Investigation of H$^+$ implanted Fe-Al alloys

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Abstract. In the present work hydrogen interaction with vacancies was investigated in Fe-Al alloys with various concentration of vacancies. The Fe-Al samples were implanted with low energy H$^+$ ions (100 keV). This procedure introduced high hydrogen concentration into relatively narrow sub-surface region in the depth of $\sim$500 nm. Variable energy positron annihilation spectroscopy (VEPAS) was employed for investigation of hydrogen interaction with vacancies in the sub-surface region. This study revealed formation of vacancy-hydrogen complexes in the sub-surface region. Thermal stability of vacancy-hydrogen complexes was investigated as well.

1. Introduction

Iron aluminides are widely considered as prospective materials due to high specific mechanical strength and enhanced corrosion resistance at elevated temperatures. However, work machinability of these alloys suffers from poor ductility at room temperature. Since it has been shown that the ductility of Fe-Al alloys is remarkably improved in the absence of hydrogen and water vapor [1], environmental hydrogen embrittlement was suggested to take place in Fe-Al alloys. In addition to this, Fe-Al alloys are well known for a low vacancy formation enthalpy. As a consequence, the equilibrium concentration of vacancies in Fe-Al alloys is substantially high compared to pure metals. Thermal vacancies formed at elevated temperatures in Fe-Al alloys can be relatively easily quenched to room temperature. Hydrogen interaction with vacancies could play very important role in the embrittlement process. The importance of hydrogen interaction with vacancies is further amplified by high mobility of hydrogen in Fe-Al lattice.

In this work we employed VEPAS for investigation of defects introduced by H$^+$ implantation and interaction of implanted hydrogen with vacancies in Fe-Al alloys with various composition.

2. Experimental

Fe-Al alloys of Al concentration $c_{Al}$ 27 and 35 at.% were prepared by arc melting from high purity Fe (99.99%) and Al (99.99%) in Ti-gettered Ar atmosphere. As-cast alloys exhibited coarse grains with the mean diameter of a few mm. Specimens were quenched to room temperature after one hour of annealing at 1000 °C. The Fe$_{73}$Al$_{27}$ sample was subsequently annealed at 520 °C for one
hour. The samples were implanted by H$^+$ ions with the energy of 100 keV up to a fluence of $3 \times 10^{18}$ at./cm$^2$. The implantation was performed at room temperature on a cascade accelerator using the accelerating voltage of 100 kV.

Variable energy positron annihilation spectroscopy (VEPAS) measurements were performed using magnetically guided energy variable positron beam "SPONSOR" [2] with positron energy adjustable in the range from 30 eV to 35 keV. Energy spectra of annihilation $\gamma$ rays were measured by HPGe detector having an energy resolution of $(1.06 \pm 0.01)$ keV (FWHM at 511 keV). The Doppler broadening of annihilation profile was evaluated using the line-shape $S$-parameter.

3. Results and discussion

The aim of this study was to investigate the interaction of hydrogen with vacancies in Fe-Al alloys. For this purpose the Fe-Al alloys with known vacancy concentrations were prepared, Fe$_{73}$Al$_{27}$ sample exhibits low concentration of vacancies $c_V \approx 4 \times 10^{-6}$ while Fe$_{65}$Al$_{35}$ contains high vacancy concentration of $c_V \approx 5 \times 10^{-3}$ [3], consistent with $c_V \approx 3 \times 10^{-3}$ for Fe$_{64}$Al$_{36}$ [4].

![Figure 1](image-url) 

Figure 1. $S(E)$ curves of (a) Fe$_{73}$Al$_{27}$ and (b) Fe$_{65}$Al$_{35}$ alloy in the as-prepared state, implanted with 100 keV H$^+$ ions and subsequently annealed at 400 $^\circ$C, 500 $^\circ$C and 600 $^\circ$C. The hydrogen implantation profile plotted as a gray histogram was calculated by SRIM [5].

The implantation profile of H$^+$ ions calculated by SRIM code [5] is plotted in Fig. 1 as gray histograms. The mean H$^+$ penetration depth is $\bar{z}_{H^+} \approx 520$ nm and the width of the implantation profile is characterized by FWHM of $\approx 130$ nm.

