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Radiation-induced segregation of deuterium in austenitic steels and vanadium alloys

V.L. Arbuzov *, G.A. Raspopova, V.B. Vykhodets

Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, 18 S. Kovalevskaya St., 620219 Ekaterinburg, GSP-170, Russian Federation

Abstract

The accumulation and distribution of implanted deuterium were studied through simultaneous analysis using the nuclear reaction D(d,p)T for some austenitic, austenitic–martensitic steels, Fe–16% Cr, V–4% Ti–4% Cr, V–10% Ti–5% Cr alloys, and vanadium. The implantation was carried out by 700-keV deuteron irradiation at room temperature with a total implantation dose of about 2×10^{18} cm^{-2}. It is shown that the deuterium segregation induced by ion irradiation in vanadium and the Fe–16% Cr alloy remained unchanged during room temperature holding after implantation. On the other hand, in the two-phase steel and the V–Ti(–Cr) alloys the holding led to a partial elimination of the concentration inhomogeneity of the implant in the irradiated portion, while in the austenitic steel deuterium segregation increased probably due to the migration of deuterium from the unirradiated volume to the irradiation zone. Possible reasons for different behavior of the implanted deuterium in different materials will be briefly discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

It is known that implantation of hydrogen in steels and alloys at low temperatures is accompanied by accumulation of the implant in the irradiated areas. That concentration inhomogeneity is not eliminated completely even when the mobility of hydrogen is high. For example, the concentration of the implanted hydrogen in radiation-damaged areas of the samples of the 316 stainless steel remains to be high even at temperatures of 500–600 K [1]. In pure vanadium, titanium and their alloys this phenomenon was detected at room temperature [2,3]. An inhomogeneous distribution of hydrogen, which was found in hydrogen-containing metal targets irradiated with light (helium) and heavy (metal) ions, is caused by a redistribution of hydrogen from the volume of the target to the region having a high concentration of radiation-induced defects (RIDs) [4–8]. All these experimental results reflect a single phenomenon called as ‘ion-irradiation-induced segregation of hydrogen’ [2].

Up to now certain concepts have been proposed with respect to the ion-irradiation-induced segregation of hydrogen in metals. These concepts are as follows. The concentration distribution inhomogeneity of the implanted hydrogen at temperatures where the diffusion mobility of hydrogen is high is due to trapping of some hydrogen atoms by RID’s. The remaining hydrogen is in the ‘free’ state and is distributed uniformly in the whole volume of the target sample. This feature was observed when vanadium was bombarded with deuterium ions at room temperature [3].

The stability of the defect structure, which is formed during implantation at room temperature, and the hydrogen segregation induced by ion irradiation was investigated in this study.

2. Materials and methods

The materials studied were steels and alloys, which are structural candidates for fusion reactors:

1. V–4% Ti–4% Cr and V–10% Ti–5% Cr alloys; commercially pure vanadium.
2. Austenitic stainless steel type Cr16Ni15Mo3Ti1.

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[*] Corresponding author. Tel.: +7-3432 499 038; fax: +7-3432 745 244; e-mail: segregat@ifm.e-burg.su

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3. Two-phase austenitic–martensitic steel type Cr16Ni8-Mo3.
4. Fe–16 at.% Cr alloy was taken to simulate the BCC component of the two-phase steel.

Diffusion coefficients of hydrogen in materials whose compositions are similar to those of the targets studied are as follows: 2.3×10^{-5} in vanadium [9]; 5.3×10^{-6} in V5Ti [9]; 2.3×10^{-6} in V10Ti [9]; 2.7×10^{-7} in Fe(15–18.5)Cr [10]; 1.6×10^{-11} in the 304L austenitic stainless steel [11], $(0.23–1.3) \times 10^{-11}$ in the martensitic stainless steel [12,13].

