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Annealing behaviour of plastically deformed stainless steel 1.4307 studied by positron annihilation methods

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Abstract. Isochronal and isothermal annealing of stainless steel 1.4307 samples deformed by compression were investigated using Doppler broadening measurements of the annihilation line. We made an attempt to describe the obtained dependencies in terms of vacancy migration and sinking to the grain boundaries. The model assumed spherical grains with a homogeneous initial distribution of vacancies. The model was capable of following the isochronal annealing data quite accurately. However, the obtained activation energy of vacancy migration equal to 0.44 ± 0.05 eV seemed too low. The isothermal annealing dependency was reproduced less precisely. The reason for this may be the presence of the α'-martensite particles in the samples, which can introduce additional defects seen by positrons in the temperature range in which the martensite reversion takes place.

Key words: plastic deformation • positron annihilation • stainless steel

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Introduction

Positron annihilation spectroscopy is a well-established tool for microstructure investigations of condensed matter. The interaction of positrons with matter is used to study configuration and properties of materials at the atomic level. Positrons implanted into a metallic system localize in regions where electron density is lower than in a perfect crystal lattice, i.e. open volume defects, and then annihilate with electrons. In case of vacancies and small vacancy clusters the relationship between the positron lifetime and the size of open volume defects is well known.

Efforts are made to apply positron annihilation techniques as a non-destructive method of material evaluation for mechanical engineering. In particular, this concerns structural modification of metals and alloys caused by plastic deformation. Crystal lattice defects generated during plastic deformation, i.e. open-volume defects such as vacancies and their agglomerates and to some extent dislocations can be investigated using positron annihilation techniques. Generation of defects by plastic deformation or fatigue and their evolution during annealing treatment exemplify problems studied. In case of alloys, the annihilation of positrons with the bound electrons of atoms surrounding open volume defects deliver unique signature which may be used for their identification. Then, positron annihilation can also shed light on the interactions of open volume defects with alloying components' atoms, which is important for structural materials containing many elements.

Table 1. The chemical composition of the studied samples (wt.%)

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V
1.4307	0.012	0.29	1.13	0.028	0.026	18.37	8.12	0.36	0.35	0.09

Austenitic stainless steel is such widely used structural material. Defects production and their interactions with alloying elements' atoms due to plastic deformation in stainless steel are much more complex than in dilute binary alloys. However, understanding of these processes is important from the application point of view.

Interpretation of previous positron annihilation annealing experiments performed for stainless steel samples after plastic deformation or fatigue treatment [6, 9] are based on the theoretical [11, 12] and experimental evidences [8] that dislocations and their dilatation zones are shallow traps for positron in room temperature in iron or in stainless steel. In addition, dislocation density does not change significantly in the temperature range in which the changes of the positron annihilation characteristics were observed [8]. Thus, the observed changes were explained by the behaviour of vacancies, i.e. their migration to grain boundaries or other sinks, and creation of carbide precipitates at higher temperatures [2, 6], whose mismatch with austenite matrix is compensated with misfit dislocations.

The aim of the presented investigations was to study the annealing behaviour of deformed austenitic stainless steel 1.4307 (EN) in terms of annealing of defects detected by positron annihilation methods.

Experimental details

The material under investigation was a commercial stainless steel 1.4307 (EN) equivalent to AISI 304L. Its chemical composition determined using an atomic emission spectrometer with spark excitation is shown in Table 1.

Samples in shape of discs, 4 mm high and 10 mm in diameter, were annealed for 1 h in the flow of N_2 gas at a temperature of 650°C, and then slowly cooled to room temperature to remove any deformation effects due to cutting and surface polishing. After annealing, the surface layer was removed by etching in hydrofluoric acid and 25% solution of nitride acid in distilled water. It was checked that the applied treatments allow us to obtain samples with a relatively low density of crystal lattice defects and clean surfaces. Though stainless steel 1.4307 is austenitic, the X-ray diffraction performed for initial samples revealed also peaks of α'-martensite. X-ray diffraction was carried out in a Philips X-Pert diffractometer using K_αCu radiation.

