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The interaction of deuterium and tritium with radiation and other defects in austenitic steel and nickel

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Abstract

The methods of residual resistivity, annihilation of positrons, and nuclear reactions in nickel and austenitic steels were used to examine the interaction of deuterium and tritium with defects produced by electron- neutron- or ion-irradiation and plastic deformation. It was found that vacancies, dislocations and three-dimensional vacancy clusters captured hydrogen in nickel. Vacancy clusters were formed in the presence of deuterium and tritium at room temperature, when single vacancies were immobile. The type of the hydrogen isotope determined configurations of those clusters. Hydrogen atoms interacted with interstitial atoms at 150 K in nickel and at 220 K in steel. Deuterium segregation occurred both in nickel and austenitic steel under irradiation with deuterium ions, but the segregation exhibited a different behavior. A possible scheme of formation and evolution of deuterium segregation in the studied materials was proposed.

1. Introduction

The behavior of hydrogen in reactor materials presents a topical problem today as well. It is known that the structure and properties of materials can change dramatically under neutron- or ion-irradiation in the presence of hydrogen [1,2]. The effect of hydrogen is due to the interaction with both radiation-induced defects and pre-irradiation defects. However, details of this interaction are not fully understood.

This study is dedicated to the interaction of deuterium and tritium with structural defects, which were produced in nickel and austenitic steel subject to electron- neutron- or ion-irradiation and plastic deformation. Electron-irradiation caused a uniform distribution of interstitials and vacancies. Additionally, defect clusters in displacement cascades were distributed uniformly under neutron-irradiation. Ion-irradiation led to a non-uniform distribution of both radiation defects and implanted hydrogen. Plastic deformation was followed by a uniform distribution of vacancies and dislocations.

The method of residual resistivity, the positron annihilation method and the method of nuclear reactions were used.

2. Experimental

The subject of this study was nickel of 99.999% purity and a stainless austenitic steel $Cr_{16}Ni_{15}Mo_3Ti_1$, which is a modification of the SS316 steel containing ~1% titanium. The concentration of interstitial impurities in the stainless steel was ~1000 at. ppm.

The samples were doped with tritium and deuterium at 873 K from the gaseous phase to 80 at. ppm for Ni–DI, 300 at. ppm for Ni–DII, 140 at. ppm for Ni–T, and 150 at. ppm tritium for steel. Concentrations of D and T in nickel were determined from resistivity increments [3] and solubility data [4]. The samples were kept in liquid nitrogen to prevent of gassing. After doping the part of

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nickel samples were deformed at ~273 K. Mounting of the samples to the sample holder at 273K for 10 min excluded any appreciable loss of hydrogen.

The samples were exposed to irradiation with 5 MeV electrons at 80 K, neutrons at 80 and 340 K, and 700 keV deuterons at room temperature (profiles were taken simultaneously).

3. Results and discussion

3.1. Electron- and neutron-irradiation

When doped nickel samples exposed to the electron fluence of up to 7×10^{17} cm^2, increments of their residual resistivity were 20% higher than the increment in pure nickel (concentration of Frenkel pairs of about 10 at. ppm). Results of isochronous annealing of these samples are shown in Fig. 1 as differential curves. From these curves, the main distinction between the doped nickel and pure nickel is the annealing peak at 150 K. This peak may be connected with the presence of deuterium or tritium through the following mechanisms:

1. Dissociation of 'hydrogen atom–self interstitial atom (SIA)' complexes resulting from migration ($E_m = 0.15$ eV) and capture of SIA during irradiation (the binding energy estimated from location of the peak is about 0.3 eV).
2. The capture of hydrogen atoms, which migrate at about 150 K ($E_m \sim 0.4$ eV [2]), at vacancies and the formation of complexes (up to six hydrogen atoms per vacancy [5]).

If hydrogen atoms are captured at vacancies, the peak at 150 K should have the same value for all the samples. When the deuterium concentration is increased, this peak grows by 30%. Therefore the mechanism of dissociation seems to be more probable.