Other researchers used deuterons having an energy of tens of keV as the implants to simulate the processes that take place in fusion reactors. This choice of energies makes it difficult to interpret the obtained results from the viewpoint of the interaction between hydrogen atoms and RID's. The reason of this difficulty is that the implant is accumulated near the surface and the distribution of the implant may be affected both by contamination of the irradiated volume with interstitial impurities from the sample's surface, and by the fact that the surface represents an effective sink of defects. In type 316 stainless steel the projective path of deuterons equals 3.21 μm at the deuteron energy of 700 keV (which is used in this study) and is within 0.07–0.135 μm at the deuteron energy of 10–20 keV.

The D(^{3}He,p)^{4}He reaction was used in previous work [14] dealing with the study of the distribution of implanted hydrogen in metal targets by the nuclear reaction method. In spite of unquestionable merits (a high sensitivity and resolution), the helium reaction has considerable drawbacks: an additional component (helium) and an additional (apart from the implantation-induced) radiation damage outside the deuterium implantation zone are introduced in the sample. These drawbacks may be eliminated if the processes of implantation and measurement coincide in time and space. The D(d,p)T reaction was, hence, used in this study to determine the deuterium concentration.

The main feature of the implantation and measurement procedures was as follows. A van de Graaf accelerator served as the source of accelerated deuterons for implantation and D(d,p)T analysis. The implanted deuterons had an energy of 700 keV. The incident beam was perpendicular to the test target. The proton detection angle was 120°. Measurements were made at implantation doses of $(1–200) \times 10^{16}$ cm^{-2}.

A $TiD_{1.78}$ reference sample was used to determine the concentration and distribution of deuterium. The TRIM 95 program was employed to calculate the analyzable depth of the implanted deuterium and the distribution of vacancies in the analyzable zone.

An integral parameter – an average concentration of the implanted deuterium, C_D, measured in the analyzable zone – was introduced for the interpretation of the measured results. Average concentrations of the implanted deuterium, $C_{D(calc.)}$, and the fraction of deuterium retained in the analyzable zone, $\alpha = C_D/C_{D(calc.)} \times 100\%$, were calculated under the assumption that all the deuterium is preserved in this zone.

3. Results and discussion

The distribution of the implant from the surface to the bulk of the samples and the accumulation of the implanted deuterium in the test targets have revealed some features in common:

1. The maximum deuterium concentration appears near the maximum distribution of vacancies (Fig. 1).
2. The amount of the implanted deuterium increased along the whole depth of the analyzable zone when the implantation dose was raised up to saturation, if it took place.

Besides these common features, the test targets were characterized by considerable differences in the time stability of the deuterium segregation formed under the ion irradiation and in the accumulation kinetics of the implanted deuterium.

Among the targets studied, it was observed only in vanadium and the Fe–16% Cr alloy that the deuterium distribution, which was formed during implantation, remained unchanged after the ion bombardment was stopped. Despite obvious distinctions such as chemical

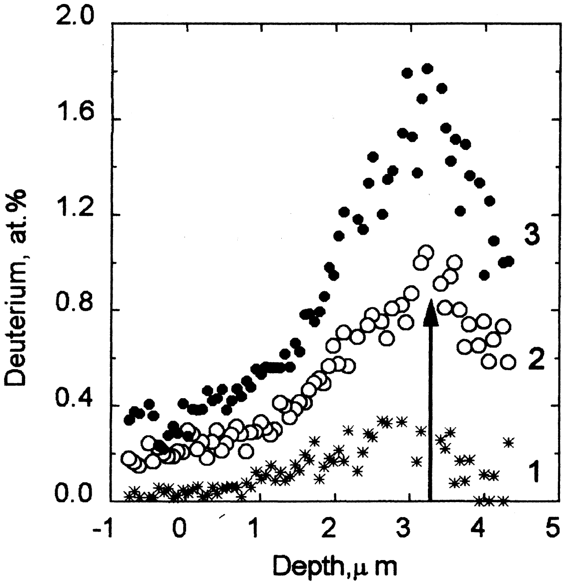

Fig. 1. The distribution of the implanted deuterium in the samples of the austenitic steel (1), the Fe–16% Cr alloy (2) and the two-phase steel (3) after bombardment with deuterons at a dose of $(52–54) \times 10^{16}$ cm^{-2}. (The arrow indicates the location of the maximum distribution of vacancies calculated by the TRIM program.)