From the H$^+$ implantation profile one can calculate that 75% of implanted hydrogen is stopped in a sub-surface layer located at a depth from 470 to 600 nm below the surface. Using the total fluence of H$^+$ implantation one can easily estimate that hydrogen concentration in this layer is as high as 2.5 H per one host metal atom (Fe, Al). Hence, the hydrogen concentration in the sub-surface region 470-600 nm is much higher than the concentration of vacancies.

The VEPAS results for Fe$_{73}$Al$_{27}$ alloy are plotted in Fig. 1(a). In the virgin Fe$_{73}$Al$_{27}$ sample the $S$-parameter decreases with increasing positron energy from the surface value to the bulk value. Fitting of the $S(E)$ dependence resulted in positron diffusion length $L_+ = (130 \pm 7)$ nm which is in agreement with low concentration of defects in this sample. One can see in Fig. 1(a) that Fe$_{73}$Al$_{27}$ alloy implanted with H$^+$ exhibits a bump with significantly enhanced $S$ parameter in the sub-surface region influenced by hydrogen implantation. This is obviously due to new defects created in the sample by H$^+$ implantation. Protons with energy 100 keV implanted into the sample lose their kinetic energy in collisions with Fe and Al atoms and produce Frenkel pairs in the host lattice. Some of them recombine, i.e. vacancy is filled by interstitial atom, but other ones remain in the sample since the displaced atom was kicked out to sufficient distance from
the vacancy. The increase of the \( S \) parameter in the sub-surface region in \( \text{Fe}_{73}\text{Al}_{27} \) sample is due to positron trapping at such vacancies created by \( \text{H}^+ \) implantation. Since it is known that an attractive interaction exists between hydrogen and vacancies \([6]\), vacancies introduced by \( \text{H}^+ \) implantation are likely associated with hydrogen. However, since the concentration of implanted hydrogen in the sub-surface region exceeds the concentration of vacancies by several orders of magnitude the majority of hydrogen atoms are located in the interstitial sites of Fe-Al lattice.

Fig. 1(b) shows \( S(E) \) curves for the \( \text{Fe}_{65}\text{Al}_{35} \) alloy. On the contrary to \( \text{Fe}_{73}\text{Al}_{27} \) alloy, the \( \text{Fe}_{65}\text{Al}_{35} \) alloy contains a high concentration of vacancies already in the virgin state, i.e. prior to \( \text{H}^+ \) implantation. This is demonstrated by a very short positron diffusion length \( L_+ = (10 \pm 2) \text{nm} \) measured in the virgin sample. From inspection of Figs. 1(a), 1(b) one can deduce that the bulk \( S \) parameter in the virgin \( \text{Fe}_{65}\text{Al}_{35} \) sample is higher than \( S \) in the \( \text{H}^+ \) implanted region in \( \text{Fe}_{73}\text{Al}_{27} \). It indicates that \( \text{Fe}_{65}\text{Al}_{35} \) sample in the virgin state contains higher concentration of vacancies than the sub-surface region in \( \text{H}^+ \) implanted \( \text{Fe}_{73}\text{Al}_{27} \). Protons implanted into \( \text{Fe}_{65}\text{Al}_{35} \) creates vacancies in a similar manner as in \( \text{Fe}_{73}\text{Al}_{27} \) but at the same time hydrogen implanted into the sub-surface region is trapped at vacancies existing already in the sample. The former process increases the \( S \) parameter while the latter leads to a decrease of \( S \) due to the fact that the electron density in vacancy is enhanced by the presence of hydrogen and therefore reduced positron localization. One can see in Fig. 1(b) that the latter effect prevailed and \( \text{H}^+ \) implanted \( \text{Fe}_{73}\text{Al}_{27} \) exhibits lowered \( S \) parameter in the sub-surface region influenced by implantation. Similar effect of decrease of the \( S \) parameter caused by \( \text{H}^+ \) implantation was recently observed in \( \text{Fe}_{52}\text{Al}_{48} \) \([7]\) which presumably contains very high concentration of vacancies in orders of \( 10^{-2} \) due to its high Al content \([3]\).

The implanted samples were subjected to annealing for 1 h in vacuum at various temperatures in order to examine the thermal stability of defects. The \( S(E) \) curves for annealed \( \text{Fe}_{73}\text{Al}_{27} \) and \( \text{Fe}_{65}\text{Al}_{35} \) alloys are plotted in Figs. 1(a) and 1(b), respectively.