The large annealing peak at 370–380 K, which corresponds to annealing of vacancies in pure nickel, appears for all the samples. However, this peak is larger for the doped nickel and increases with hydrogen concentration. At temperatures above 450 K resistivity remains constant and in the doped nickel proves to be lower than the initial resistivity by the value corresponding to the hydrogen contribution. This means that annealing of vacancies in the doped samples is accompanied by the release of hydrogen. This is in agreement with the previous findings [3].

The dissociation energy of 'vacancy–deuterium atom' complexes is 0.98 eV and these complexes dissociate at about 305 K [6]. Annealing spectra registered at this temperature do not exhibit any pronounced peak. This dissociation is not observed either because trapping occurs again when the sample is cooled to the measurement temperature (4.2 K) or because the contribution from the complexes nearly equals the contribution from their constituent components. This inference agrees with the first mechanism. Release of the hydrogen isotopes from unirradiated samples was observed at temperatures near 450 K.

Figs. 2 and 3 present results of isochronous annealing and differential curves for tritium-doped and undoped steel exposed to electron and neutron irradiation at 80 K,

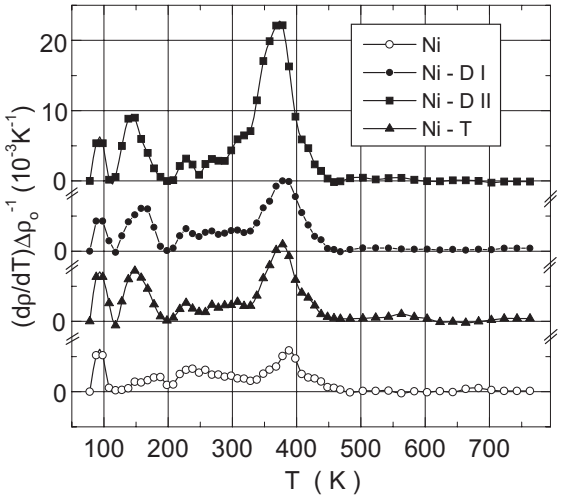

Fig. 1. The annealing spectrum of residual resistivity (differential curves) for D- or T-doped Ni after electron-irradiation at 80 K and isochronous annealing.

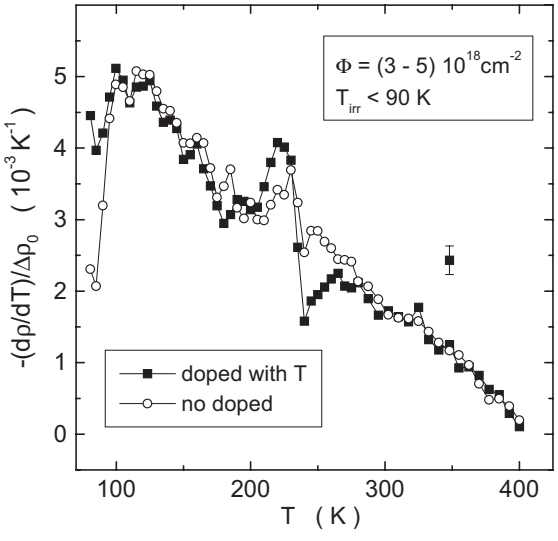

Fig. 2. Annealing spectrum of residual resistivity (differential curves) for tritium-doped and undoped austenitic steel after electron-irradiation at 80 K. Normalized to the initial increment.

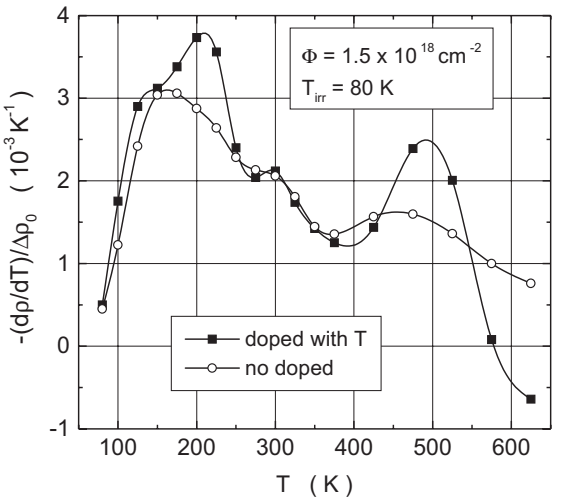

Fig. 3. Annealing spectrum of residual resistivity (differential curves) for tritium-doped and undoped austenitic steel after neutron-irradiation at 80 K. Normalized to the initial increment.

respectively. Resistivity of doped and undoped steel drops to the initial value during annealing. Annealing peaks are observed at ~110 and ~220 K both upon electron- and neutron-irradiation, respectively. The annealing peak at 220 K is larger for tritium-doped steel than for undoped steel.