After that, the samples were plastically deformed using hydraulic press with a pressure of 18 MPa, which gave a thickness reduction equal to 6%. Two procedures of annealing and measurement were performed. The first was isochronal annealing for 1 h in the temperature range from room temperature to 725°C. The second was isothermal annealing at 375°C.

After each annealing, the positron measurement was performed using a Doppler broadening (DB) spectrometer with a coaxial HPGe (high purity germanium) detector with interpolated energy resolution of 1.4 keV full width at half maximum (FWHM) at 511 keV and less than a 10 μCi ^{68}Ge/^{68}Ga positron source. The reciprocal value of the linear absorption coefficient for positron emitted from this isotope into iron is equal to ca. 150 μm [5].

Additionally, there were performed positron lifetime measurements for initially annealed samples, deformed samples and samples after completion of the annealing cycles. The positron lifetime spectra of more than 1.5×10^6 counts were measured using a fast-fast spectrometer with BaF_2 scintillators. The time resolution of the system was 280 ps (FWHM). The 70-μCi activity positron source containing ^{22}Na isotope enveloped in a 7-μm thick kapton foil was sandwiched between stainless steel samples. The average implantation depth, which is the reciprocal value of the linear absorption coefficient, for positron emitted from ^{22}Na into iron is about 29 μm. All the obtained spectra were analyzed using the LT code [13].

Results and discussion

The positron lifetime measured for the initially annealed reference sample was equal to 109 ± 1 ps, which may be attributed to annihilation of positrons in the perfect lattice. The mean positron lifetime for the sample after plastic deformation was equal to 163 ± 1 ps. For comparison, the lifetime of positron trapped in the vacancy in the perfect lattice of iron is equal to 175 ps [15]. Lower value of the positron lifetime may suggest that part of the vacancies in which positrons are localized is on the dislocation lines, where atomic surrounding is distorted. This gives lower values of positron lifetime [10, 12].

Figure 1 presents the results of Doppler broadening measurements for isochronal annealing of the deformed steel samples. The S-parameter, which is defined as the ratio of the area under the fixed central part of the annihilation line to the area under the whole annihilation line, exhibits decrease with annealing temperature after a small initial increase for the temperatures between 100 and 200°C. Since the S-parameter is sensitive to the annihilation of positrons with low momentum electrons which are present in open volume defects decrease of the S-parameter indicates annealing of these defects. Similarly to the former papers [6, 9], we made an attempt to describe the obtained dependency by the vacancy migration model. The model assumes that vacancies detected by positron annihilation method diffuse to the grain boundaries or other sinks where they annihilate. The grains are in the form of spheres of radius R. The concentration of vacancies as a function of time and annealing temperature is given by:

$$\frac{c_v(t,T)}{c_0} = \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2}\exp\left[\frac{-D(T)k^2\pi^2 t}{R^2}\right] \quad (1)$$

where c_0 is the initial concentration of vacancies at initial time, $t = 0$, $D(T) = D_0 \exp(-Q_m/k_B T)$ is the vacancy diffusion coefficient, where Q_m is the activation energy for migration of vacancies and D_0 is a constant, T is