composition, these materials had some features in common: a monotonic descending dose dependence of the implanted deuterium retainment $\alpha(F)$ (Fig. 2), saturation of $C_D(F)$, a bcc lattice, and a relatively high mobility of deuterium. Moreover, they were characterized by saturation of the dose dependence of the implanted deuterium accumulation in the irradiated volume.

Let us consider the experimental findings and the representation of the model advanced in this study.

Pure vanadium: We have proposed a model of interaction between the implanted atoms and radiation-induced defects in pure vanadium elsewhere [3]. According to this model, the deuterium traps are vacancy-type defects. These defects and the implanted atoms form rather stable complexes and the concentration inhomogeneity of the implant is stable at room temperature. The saturation of $C_D(F)$ is explained by self-annealing of the defects and establishment of a constant concentration of traps. The monotonic dependence $\alpha(F)$ may be related in terms of the proposed model to a decrease in the fraction of the retained deuterium. This decrease is due to a partial self-annealing of the defects-traps before $C_D(F)$ comes to saturation.

The Fe–16% Cr alloy: Since the dependence $C_D(F)$ and $\alpha(F)$ exhibited similar behavior in this alloy and vanadium, the obtained results may be explained along the same lines of reasoning as those for vanadium.

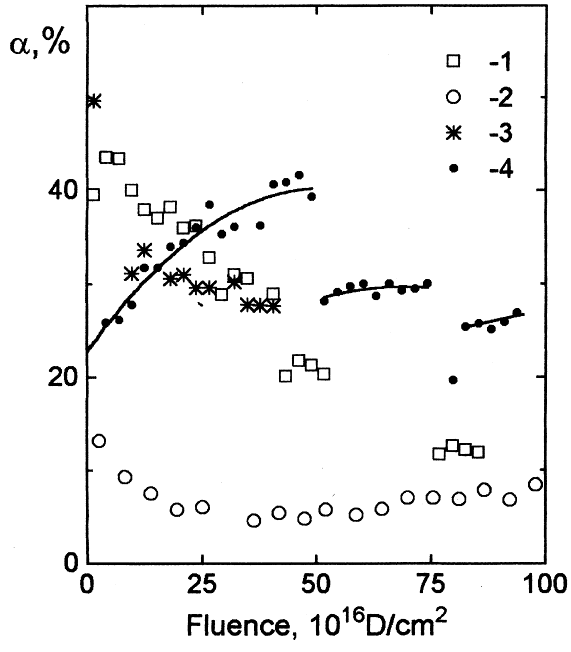

Fig. 2. The effect of the implantation dose on the retainment of the implanted deuterium in the analyzable zone in the samples of the Fe–16% Cr alloy (1), the austenitic steel (2), the vanadium (3) and the two-phase steel (4).

When irradiation of all the targets, except vanadium and the Fe–16% Cr alloy, was stopped, the concentration of the implanted deuterium in the radiation-damaged volume was altered.

V–Ti(–Cr) alloys: We have shown [3] that accumulation of the implanted deuterium in irradiated areas of the targets depends on both the implantation dose and the titanium content of these areas.

Additional experiments on the V–Ti(–Cr) alloys revealed the following. A pause in the implantation process was accompanied by a decrease in C_D and α, i.e. led to a partial clean-out of the initial distribution of the implant. The variation in the accumulated concentration and the fraction of the retained deuterium was most intensive at the initial stages after the irradiation termination and then slowed down. The redistribution of the implanted deuterium continued until a certain concentration of deuterium was reached in the irradiated volume. The instability of the implant distribution formed under the ion bombardment may be due to the fact that the diffusion drain of the implant from the irradiation zone is hampered. The mobility of the implanted deuterium in the V–Ti alloys decreases monotonically with increasing titanium concentration [9] and is lower in the vanadium alloys than in pure vanadium.