It is known that annealing of stainless austenitic steels exposed to low-temperature irradiation can cause migration of interstitial atoms (below 200 K to short distances only, within Frenkel pairs) and vacancies above 280 K [7,8]. Therefore, one may think that the annealing peak at 110 K corresponds to annihilation of nearest pairs, while the peak at 220 K corresponds to the long-range migration of SIAs and their annihilation at vacancies or trapping. The effect of tritium loading (growth of the peak at 220 K) is probably due to the increase in SIAs annihilated at vacancies, because tritium occupies traps of interstitial atoms. At large values of the neutron fluence no difference exists between tritium-doped and undoped steel.

The annealing peak at ~500 K most likely corresponds to release of vacancies from traps and annealing of these vacancies at sinks. The larger peak, is in tritium-doped steel, then it is in undoped steel (see Fig. 3), suggests a dissociation of complexes of one species, probably those containing tritium atoms, which can leave the solid solution and accumulate at lattice inhomogeneities. Neutron-irradiation at 340 K and subsequent isochronous annealing did not reveal any distinctions between tritium-doped and undoped steel. This fact testifies to release of tritium from the solid solution upon irradiation.

3.2. Plastic deformation

Changes in the shape of the angular correlation spectra were checked using the *S*-parameter, which depends both on the concentration and type of defects, and the *R*-parameter, which depends only on the type (structure) of defects [9]. The *S*-parameters as a function of the degree of deformation ε at room temperature for Ni, Ni–DI, Ni–DII, and Ni–T are shown in Fig. 4. The *S*-parameter grows faster with increasing ε, i.e., with the defect concentration, in hydrogen-doped samples. The *S*-parameter curves flattens out at $\varepsilon > 10\%$, due to saturation of the annihilation parameters when the defect concentration exceeds $\sim 10^{-4}$. The plateau value of the *S*-parameter characterizes defects representing dominant traps of positrons. It is known [10] that single vacancies (S_v is the saturation parameter) serve as dominant traps in pure nickel deformed to $\varepsilon > 10\%$. Hence, the larger plateau value of the *S*-parameter for hydrogen-doped Ni characterizes dominant traps other than single vacancies and dislocations.

Growth of the *S*-parameter in excess of S_v is explained [11] by annihilation of positrons at three-dimensional vacancy clusters (VC). This is confirmed by the *R*-parameter, which is known to be larger for VC than for single vacancies. It is worth noting that the VC configuration is altered (the *R*-parameter increases) and remains unchanged (the *R*-parameter is constant) in Ni–D and Ni–T, respectively, when the degree of deformation is increased.

Probably, mobility of 'vacancy–hydrogen atom' complexes is higher than that of vacancies. As a result, vacancy clusters comprising deuterium or tritium atoms

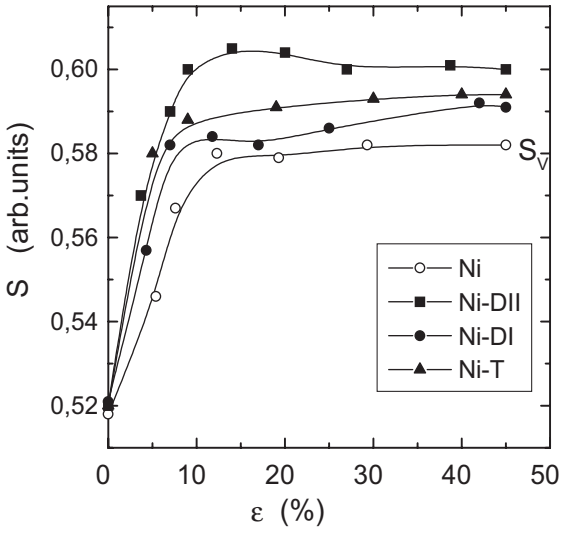

Fig. 4. Changes in the *S*-parameter versus the degree of deformation of initial and deuterium- or tritium-doped Ni.

are formed and play a stabilizing role. Analogous results were obtained in experiments [12] when hydrogen was implanted in deformed nickel samples.

