns. A high resolution digital spectrometer [5] with a time resolution of 150 ps (FWHM, $^{22}$Na) was employed. At least $10^7$ annihilation events were accumulated in all LT spectra.

SPIS studies were performed on magnetically guided variable energy positron beam “SPONSOR” [6]. The energy of incident positrons was varied in the 0.03 to 36 keV range. The Doppler broadening of the annihilation line was measured by an HPGe detector with an energy resolution of $(1.09 \pm 0.01)$ keV at 511 keV and evaluated in terms of the $S$ parameter. The $S$ parameter values in this paper were normalized to the bulk $S$ parameter for the Fe$_3$Al sample measured at a positron energy of 36 keV.

3. Results and discussion
The SM Fe$_3$Al alloy exhibits a two component LT spectrum. The shorter component with the lifetime $\tau_1 = (27 \pm 9)$ ps and intensity $I_1 = (10.5 \pm 0.6)$ % represents a contribution of free positrons. The longer component with the lifetime $\tau_2 = (182.4 \pm 0.3)$ ps and intensity $I_2 = (89.5 \pm 0.8)$ % can be attributed to...
positrons trapped at quenched-in defects. The lifetime $\tau_2$ agrees well with the calculated lifetime of positrons trapped in Fe-vacancy ($V_{Fe}$) surrounded by 4 Fe and 4 Al nearest neighbours [7]. The quantity $\tau_f = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1} = 114$ ps agrees well with the bulk positron lifetime of 112 ps measured on annealed Fe$_{76.3}$Al$_{23.7}$ [8]. This testifies that the Fe$_3$Al sample contains a single type of uniformly distributed traps and their concentration can be calculated using the two state simple trapping model

$$ c = \frac{1}{\nu} \frac{I_2}{I_1} \left( \frac{1}{\tau_f} - \frac{1}{\tau_f} \right). $$

Here $\nu = 4 \times 10^{14}$ at. s$^{-1}$ is the specific positron trapping rate for $V_{Fe}$ [8]. From equation (1) one obtains that the concentration of $V_{Fe}$ in Fe$_3$Al sample is $c = (5 \pm 1) \times 10^{-3}$ at.%. All non-SM alloys exhibit single component LT spectra with the lifetime in the range 191–195 ps which obviously represents a contribution of positrons trapped at quenched-in defects. Hence, non-SM alloys have a very high density of defects ($c > 2 \times 10^{-2}$ at.% [7]), which causes saturated positron trapping, i.e. the free positron component is too short and small to be resolved. Figure 1 shows the lifetime of positrons trapped at defects plotted as a function of $C$(Al). In the Fe$_{76}$Al$_{24}$ alloy, a lifetime of 191 ps is detected, which agrees with the calculated lifetime of positrons trapped in $V_{Fe}$ associated with an Fe antisite atom ($V_{Fe}$+$FeAl$). On the other hand, Al-rich alloys ($C$(Al) > 25 at.%) are characterized by a longer lifetime of 195 ps which is close to the calculated lifetime of a triple defect consisting of two $V_{Fe}$ aligned in the [100] direction and connected by an FeAl atom (TDFe-A type) [3].

![Figure 3. Bulk parameters obtained from fitting of $S(E)$ curves measured on Fe-Al alloys with various Al content: $S$ parameter (full circles), positron diffusion length $L_+$(open circles).](image)

The dependence of the $S$ parameter on the incident positron energy is plotted in figure 2. At very low energies $E \approx 30$ eV almost all positrons annihilate on the surface. A drop of $S$ at positron energies $E < 10$ keV is due to a contribution of positrons annihilating in an oxide layer with a thickness of 10-40 nm formed on specimens during annealing. Almost no influence of the oxide layer on the $S(E)$ curve was found in the Fe$_3$Al alloy. Solid lines in figure 2 show results of fitting of the experimental points using the VEPFIT software package [9]. A two-layer model consisting of (i) an oxide surface layer and (ii) the bulk region were assumed in fitting with the exception of the Fe$_3$Al sample where no oxide layer was considered. The $S$ parameter and positron diffusion length $L_+$ for the bulk region obtained from fitting are plotted in figure 3. The SM Fe$_3$Al alloy exhibits the lowest $S$ parameter and the longest positron diffusion length. Non-SM Fe-Al alloys have significantly higher $S$ parameters and shorter positron diffusion lengths indicating higher concentrations of quenched-in vacancy-like defects. The concentration of defects can be calculated from SPIS results using expression

$$ c = \frac{1}{\nu} \left( \frac{L_+^2}{L_{B,+}^2} - 1 \right), $$

where $L_{B,+} \approx 180$ nm [7] is the positron diffusion length in a defect-free Fe-Al alloy and $L_+$ is the positron diffusion length measured in the studied sample. It has been demonstrated [7,10] that $L_+$ can be reliably determined even in samples with a very high concentration of defects. Figure 4 shows the
dependence of the concentration of quenched-in vacancy-like defects found using equation (2) on \( C(\text{Al}) \). Note that for triple defects we used \( \nu = 8 \times 10^{14} \text{ at. s}^{-1} \) since their open volume is roughly twice that of \( V_{\text{Fe}} \). The concentration of quenched-in vacancies in \( \text{Fe}_3\text{Al} \) calculated from LT data using equation (1) is also shown in the figure and agrees well with that calculated from SPIS data. One can see in figure 4 that the SM \( \text{Fe}_3\text{Al} \) alloy exhibits the lowest concentration of quenched-in vacancies among the studied samples. Non-SM alloys feature a significantly increased \( c \) both for the under-SM composition (\( \text{Fe}_{76}\text{Al}_{24} \)) and for the over-SM one (\( C(\text{Al}) > 25 \text{ at.\%} \)).

![Figure 4.](image)

**Figure 4.** Concentration of vacancy-like defects deduced from SPIS data (full points) and LT data (open circles). The dashed line shows the maximum density of defects which can be determined by LT spectroscopy.

4. Conclusions

Open-volume defects in Fe-Al alloys quenched from 1000°C were identified as Fe-vacancies in the \( \text{Fe}_3\text{Al} \) alloy, Fe-vacancies associated with Fe-Al atoms in the alloy with \( C(\text{Al}) < 25 \text{ at.\%} \) and triple defects consisting of an Fe-divacancy plus an Fe-Al atom in alloys with \( C(\text{Al}) > 25 \text{ at.\%} \). It was demonstrated that the concentration of defects can be reliably determined from SPIS results even in cases when the free positron component cannot be resolved in LT spectra. The concentration of vacancies in order of \( 10^{-2} \text{ at.\%} \) was found in the \( \text{Fe}_3\text{Al} \) alloy. Roughly 10 times higher concentration was found in the alloy with \( C(\text{Al}) < 25 \text{ at.\%} \). Almost three orders of magnitude higher concentration of defects approaching 10 at.\% was determined in Al-rich alloys (\( C(\text{Al}) > 25 \text{ at.\%} \)).

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