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LONG-TERM ISOTHERMAL ANNEALING OF AN AUSTENITIC STAINLESS STEEL 1.4301 STUDIED USING POSITRON ANNIHILATION SPECTROSCOPY*

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Samples of stainless steel 1.4301 (EN) deformed by compression were subjected to cumulative isothermal annealing and studied using the Doppler broadening of the annihilation line spectroscopy. The initial plastic deformation induced not only generation of crystal lattice defects but also transformation from austenite to α'-martensite. Annealing at the temperature below the range of the α'-martensite reversion, *i.e.*, 375°C allows us to remove gradually some defects induced by plastic deformation, *i.e.*, vacancies which migrate to the sinks at grain boundaries. However, the final S-parameter value is significantly higher than prior the deformation. This behavior can be connected with anomalous evolution of the martensitic phase observed for annealing at temperatures between 300°C and 400°C. Annealing at 450°C caused reverse transformation of α'-martensite and annealing of positron trapping defects. The final value of the S-parameter slightly higher than prior the deformation and higher microhardness value may be linked to sensitization and carbide precipitation resulting from the long-time annealing.

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1. Introduction

Knowledge about structural changes occurring after plastic deformation is of great value in terms of industrial materials applications due to the impact on their physical, mechanical, technological and functional properties. Generally, mechanical damage starts with changes in the microstructure. Plastic deformation of metastable stainless steel induces not only generation of crystal lattice defects due to dislocation hardening and mechanical twinning but also phase transformation from austenite to martensite. Annealing of plastically deformed austenitic stainless steel can induce martensite reverse transformation, which may be accompanied by other processes such as recovery, recrystallization and carbide precipitation [1, 2].

Microstructural changes can be observed using standard material engineering methods, *i.e.* optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It is also useful to study properties that change with microstructure, *e.g.*, microhardness. Microstructure modifications influence also defects of the crystal lattice at the atomic level and positron annihilation spectroscopy allows us to investigate these changes [3–6]. The studies can also be performed for the sample layer of the depth of a few micrometers at the surface using variable energy positron beams [7–9].

The aim of the research presented in this paper was to study the effect of long-term isothermal annealing of plastically deformed austenitic stainless steel 1.4301 on changes of the crystal lattice defects in the material, detected by positron annihilation spectroscopy. XRD and microhardness measurements supplemented these studies. Additionally, microscopic observations of the samples subjected to a corrosion treatment were performed.

2. Experimental details

The material under investigation was commercial austenitic stainless steel 1.4301 with the chemical composition shown in Table I. The chemical composition was determined using an atomic emission spectrometer with spark excitation. Steel samples for study were cut from a 10 mm diameter rod using the diamond saw with a low cutting speed. Samples in shape of discs, 4 mm high and 10 mm in diameter, were annealed for 1 h in the flow on N_2 gas at temperature of 700°C, and then slowly cooled to room temperature in order to remove any deformation effect due to cutting. After annealing, the surface layer was etched by the TS-K 2000 paste containing 5–10% hydrofluoric acid and 25–30% nitric acid. Next, the samples were plastically deformed by uniaxial compression up to 6% thickness reduction relative to the initial value. Two sets of samples were isothermally annealed at 375°C and 450°C, respectively. To obtain the dependencies of the positron

TABLE I

The chemical composition of the investigated steel (wt%).

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

annihilation parameters on annealing time, after each annealing carried out for a given time, the samples were quenched in water, additionally, possible oxides formed on the surface were removed by the TS-K 2000 paste etching, and then the positron annihilation measurement was performed at room temperature. For this purpose, a coaxial high-purity germanium (HPGe) detector with energy resolution equal to 1.38 keV (FWHM) interpolated at 511 keV was used for monitoring the Doppler broadening of the annihilation line. The ^{68}Ge/^{68}Ga isotope (activity 10 μCi) enveloped in a 7 μm-thick kapton foil was used as a positron source. A typical measurement geometry was applied, *i.e.*, the source was placed between two identical samples with a flat surface. Thanks to that, the positrons were emitted into the samples in a full solid angle. Number of counts in the spectrum in the area of the annihilation line were 10^6. The obtained spectrum was analyzed using the SP-1 program [10] by determining a so-called S-parameter. The S-parameter is defined as the ratio of the area under the fixed central part of the annihilation line (for energy close to 511 keV) to the area under the whole annihilation line. It is sensitive to the annihilation of positrons with low momentum electrons which are present in open volume defects.

The X-ray diffraction measurements were carried out using CuK$_\alpha$ radiation on a Philips X-Pert diffractometer. Microhardness measurements were carried out using hardness tester TUKON 2500 manufactured by Wilson Hardness. Additionally, the corrosion behavior of the sample after long-time annealing at 450°C was studied. For this purpose, the sample was studied by an optical microscope: Axio Imager M1m ZEISS after 6 h immersion in a dilute etching solution of TS-K 2000 (1:10 in distilled water).

3. Results and discussion

The applied plastic deformation was relatively low (*i.e.*, 6% reduction in thickness only). However, it was sufficient not only to generate crystal lattice defects but also the phase transformation from austenite to α'-martensite to occur. The peaks from α'-martensite are clearly visible beside the peaks from austenite in the diffraction pattern for the sample after deformation shown in Fig. 1.