Our annealing experiments revealed that VC decorated with deuterium atoms have two types of atomic configurations with the binding energy of nearly 0.73 and 1.05 eV, respectively, but clusters of one configuration are formed in Ni–T with the binding energy equal to 1.05 eV. Vacancy clusters are not detected in pure nickel either during deformation or upon subsequent annealing.

The experiments suggest that tritium atoms do not contribute to formation of vacancy-type defects in steel. In our opinion, this is due to the large concentration of interstitial impurities (nitrogen and oxygen), which also represent vacancy traps.

3.3. Ion-irradiation

The depth distribution and the average concentration C_D of deuterium were measured in the zone 4 μm thick and 3 mm^2 in cross-section. The calculated value of 0.3 dpa corresponds to the irradiation dose equal to $\sim 1\times10^8$ cm^{-2}. Experimental profiles of deuterium distribution proved to agree qualitatively with the theoretical distribution of vacancies, which was computed by the TRIM 95 program.

The all-implanted deuterium concentration C_D(calc.) and the amount of retained deuterium $\alpha = C_D/C_D$(calc.) were calculated. Three types of samples were prepared:

1. Well annealed pure nickel.
2. Deformed nickel. The concentration of deformation vacancies was 10^{-4} and the density of dislocations was equal to 10^{11} cm^{-2}.
3. Deformed and annealed at 500 K nickel. The final density of dislocations was about 10^{11} cm^{-2}.

Deuteron-irradiation of all the nickel targets was followed by a monotonic increase in the deuterium concentration C_D (Φ) (Fig. 5). The concentration C_D decreased when implantation was interrupted. The experiments showed the decrease increased, with larger dose and longer interruption time.

The contribution made to C_D by vacancies and dislocations with increasing in dose is shown in Fig. 6, and was determined from the following expressions:

$$\Delta C_D(\text{vac.}) = C_D(\text{Ni def.}) - C_D(\text{Ni ann.})$$

and

$$\Delta C_D(\text{disl.}) = C_D(\text{Ni ann.}) - C_D(\text{Ni}).$$

Note that ΔC_D (vac.) reflects the contribution of deformation vacancies in the presence of dislocations and radiation defects, while ΔC_D (disl.) reflects the contribution of dislocations in the presence of radiation defects only. Vacancy traps dominate over dislocation traps at the beginning of irradiation. At $\Phi > 5\times10^{17}$ cm^{-2} the contribution of dislocations prevails.

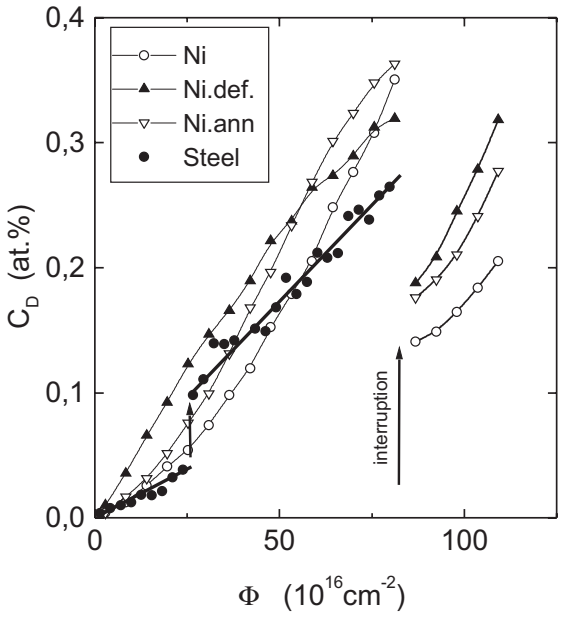

Fig. 5. Effect of the ion-irradiation interruption on accumulation of deuterium in nickel samples (starting, deformed and annealed Ni) and in austenitic steel.

