Quenched-in Vacancies and Hardening of Fe–Al Intermetallics

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The role of vacancies in hardening of Fe–Al intermetallic alloys was studied in the present work for a wide range of Al concentrations from 20 to 50 at\%. The alloys quenched from 1000 °C as well as those annealed subsequently at 520 °C for 1 h were subject to study. Slow-positron beam experiments combined with Vicker’s microhardness tests were utilised. Hardness of Fe–Al alloys exhibited a somewhat complex dependence on Al content which could not be fully explained purely by consideration of intermetallic phases formed. This happens due to additional hardening effect caused by quenched-in vacancies. The concentrations of vacancies were estimated from positron back-diffusion data and found to rise for Al content above 25 at\%. Correlation of vacancy concentrations with hardness data for the quenched and annealed alloys has revealed that hardening of alloys with a low Al content (<30 at\%) is originated predominantly by anti-phase boundaries while hardening induced by quenched-in vacancies dominates for alloys with a higher Al content (30–50 at\%).

1. Introduction

Iron–aluminum intermetallic alloys belong to attractive materials for industrial use. Particularly, they exhibit a low density, a high strength, and a good corrosion resistance. A low production cost of Fe–Al alloys is also advantageous.

Physical and functional properties of Fe–Al intermetallics are influenced by point defects and atomic ordering during slow cooling from high temperatures to room temperature (RT). The ordering appears to depend on Al content \cite{1}. At \(\approx 1000^\circ\text{C}\), the Fe–Al alloys exist in the disordered A\(_2\) phase. The Fe–Al alloys with a high Al concentration of 30–50 at\% undergo transformation from the A\(_2\) phase to the partially ordered B\(_2\) structure when cooled down to RT. The Fe–Al alloys with a lower Al content (20–30 at\%) pass first also through the A\(_2\) → B\(_2\) transition during cooling, but ordering continues with decreasing temperature reaching eventually the ordered D\(_03\) phase at RT. At high temperatures, the equilibrium concentrations of vacancies in Fe–Al alloys become as high as several at\% \cite{2}. Vacancies were for example shown to have a significant influence on hardness of these systems \cite{3}. Thus comprehensive research on vacancies in Fe–Al alloys in a wide range of Al content is essential for complete understanding of physical and mechanical properties of these alloys.

The positron annihilation spectroscopy (PAS) has already been applied to defect studies of Fe–Al alloys several times \cite{4–9}. The present work was aimed to expand knowledge of Fe–Al intermetallics and to gain more insight into the hardening role of quenched-in vacancies in Fe–Al alloys and effects of annealing, covering a wide range of Al concentrations (from \(\approx 20\) at\% to \(\approx 50\) at\%). The variable energy positron annihilation spectroscopy (VEPAS) was combined with Vickers microhardness (HV) measurements.

2. Experimental

2.1. Materials

A series of Fe–Al alloys, \(\text{Fe}_{100-c_{\text{Al}}}\text{Al}_{c_{\text{Al}}}\), with Al concentrations, \(c_{\text{Al}}\), covering the range from 18 to 49 at\% were prepared by arc melting of high-purity (99.99\%) iron and aluminium in Ti-gettered argon atmosphere. Disk-shaped Fe–Al specimens (\(\approx 15\) mm diameter, \(\approx 0.5\) mm thickness) were cut from the cast ingot, annealed at \(1000^\circ\text{C}\) for 1 h in evacuated quartz ampoules and promptly quenched into water at RT. The as-quenched specimens were first characterised by VEPAS or HV. Selected quenched specimens then underwent vacuum annealing at \(520^\circ\text{C}\) for 1 h finished by quenching into RT water and followed by the measurements.
2.2. Apparatus and data taking

VEPAS investigations were carried out using a $^{22}\text{Na}$ based continuous magnetically guided slow positron beam [10]. Positron energies $E_+$, covered the interval from 0.03 to 35 keV. The $\gamma$-spectra were measured with a HPGe spectrometer exhibiting an energy resolution of 1.06 keV (FWHM) at 511 keV. At least $2.5 \times 10^5$ counts were accumulated in each annihilation peak. The Doppler-broadened peak shapes were characterised through ordinary sharpness ($S$) and wing ($W$) parameters and normalised to values $S_0 = 0.5085 \pm 0.0010$ and $W_0 = 0.1044 \pm 0.0004$, to which measured $S$- and $W$-values were found to level for the quenched Fe$_{77}$Al$_{23}$ reference alloy above $E_+ \approx 20$ keV. The dependencies $S$ vs. $E_+$ were analysed by means of the VEPFIT code [11].

Vickers microhardness tests were carried out by applying 100 g load for 10 s using the STRUERS Duramin-2 micro-tester. Resulting HV-values were obtained by averaging at least 10 repeated tests.

3. Results And Discussion

3.1. VEPAS data

The dependences of $S$-parameters on positron energy $E_+$ measured for Fe–Al alloys in the present work, exhibited patterns illustrated in Fig. 1. For $E_+ < 2$ keV, a pronounced fall of the $S$-values with increasing $E_+$ was seen, which should be attributed to an oxide layer, that Fe–Al alloys are known to be covered with [8]. Above $E_+ \approx 2$ keV, gradual approach of $S$-parameters toward $c_{\text{Al}}$-specific bulk values, $S_{\text{bulk}}$ ($c_{\text{Al}}$), was clearly visible, reflecting decreasing portion of positrons that could diffuse back to the surface, when $E_+$ was increased.