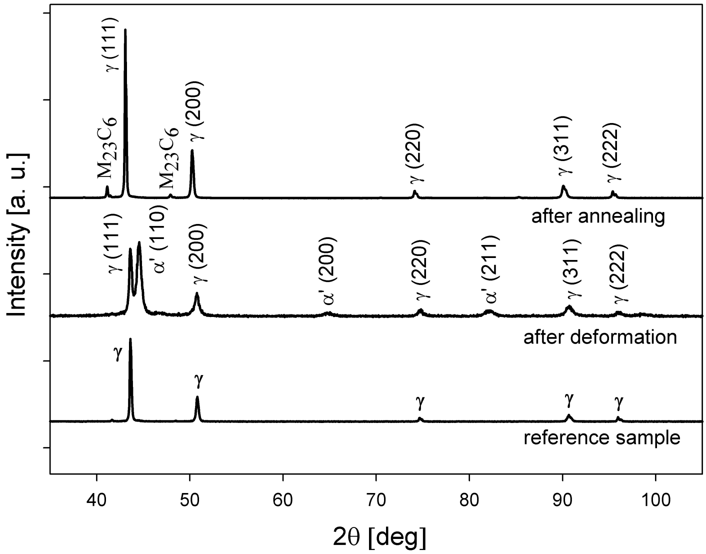

Fig. 1. The comparison X-ray patterns for annealed sample, after deformation and after annealing for *ca.* 6 000 minutes at 450°C.

The S-parameter dependencies on the annealing time at two temperatures are depicted in Fig. 2. The temperature of 375°C was chosen in the middle of the S-parameter decrease obtained for isochronal annealing attributed to migration of vacancies to their sinks at grain boundaries [11, 12]. Nonetheless, it is lower than the temperature of α'-martensite reversion which occurs above 400°C [1]. The second temperature selected for this study, *i.e.*, 450°C is high enough for α'-martensite reversion to occur. The values of the S-parameter for the samples prior the deformation described as the reference value and after deformation described as as-deformed one are also shown in Fig. 2.

It can be noticed that for annealing at 375°C, the S-parameter decreases in the whole range of annealing time. This indicates that defects induced by plastic deformation are gradually annealed, *i.e.*, their concentration decreases. The largest decrease of the S-parameter is observed after first 3 minutes of annealing. For times higher than 10 minutes, the S-parameter decrease becomes slower as indicated by a change in the slope. For the temperature of 450°C, even larger decrease of the S-parameter occurs for the 3 minutes of annealing and then after the annealing time of 1 000 minutes, the S-parameter reaches the value only slightly higher than that obtained for the reference sample (*i.e.*, sample before deformation) and this state persists after further annealing. Then, the selected parameters, *i.e.*, time and temperature are sufficient for the α'-martensite reverse transformation to take place. This is confirmed by the XRD pattern measured for the sam-

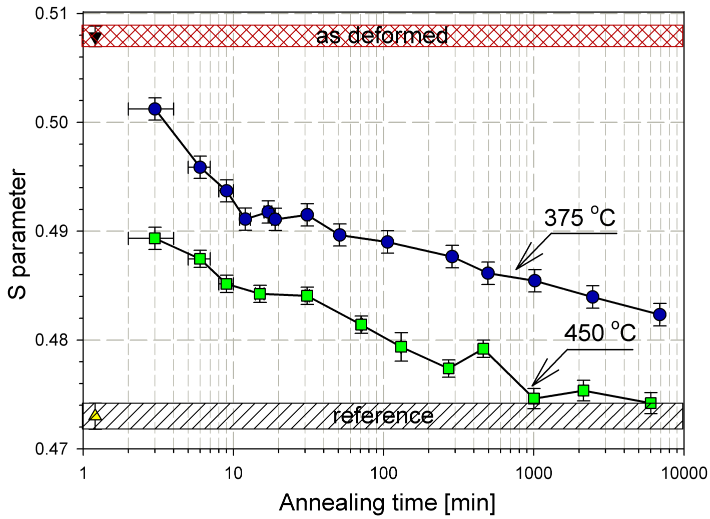

Fig. 2. The S-parameter as a function of annealing time for isothermal annealing of stainless steel 1.401 at 375°C and 450°C. The samples were deformed by compression to 6% thickness reduction. The upper hatched area indicates the initial value of the S-parameter after deformation. The lower hatched area shows the reference value of the S-parameter for the well-annealed sample before deformation.

ple after *ca.* 6 000 minute annealing at 450°C (Fig. 1) for which no peaks from α'-martensite were noticed. Peaks from austenite are clearly visible, however, additional weak peaks attributed to metal carbides $M_{23}C_6$ are also present.

For the sample annealed at 375°C, the decrease in the S-parameter (Fig. 2) is slower than that for the sample annealed at 450°C and it does not reach the value obtained for the well-annealed reference sample even after long-time annealing. Not only α'-martensite reversion does not take place but according to the literature, annealing at a temperature between 300°C and 400°C can cause an increase in the α'-martensite volume fraction [13,14]. This process can prevent annealing of defects which trap positrons and contribute to higher value of the S-parameter in spite of the fact that vacancies induced during deformation are annealed in temperatures above 200°C, *i.e.*, during the first stage of recovery.