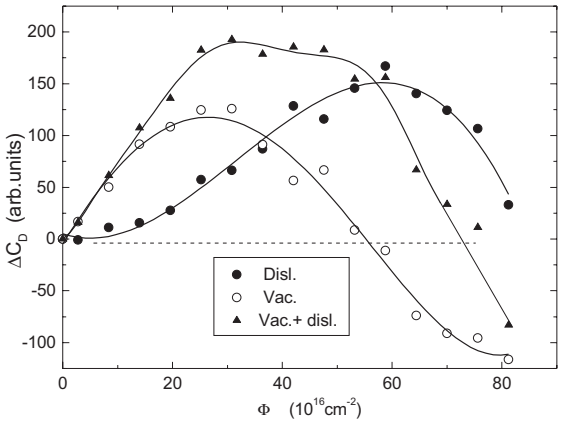

Fig. 6. Contribution of dislocations and deformation vacancies to accumulation of deuterium in nickel.

The quantity of retained deuterium in the analyzed zone proved to be 4–12% for all the nickel targets. This means that most of the implanted deuterium was redistributed to the target volume during irradiation. In the presence of dislocations, deuterium segregation tends to saturation with increasing irradiation dose, unlike in pure nickel. We showed that even if the target contains

vacancy defects only, the increase in the defect concentration with growing Φ could cause the total capacity of hydrogen traps to stabilize (vanadium, V–Ti alloys [13]). A scheme explaining the effect of dislocations and deformation vacancies on deuterium segregation in nickel is proposed:

1. If the density of radiation vacancy defects is small, dislocations represent low-efficiency hydrogen traps and insignificantly contribute to C_D, but the deformation vacancy play the main role.
2. If the density of radiation vacancy increases, dislocations interact with these defects and acquire kinks. The kinks improve efficiency of dislocation hydrogen traps and considerably increase C_D.
3. If the density of radiation vacancy is high, the presence of dislocations decrease C_D, because the number of vacancy traps (vacancy clusters) is reduced.

The structural evolution of vacancy defects is probably superimposed on competition of the last two factors. Deformation vacancies present in the target should shift all the observed effects to lower doses of ion-bombardment.

Ion-bombardment was interrupted for 2 h and 40 min (see Fig. 5), when presumably the dislocation structure evolution was complete (kinks were formed). This accounts for the relative trend of $C_D(\Phi)$ in the interruption: the maximum and minimum segregations correspond to deformed and pure annealed nickel, respectively.

The comparison of the behaviors of nickel and austenitic steel yielded the following results. Deuterium accumulates similarly in nickel and in steel at small doses, but when Φ exceeds 10^{17} cm^{-2}, C_D proves to be higher in nickel than in steel and the difference is enhanced with increasing Φ (see Fig. 5). Segregation diminishes in nickel and increases in austenitic steel during the interruption. That is, in the latter case the flow of deuterium from the target volume to the radiation-damaged zone is enhanced.

The last result is unusual for metal targets. A similar effect is observed in titanium single crystals only [14]. This effect is attributed to formation of large-capacity traps.

In austenitic steel, sinks are distributed uniformly over the target volume. It is not improbable that large-capacity immobile traps, which are formed in steel, represent small-size hydrogen bubbles.

4. Conclusions

1. It was shown that hydrogen atoms interacted with interstitial atoms at 150 K in nickel and 220 K in steel.
2. Deuterium and tritium atoms were found to stimulate formation of vacancy clusters in nickel subject to plastic deformation at room temperature. The structure of the vacancy clusters depended on the isotope composition. Tritium had no effect on formation of vacancy clusters in deformed samples of austenitic steel.
3. Deuterium segregation caused by deuteron-irradiation was detected in nickel and austenitic steel. The segregation was unstable at room temperature. If irradiation was interrupted, deuterium was drained to the target volume in nickel and from the target volume to the analyzed zone in austenitic steel.
4. Deformation vacancies and dislocations were shown to be deuterium traps in pure nickel. When the ion-irradiation dose was increased, capacity of the deuterium dislocation traps was enhanced in nickel, thanks to changes in the trap structure.
5. At ion-irradiation doses over 8×10^{17} cm^{-2} the initial defect structure of nickel no longer contributed to formation of the deuterium segregation.

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