The measured $S(E_+)$ dependences were analysed by means of VEPFIT code [11]. In accordance with the observed shapes of these dependences, the fitting model included the two depth regions: (i) the thin (a few tens of nm) surface oxide layer, and (ii) the Fe–Al bulk. Below, we will focus on the bulk region characterised by shape parameters $S_{\text{bulk}}$ and $W_{\text{bulk}}$, and the mean positron diffusion length $L_{+,\text{bulk}}$. VEPFIT analysis of measured $W(E_+)$-dependences appeared to be less meaningful. $W_{\text{bulk}}$ parameters could, however, be estimated by averaging measured $W$-values over the plateau region ($E_+ \geq 20$ keV). The bulk shape parameters were arranged in the $S_{\text{bulk}}$-$W_{\text{bulk}}$ plot in Fig. 2. Roughly linear behaviour is featured by this plot for the quenched as well as annealed Fe–Al alloys, suggesting that the same defect species were dominating positron traps in the bulk region for all the Fe–Al alloys with Al content between 26 and 50 at%. For the quenched Fe–Al alloys, the evolution of $S_{\text{bulk}}$- and $W_{\text{bulk}}$-values with $c_{\text{Al}}$ show a non-monotonicity around $c_{\text{Al}} = 26$ at%, reaching the minimum in $S_{\text{bulk}}$ (maximum in $W_{\text{bulk}}$) at $c_{\text{Al}} = 26$ at%. Then, $S_{\text{bulk}}$-values were found to grow ($W_{\text{bulk}}$ to decline) monotonically, see Fig. 2. For the annealed Fe–Al alloys, the evolution of the plot remains similar to the quenched alloys, however, the $S_{\text{bulk}}$-values are altogether lower ($W_{\text{bulk}}$-values higher) than corresponding data for the quenched alloys. The decrease in $S_{\text{bulk}}$-values for annealed alloys with respect to the quenched ones becomes more pronounced for $c_{\text{Al}} > 40$ at%. The negative slope of the $S_{\text{bulk}}$-$W_{\text{bulk}}$ line for the annealed alloys seems to be slightly higher than that for the quenched ones. In Fig. 3, $L_{+,\text{bulk}}$-values obtained using VEPFIT analysis were plotted against the Al content. A decrease in diffusion lengths with increasing $c_{\text{Al}}$ can be clearly seen in the figure, being more pronounced for the quenched alloys at higher Al content. The trends in $S_{\text{bulk}}$, $W_{\text{bulk}}$- and $L_{+,\text{bulk}}$-values displayed in Figs. 2 and 3 should be understood as a manifestation of increasing role of defects in the bulk region of
with increased Al content was observed. In addition, a drop in the vacancy concentration in the annealed samples, compared to the quenched ones, is seen in Fig. 4, progressing markedly with increasing Al content above $c_{Al} \approx 26$ at%.

### 3.2. HV data

Microhardness values measured for quenched and annealed Fe–Al alloys were collected in Fig. 5 as functions of Al concentration $c_{Al}$. Similarly to the VEPAS results, the data showed a non-monotonic behaviour: For quenched alloys, the HV-values first grew from $c_{Al} \approx 20$ at% reaching a broad maximum at $c_{Al} \approx 27$ at%. Then they exhibited a visible drop between $c_{Al} \approx 27$ and $\approx 30$ at%. Above $c_{Al} \approx 30$ at%, another rise up of HV toward alloys with higher Al content was seen. After annealing at 520°C per 1 h, only minor differences in hardness between quenched and annealed Fe–Al samples were found below $c_{Al} = 27$ at%. Whereas, a remarkable decline of HV with respect to the quenched samples for AI content above $\approx 27$ at% took place and this difference became gradually enlarged with increasing Al concentration, obviously reflecting an increasing vacancy concentration $c_V$ revealed in this $c_{Al}$ region by the VEPAS data of Sect. 3.1 as well as by earlier LT results [8]. Undoubtedly, such decrease should be due to annihilation of quenched-in vacancies during annealing. In annealed alloys, the HV-values were kept roughly stable between $C_{Al} \approx 30$ and $\approx 40$ at% indicating that applying of annealing at 520°C for 1 h had been sufficient to anneal out a majority of quenched-in vacancies. Then a slight increase in HV was observed, see Fig. 5, resulting probably from contribution of triple defects (two aligned Fe vacancies in the A sublattice associated with an antisite Fe atom in the B sublattice). In fact, an increasing role of triple defects, which in Al-rich alloys is around $c_{Al} \approx 50$ at%, was evidenced in our earlier positron lifetime measurements [8].
In this case, HV values measured for the annealed alloys approximate sufficiently the HV values Quenched-in vacancies are obstacles pining dislocations. In turn the second hardening mechanism, viz., vacancy-induced hardening, contributes to hardening in the Fe–Al alloys with higher Al content (> 30 at%).
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References