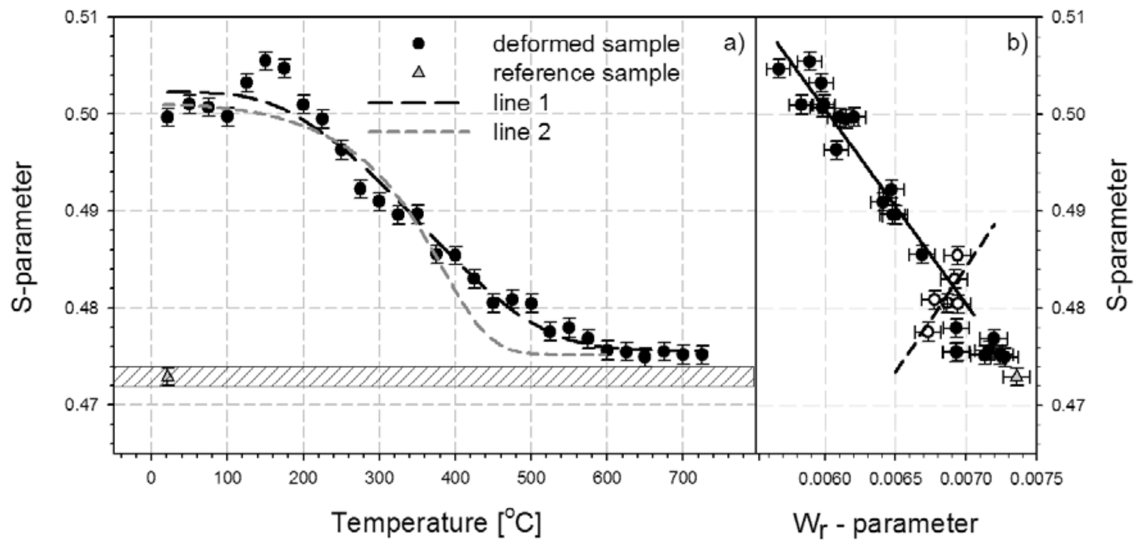

Fig. 1. (a) The S-parameter as a function of annealing temperature for 1 h isochronal annealing of 1.4301 (EN) stainless steel deformed using hydraulic press with pressure of 18 MPa, which gave thickness reduction 6%. The dashed line 1 presents the curve obtained by fitting Eq. (2) to the experimental data. The dashed line 2 was obtained by fitting Eq. (2) to the data from paper [1] for the irradiated stainless steel D9. The hatched area shows the value of the S-parameter for the initial sample before deformation. (b) The S-parameter as a function of the W_r-parameter. The solid straight line was fitted to the experimental points for temperature range from room temperature to 375°C. The dashed straight line was fitted to the experimental points for temperature range from 400 to 550°C denoted by open circles.

the absolute temperature, and t is the annealing time. Assuming that the positron trapping model is valid, the S-parameter as a function of time and annealing temperature is the following:

$$S(t,T) = \frac{S_f + S_v A c_v(t,T)}{1 + A c_v(t,T)} \tag{2}$$

where S_f and S_v are the S-parameter values corresponding to positron annihilation from the free state and from the state localized in vacancy, respectively $A = c_0\mu/\lambda_f$, μ is the trapping efficiency, λ_f is the free annihilation rate. The presented model can describe the experimental data obtained for both isochronal and isothermal annealing as it was shown for deformed silver [4].

The dashed line in Fig. 1a presents the curve obtained by fitting Eq. (2) to experimental data (black dashed line). The fitted curve describes the data well. However, the obtained value of the activation energy for vacancy migration, i.e. 0.44 ± 0.05 eV, is relatively low in comparison to 0.92 ± 0.02 eV for AISI 321 stainless steel [6] or 0.9 eV for 316L stainless steel [9]. Moreover, obtaining of a realistic value of the grain radius R at most of the order of dozens of micrometers causes that the diffusion pre-exponential factor D_0 takes the value of the order of 10^{-10} m^2/s, which is considerably lower than the minimal value obtained by Holzwarth *et al.* [9], i.e. 6×10^{-7} m^2/s for the grain size $R = 15$ μm.

