

Vacancy clustering behavior in hydrogen-charged martensitic steel AISI 410 under tensile deformation

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Abstract. The formation and accumulation of defects under tensile deformation of hydrogen-charged AISI 410 martensitic steels were investigated by using positron lifetime spectroscopy. During the deformation process, dislocations and vacancy-clusters were introduced and increased with increasing strains. Between hydrogen-charged and uncharged samples with the same tensile strains there was no significant difference in the dislocation density and mono-vacancy equivalent vacancy density.

1. Introduction

Hydrogen embrittlement is a serious problem responsible primarily for delayed failures that frequently occurs when high-strength martensitic steels and other metals absorb hydrogen. It is characterized by mechanical properties degradation due to hydrogen ingress, such as ductility reduction. These behaviors imply that the hydrogen embrittlement is directly correlated with lattice defects and most models on hydrogen embrittlement are based on hydrogen-defect interactions. However, the interaction between hydrogen and defects during deformation has not been revealed enough yet. Positron lifetime spectroscopy is specifically sensitive to open-volume defects, such as dislocations, vacancies and vacancy clusters. In particular, it has a distinctive advantage in detecting vacancy or vacancy cluster, and evaluating in vacancy densities through multi-component spectrum analysis based on the multi-state positron trapping model.

AISI 410 steel is one of the most popular 400 series martensitic stainless steels, and is widely used for the high strength and corrosion resistant applications. In this study, the formation and accumulation of defects in AISI 410 steel under tensile deformation were investigated by using positron lifetime spectroscopy.

2. Experimental method

The chemical composition of the commercial AISI 410 steel plates used in this study is provided in Table 1. The composition is within the typical composition range of AISI 410 steel. The steel plates with a thickness of 5 mm were machined to the tensile test specimen geometry with a gauge width of 5 mm, a gauge length of 30 mm and a thickness of 5 mm. Then tensile test specimens were polished up to grit #2000 with waterproof abrasive papers. The hydrogen charging was conducted by soaking for



Table 1. Chemical composition (wt%) of steel plates. The composition range of AISI 410 steel is also shown for comparison.

| | Fe | Cr | Mn | Si | C | Ni | P | S |
|---------------|---------|-----------|-------|-------|----------|----------|----------|----------|
| Steel studied | Balance | 12.73 | 0.45 | 0.38 | 0.14 | 0.07 | 0.022 | 0.006 |
| AISI 410 | Balance | 11.5-13.5 | 1 max | 1 max | 0.15 max | 0.75 max | 0.04 max | 0.03 max |

48h at 50°C in a 20wt% ammonium thiocyanate (NH₄SCN) solution. The diffusible hydrogen content in the hydrogen-charged samples was evaluated as 2.2 wtppm based on thermal desorption analysis.

Tensile tests were carried out at room temperature using a servo-hydraulic universal testing machine (EHF-EV101k2-A20-1A, Shimadzu Corporation) at a strain rate of $8.0 \times 10^{-6} \text{ s}^{-1}$ for hydrogen-charged and uncharged samples, and fractured and interrupted samples were prepared. In order to prevent hydrogen release from hydrogen-charged samples during the tensile deformation, the tensile test specimens were soaked in the NH₄SCN solution. A pair of samples for positron lifetime measurements was obtained from the gauge part of the tensile test specimens. The samples obtained were mechanically polished and then electrolytically polished by using an ammonium chloride solution. Positron lifetime measurements were carried out by using a digital oscilloscope system with photomultiplier tubes mounted with BaF₂ scintillators, having a time resolution (FWHM) of 175 ps. The positron lifetime measurements require data acquisition for approximately 9 hours with a Na-22 positron source of 0.7MBq activity in order to acquire 3 million counts in the positron lifetime spectrum. The measured spectra were analyzed using the programs RESOLUTION [1] and POSITRONFIT Extended [2].

3. Results

The engineering stress-strain curves for hydrogen-free and hydrogen-charged samples are shown in Figure 1. The tensile elongation was obviously reduced by hydrogen charging. The positron lifetimes τ_{one} obtained by one-component fitting of lifetime spectra are shown in Figure 2. The positron lifetime for hydrogen-charged samples showed higher values compared to uncharged samples.