Annealing at 400 °C activates a diffusion of hydrogen. The implanted hydrogen located in interstitial sites diffuses out of the narrow sub-surface region further into the sample, i.e. the hydrogen concentration profile becomes broader and vacancies located in larger distance from the maximum of the hydrogen implantation profile can be filled with hydrogen. Driving force for this process is a gradient of the hydrogen concentration. This process leads to a decrease of \( S \) in a broader sub-surface region which can be seen for \( \text{Fe}_{73}\text{Al}_{27} \) and \( \text{Fe}_{65}\text{Al}_{35} \) alloys annealed at 400 °C in Fig. 1(a) and 1(b), respectively. Positrons with kinetic energy of 16 keV exhibit the mean penetration depth of \( \sim 510 \text{nm} \) which is close to the maximum of the implantation profile of hydrogen. The implantation profiles for positrons and hydrogen are compared in Fig. 2a. Obviously, the positron implantation profile is significantly wider which testifies that the \( S \) parameter value measured at positron energy of 16 keV contains a superposition of a contribution from positrons annihilated inside the region with high hydrogen concentration and also a contribution of positrons annihilated outside this region. The broadening of the hydrogen concentration profile extends the spatial range in which vacancies are filled with hydrogen and thereby decreases the \( S \) parameter. An additional mechanism which occurs at higher temperatures is recovery of vacancies which disappear by diffusion into sinks at grain boundaries and on the surface. This process is clearly visible in Fig. 1(b) as a drop of the bulk \( S \) parameter of both alloys annealed at 500 °C. Note that enhanced \( S \) parameter at low energies in the \( \text{Fe}_{73}\text{Al}_{27} \) alloy annealed 600 °C is due to the formation of a thin oxide layer during annealing.

It is instructive to compare the temperature dependence of the bulk \( S \) parameter \( S(35 \text{keV}) \) determined at the positron energy of 35 keV and the \( S \) parameter \( S(16 \text{keV}) \) determined at energy of 16 keV where the contribution of positrons annihilated in the sub-surface region with high hydrogen concentration was maximal. The behavior of the \( S \) parameters \( S(35 \text{keV}) \) and \( S(16 \text{keV}) \) for the \( \text{Fe}_{73}\text{Al}_{27} \) and \( \text{Fe}_{65}\text{Al}_{35} \) alloys is plotted in Fig. 3b and 3c, respectively. The \( S \) parameter \( S(16 \text{keV}) \), which characterizes the sub-surface region influenced
Figure 2. (a) Comparison of the implantation profile of H$^+$ ions with the energy of 100 keV and the implantation profile of positrons with energy of 16 keV. $S$-parameter determined at positron energy of $E = 16$ keV and 35 keV for (b) Fe$_{73}$Al$_{27}$ and (c) Fe$_{65}$Al$_{35}$.

by implanted hydrogen, decreases already during annealing at 400 °C due to the spread of hydrogen concentration profile. During further annealing the decrease of $S(16$ keV) continues due to the recovery of vacancies. The $S$ parameter $S(35$ keV) for Fe$_{73}$Al$_{27}$ alloy exhibits a similar but less pronounced decrease since a fraction of positrons implanted into the sample with energy of 35 keV is still able to diffuse back into the sub-surface region containing vacancies created by H$^+$ implantation. On the other hand, in the Fe$_{65}$Al$_{35}$ alloy the $S$ parameter $S(35$ keV) is not affected by the sub-surface region containing implanted hydrogen because of very short positron diffusion length due to a high concentration of vacancies. The $S$ parameter $S(35$ keV) for the Fe$_{65}$Al$_{35}$ alloy remains approximately constant during annealing and decreases only after annealing at 500 °C where vacancies in the bulk are annealed out.

4. Conclusions
Fe-Al alloys implanted by H$^+$ ions with the energy of 100 keV were studied by the VEPAS technique. It was suggested that H$^+$ implantation creates vacancy-hydrogen complexes in a sub-surface region. Moreover, trapping of hydrogen at vacancies existing already in sample was observed. The investigation of the thermal stability of defects in H$^+$ implanted alloys revealed that hydrogen diffusion is activated by annealing at 400 °C leading to a spread of the hydrogen concentration profile. Vacancies are annealed out by further annealing at 500 °C.

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