For comparison, Fig. 1a shows also a curve which is a result of fitting Eq. (2) to the data from the paper [1] obtained for the irradiated stainless steel D9 (grey dashed line). The values of the S-parameter were proportionally rescaled. Taking into account positron lifetime values, the increase of the S-parameter after irradiation was ascribed to the presence of vacancy-like defects. The obtained, from the fit, activation energy for vacancy migration was equal to 1.00 ± 0.08 eV. The main difference between the black and grey dashed lines appears in the temperature region from 375 to 600°C. In this range the S-parameter for the studied steel 1.4307 is higher. This suggests that there are some additional defect created in the sample besides vacancies introduced by initial deformation. This is confirmed by the W_r-S dependency shown in Fig. 1b. The W_r-parameter is defined as the ratio of the area under the fixed wing region of the annihilation line to the area under the whole annihilation line. This region reflects the annihilation with high momentum electrons. The one straight line fitted to the W_r-S dependency suggests that the type of positron trapping defects does not change but their concentration changes. Different slopes of the S-W_r dependence indicate the occurrence of different types of defects in the material. The solid straight line in Fig. 1b was fitted to the experimental points for the temperature range from room temperature to 375°C. The slope of this line is equal – 20 ± 3. It seems that for the annealing temperature higher than 375°C the S-W dependence changes. The experimental points for the temperature range from 400°C to 550°C were distinguished (open circles). The slope of the fitted straight line, equals 15 ± 12 is quite different from the previous one but its error is big. This could suggest a change of the main type of the positron trapping sites for this temperature range.

Figure 2a presents the results of Doppler broadening measurements for isothermal annealing of the samples at a temperature of 375°C. The dashed line presents the curve obtained by fitting Eq. (2) to experimental data taking values of D_0 and R from the previous fit. The value of the activation energy for vacancy was equal to 0.45 eV, which agrees with that from the previous fit for isochronal annealing data, but the fitted curve does not reproduce the experimental data satisfactorily. It is worth noticing that the value of the S-parameter did not reach the value obtained after isochronal annealing. Figure 1b shows the W_r-S dependency. The solid straight line was fitted to the experimental points for the time range from 0 to 51 min. The slope of this line is equal – 20 ± 4 and it is identical to that obtained

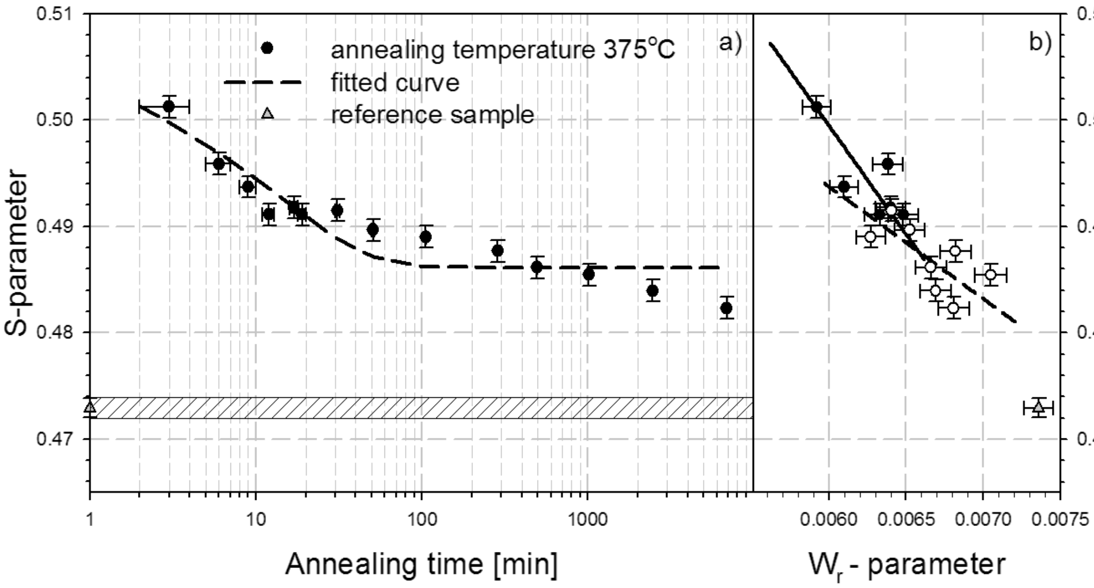

Fig. 2. (a) The *S*-parameter as a function of annealing time for isothermal annealing of 1.4301 (EN) stainless steel in temperature 375°C deformed using hydraulic press with pressure of 18 MPa, which gave thickness reduction 6%. The dashed line presents the curve obtained by fitting Eq. (2) to the experimental data. The hatched area shows the value of the *S*-parameter for the initial sample before deformation. (b) The *S*-parameter as a function of the W_r-parameter. The solid straight line was fitted to the experimental points for time range from 0 to 51 min. The dashed straight line was fitted to the experimental points for time range from 31 to 6902 min denoted by open circles.