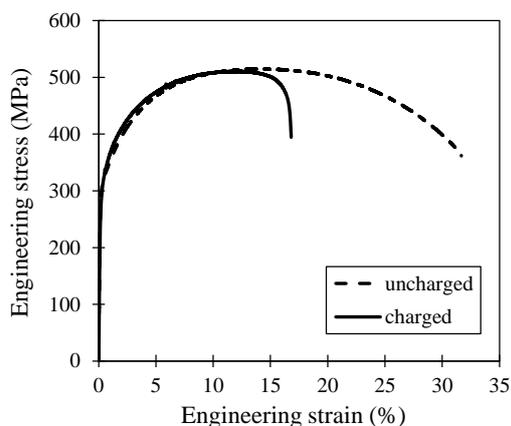


Figure 1. Engineering stress-strain curves for the hydrogen-charged and uncharged samples.

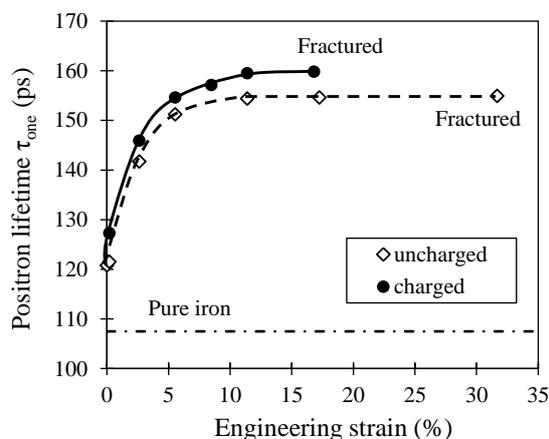


Figure 2. Positron lifetime changes with tensile strain for the hydrogen-charged and uncharged samples.

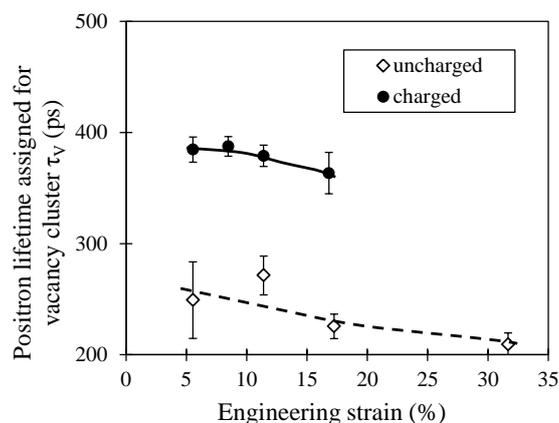


Figure 3. Changes of positron lifetime assigned for vacancy-cluster with engineering strains for hydrogen-charged and uncharged samples.

The positron lifetimes for hydrogen-charged and uncharged samples tended to increase with increasing tensile strains, and at the final fracture stages they exceeded 150 ps, which is corresponding to the positron annihilation lifetime [3, 4] at the dislocation. This implies that the vacancy-type defect which has larger positron lifetime than the dislocation was introduced during the deformation process. Then the measured positron lifetime spectra were decomposed to the three components corresponding to the positron annihilation in *free state*, at *dislocations* and the other *vacancy-type* defects which have longer positron lifetime than dislocations using the positron trapping model [5].

The positron lifetimes assigned for *dislocations* and the other *vacancy-type* defects were 145-150 ps and 200-400 ps, respectively. The positron lifetime of 145-150 ps was within the range of previously reported values for dislocations in pure iron and iron-based alloys (150 ps [3, 4], 142 ps (screw[6, 7]), 165 ps (edge[6, 7])). The longer positron lifetime of 200-400 ps is related to the calculated value for the vacancy cluster consisting of 2-15 vacancies in pure iron[8]. So, the shorter defect components were assigned as for dislocations and the longer as for vacancy clusters. Figure 3 shows the changes of positron lifetime assigned for vacancy-clusters with engineering strains for the hydrogen-charged and uncharged samples. The positron lifetime assigned for vacancy-cluster was 360-390 ps for the hydrogen-charged samples, which corresponds to the vacancy clusters consisting of 15 vacancies as reported by the theoretical study on pure iron [8]. On the other hand, in the hydrogen-free samples the number of vacancies in vacancy-clusters stayed at 2-4. These results definitely show that the vacancy cluster size formed during the tensile deformation is significantly affected by hydrogen charging.