For the sample annealed at 450°C, there were also performed the microhardness measurements as a function of the annealing time. The results are shown in Fig. 3. Initially, the value of microhardness slightly decreases, but after 1 000 minutes of annealing, some increase in hardness was registered. This hardening can be related to precipitation of metal carbides. Due to the precipitation hardening, the material hardness does not reach the value of the reference well-annealed sample.

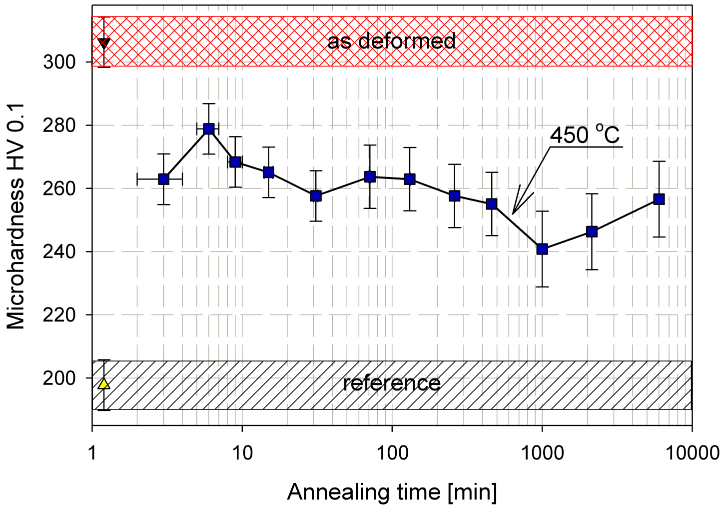

Fig. 3. Microhardness measurement as a function of annealing time at 450°C. The samples were deformed by compression to 6% thickness reduction. The upper hatched area indicates the initial value of microhardness after deformation. The lower hatched area shows the reference value of microhardness for the well-annealed sample before deformation.

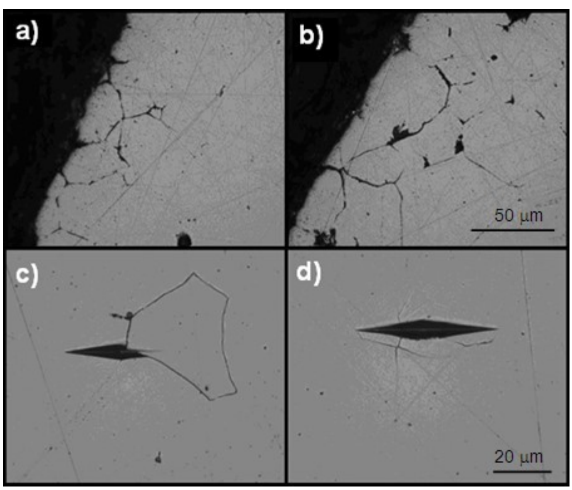

Fig. 4. The images obtained using an optical microscope for annealing stainless steel 1.4301 at temperature 450°C for *ca.* 6 000 minutes: (a), (b) visible intergranular corrosion (c), (d) cracks along grain boundaries.

The austenitic stainless steel can be prone to intergranular corrosion when it is exposed to a temperature in the range between 370 and 800°C [15, 16]. This effect, known as sensitization, results from precipitation of chromium carbides ($Cr_{23}C_6$) at the grain boundaries. Due to insufficient chromium diffusion in the matrix, the concentration of chromium decreases near the grain boundaries and chromium depleted areas (with chromium content below *ca.* 12%) are susceptible to intergranular corrosion [17]. Intergranular corrosion effects were clearly visible, especially in the near-surface region adjacent to the corrosion exposed surface of the sample, during microscopic study of the specimens after annealing for *ca.* 6 000 minutes at 450°C and then subjected to corrosion treatment. Since precipitation of chromium carbides weakens grain boundaries, distinct cracks along grain boundaries were already induced by the Knoop indenter during the microhardness tests (see Figs. 4 (c) and (d) as an example). The observed intergranular corrosion confirms sensitization of the studied stainless steel samples after long-term annealing at 450°C and indirectly indicates the presence of carbide precipitates at the grain boundaries. The sensitization can influence the S-parameter value for the annealing time higher than 1 000 minutes.

4. Conclusions

The long-time annealing behavior of austenitic stainless steel 1.4301 compressed to 6% thickness reduction were investigated using Doppler broadening spectroscopy. Annealing at the temperature below the range of the α'-martensite reversion, *i.e.*, 375°C caused annealing of some defects induced by plastic deformation, however, the S-parameter value did not return to the one prior the deformation. It can be connected with anomalous evolution of the martensitic phase. On the other hand, annealing at 450°C caused reverse transformation of α'-martensite and annealing of positron trapping defects. However, the final S-parameter value was slightly higher than the reference value. This and higher microhardness values may be connected to sensitization and carbide precipitation resulting from the long-time annealing.

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