for isochronal annealing for the temperature range from room temperature to 375°C. The dashed straight line was fitted to the experimental points for the time range from 31 to 6902 min denoted by open circles. (A few of the experimental points was considered in both fits). The slope of this line is equal to – 11 ± 4, which indicates that the main type of the positron trapping sites may be different than that for lower annealing time. However, the difference in the slopes is not so distinct as in the case of isochronal annealing. Thus, the change in the main type of positron trapping defects is not so pronounced.

The imperfect description of the studied stainless steel annealing behaviour by the vacancy migration model may be caused by the presence of martensite particles in the samples, which can introduce additional defects seen by positrons (Fig. 3). It is worth noticing that martensite did not form during plastic deformation in stainless steel studied by Holzwart *et al.* [9].

The austenite in metastable stainless steels can transform into two different types of martensite. One of them is hexagonally close packed (hcp) martensite, called ε-martensite. The other is a body centered cubic (bcc) martensite, called α'-martensite. Plastic deformation apart from introducing crystal lattice defects, can cause formation of martensite called deformation induced martensite. The fine α'-martensite grains form mainly at the intersection of shear bands inside the austenite grains. The initial α'-martensite nuclei are coherent with the parent austenite crystal lattice [3]. When the α'-martensite plates grow they become semi-coherent or incoherent. The semi-coherent austenite/martensite interfaces act as sources of dislocations increasing dislocation density in austenite phase. Then, plastic deformation takes place mainly in the austenite. Presence of martensite causes decrease of effective grains size of austenite phase contributing to strengthening of the steel [7].

During annealing, α'-martensite is stable up to 400°C [14]. Above this temperature, martensite reverses to austenite. The complete reversion may reach the temperature of the order of 750°C.

The temperature above which the reversion of martensite may start is in accordance with the temperature range where the higher values of the *S*-parameter indicate the presence of additional defects and a change of the slop of the $W_r S$ dependency may suggest a change of the main kind of places where positrons are localized and annihilate. The confirmation of the martensite reversion was obtained by X-ray diffraction. For sample after isochronal annealing, the diffraction pattern did not contain peaks of α'-martensite. Thus, it seems that the process of martensite reversion revealed in the results of positron annihilation studies of annealing behaviour of deformed stainless steel.

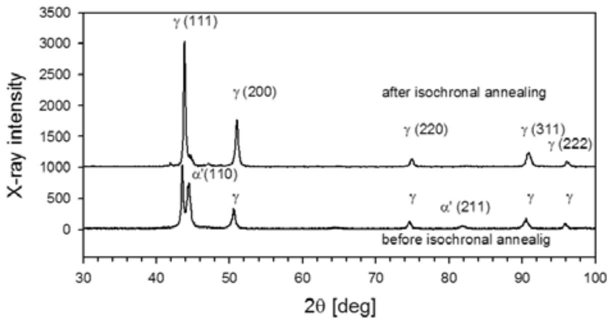

Fig. 3. X-ray diffraction patterns for the initial sample and the sample after isochronal annealing procedure.

Conclusions

Positron annihilation method allows us to investigate the annealing behaviour of deformed stainless steel in terms of defects annealing. The obtained temperature dependency of the annihilation line shape parameter, i.e. the *S*-parameter, reflects two processes in the plastically deformed stainless steel 1.4307, i.e. the migration and sinking of vacancies and the α'-martensite reversion to austenite. It seems that the latter induces additional defects beside those created by the initial deformation. This causes that the proposed vacancy migration model does not describe annealing process sufficiently giving the vacancy migration energy 0.44 ± 0.05 eV significantly lower than the values obtained for austenitic stainless steels in which deformation induced martensite does not form.

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