Then the defect densities were evaluated from the three component analysis data by using the following equations based on the trapping model;

$$C_d = \frac{1/\tau_f - 1/\tau_d + I_v(1/\tau_d - 1/\tau_v)}{1 - I_d - I_v} \times \frac{I_d}{\mu_d} \quad (1)$$

$$C_v = \frac{1/\tau_f - 1/\tau_v + I_d(1/\tau_v - 1/\tau_d)}{1 - I_v - I_d} \times \frac{I_v}{\mu_v} \quad (2)$$

where C is a defect density, I is a relative intensity of the defect component, τ is positron lifetime, μ is the specific trapping rate at the defect. The index f stands for *free-state*, d for *dislocations* and v for *vacancy clusters*. When the defect density is very high and $1 - I_v - I_d$ is very small, the dislocation density was determined by reference to the evaluation results of subsequently annealed samples up to 200°C as described later. The positron lifetime for dislocation τ_d was analytically-determined as 150 ps, based

on the data obtained for the subsequently annealed samples, and fixed in the multicomponent analysis. The specific trapping rates used in the evaluation were as follows; $\mu_d=5.1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (experimental value reported in the reference [7]) and $\mu_v \approx n \mu_{1v} = 1.1n \times 10^{15} \text{ s}^{-1}$ for the vacancy cluster consisting of n vacancies ($\mu_{1v} = 1.1 \times 10^{15} \text{ s}^{-1}$, experimental value reported as for mono-vacancy in pure iron [9]). The proportional relationship of the positron trapping rate reported in the theoretical work by Nieminen and Laakkonen [10] was assumed in the calculation. Figure 4 shows changes of (a) dislocation and (b) vacancy-cluster densities with engineering strain for the hydrogen-charged and uncharged samples. The change of mono-vacancy equivalent vacancy densities is also shown in the figure. The defect densities show significant increases with increasing strain especially in the early stage of the tensile deformations of hydrogen-charged and uncharged samples. However, there were no significant differences in the dislocation density and the equivalent vacancy density between the hydrogen charged and uncharged samples.

In order to investigate the thermal stability of vacancy-cluster, the fractured samples were subjected to the subsequent isochronal annealing for 1 hour at 100, 200, 300 and 400 °C. The measured positron

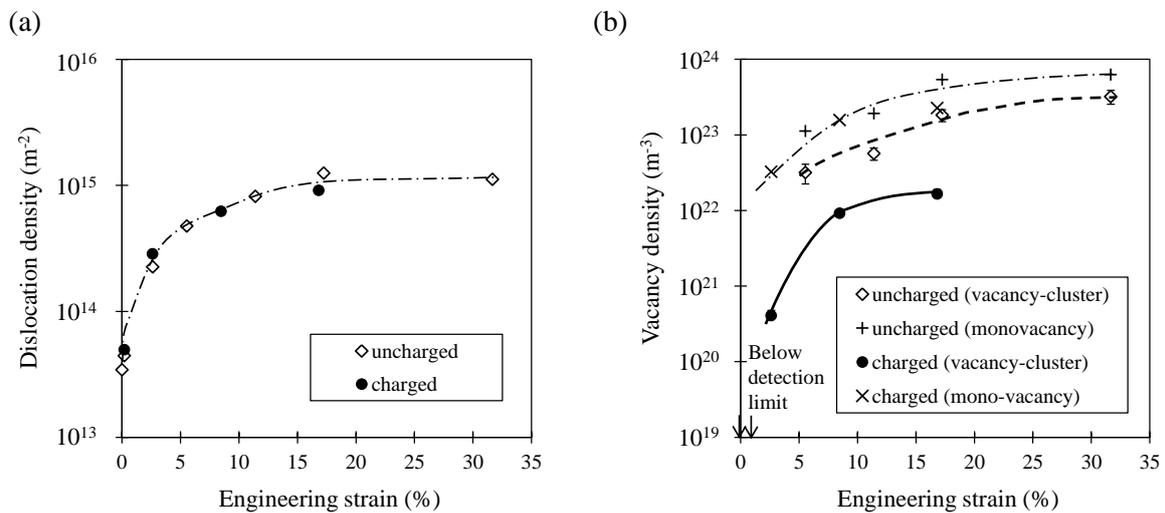


Figure 4. Changes of (a) dislocation and (b) vacancy-cluster densities with engineering strain for the hydrogen-charged and uncharged samples.

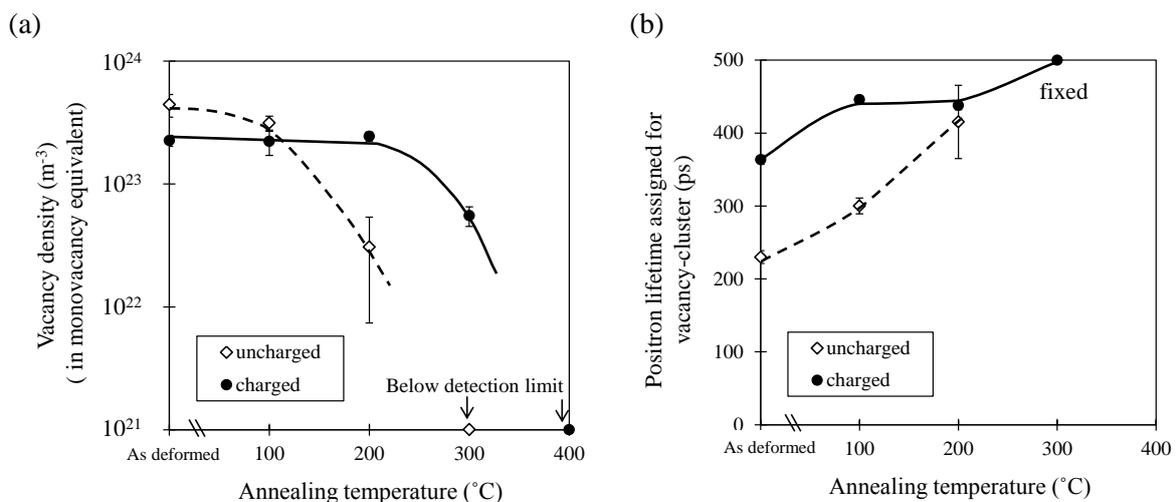


Figure 5. Changes of (a) Vacancy-cluster density and (b) positron lifetime with annealing temperature for the hydrogen-charged and uncharged samples.

lifetime spectra were decomposed to the three components and the defect densities were evaluated in the same manner as described above. In case of the hydrogen-charged sample annealed up to 300°C, the positron lifetime component assigned for vacancy cluster was about 600 ± 100 ps. So, in the multicomponent analysis, it was fixed to the value of 500 ps, which is corresponding to the saturation value of positrons lifetime for three-dimensional vacancy-cluster (voids) [11, 12]. Figure 5 shows the changes of (a) vacancy-cluster density and (b) positron lifetime assigned for vacancy-cluster with annealing temperature. It shows that the vacancy-cluster densities for the hydrogen-charged and uncharged samples decrease and vacancy-cluster sizes increase with increasing annealing temperature. This is typical vacancy clustering behavior where the excess vacancies introduced by irradiation or deformation migrate and partly merge into the larger vacancy clusters during annealing. The recovery stage of the vacancy-clusters shifts to higher temperature with hydrogen-charging, and this clearly shows that hydrogen has a significantly facilitative effect on the vacancy-clustering behavior during the deformation.

4. Discussion

In this work the facilitative effect on vacancy-clustering during tensile deformation due to hydrogen charging is obviously demonstrated and no large increase in the mono-vacancy equivalent vacancy density is also shown. These results show a partly consistent with Hydrogen Enhanced Strain Induced Vacancy Formation (HESIV) mechanism which claims that the formation of vacancies and nanovoids are facilitated under strain in the presence of hydrogen, and leads to ductile crack growth by deformation localization [13]. By thermal desorption studies [14], the increase of desorbed hydrogen contents are observed and the authors claim that the formation of vacancy-type defects are facilitated by hydrogen charging. Their results indicate that desorbed hydrogen contents obtained by the thermal desorption analysis are significantly affected not only by vacancy density but also by vacancy-cluster size. Thus the evaluation of vacancy-cluster behavior through the thermal desorption analysis has difficulty in distinguishing the density and cluster size effect. On the other hand, positron lifetime spectroscopy is the established method to detect mono-vacancy and/or small vacancy cluster, and to evaluate their densities. Further positron annihilation studies are required to understand the effect of hydrogen on the vacancy behavior under tensile deformation.

5. Conclusion

In this study, the formation and accumulation of defects under tensile deformation of hydrogen-charged AISI 410 martensitic steels were investigated by using positron lifetime spectroscopy. During the deformation process, dislocations and vacancy-clusters were introduced and increased with increasing strains. Between hydrogen-charged and uncharged samples with the same tensile strains there was no significant difference in dislocation density and the mono-vacancy equivalent vacancy density.

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