If the ion bombardment is resumed, α gradually reaches a certain quasi-equilibrium level. Subsequently the dependence $\alpha(F)$ obtained before the irradiation was interrupted continues.

Steels: The implanted deuterium accumulated faster in the two-phase steel than in the austenitic steel over the whole range of the implantation doses studied.

The two-phase steel: As the continuous implantation dose was increased, the concentration of the implanted deuterium in the irradiated volumes, C_D, rose and the fraction of the implant retained in these volumes, α, increased in the samples. The dependence $\alpha(F)$ tends to saturation (Fig. 2).

When the implantation process was stopped at the stage of the $\alpha(F)$ saturation, C_D and α decreased. The accumulated concentration left by the end of the pause decreased exponentially with increasing time of the pause. After the ion bombardment was resumed, the fraction of the retained deuterium, α, remained almost unchanged, but it was proved to be smaller than that before the pause.

The sum of the obtained results permits stating the following. In the two-phase steel part of the implanted deuterium not bound to traps at the time of implantation does not redistribute between the implantation zone and the irradiated volume of the target because of a low diffusion mobility of deuterium. After the ion irradiation is stopped, the implant is redistributed. Therefore C_D

and α decrease. During a continuous irradiation the dependence $\alpha(F)$ came to saturation. This means that a sort of a metastable equilibrium is established between the in-flow of the implant and its drain to the volume of the target. Obviously, the achievement of this 'equilibrium' depends not only on the concentration of deuterium in the irradiated volume but also on a set of other factors (density of the ion current, the steel structure, etc.).

The austenitic steel: The dose dependence of the accumulated concentration of the implanted deuterium in irradiated volumes of the austenitic steel, $C_D(F)$, had a monotonic trend. When the implantation dose F was increased, the accumulated concentration C_D grew over the whole range of the doses studied. The concentration C_D was much lower in the austenitic steel than in the two-phase steel.

The fraction of the retained deuterium, α, also was proved to be much lower than in the two-phase steel and lower than in the Fe–16% Cr alloy (Fig. 2). The dependence $\alpha(F)$ was non-monotonic: up to the implantation dose of $\sim 40 \times 10^{16}$ cm^{-2} α was lowered with increasing implantation dose and then increased but remained smaller than in all the other targets studied.

The room temperature holding of the implanted samples of the austenitic steel led, unlike in the two-phase steel, to an increase in the accumulated concentration and retainment of deuterium in the analyzable zone. The profile analysis showed that when an intermediate holding was inserted during the implantation process, the deuterium concentration rose along the whole depth of the analyzable zone (especially in the region of the implantation maximum). The increase in the deuterium concentration in the analyzable zone exhibited a complicated dependence on the preliminary implantation dose and the irradiation pause duration: the increase was the larger, the higher the concentration of the implanted deuterium in the austenitic steel sample by the moment irradiation was stopped. Holding for 43 h after implantation at a dose of 12.6×10^{16} cm^{-2} turned out to be equivalent to a continuous implantation at a dose of 80×10^{16} cm^{-2}.

Certain contradictions may be found in the results obtained on the austenitic steel. For example, while the activation energy of hydrogen diffusion in austenitic steels is relatively high, the accumulated concentration of the implant proved to be the lowest among all the targets studied. This fact indicates a high draining of deuterium from the volume of the target to the radiation-damaged area.

This contradiction may be resolved if one assumes a radiation-accelerated diffusion of the implant in the steel and a low capacity of the deuterium traps formed during implantation. In this case the 'radiation defect-deuterium atom' complexes could serve as the carriers of deuterium atoms. The formation of these mobile complexes has been suggested to account for the radiation-accelerated diffusion of deuterium in titanium [2]. A small sum capacity of the traps may be due either to a low concentration of the traps or to a small binding energy of deuterium in the traps.

The instability of the concentration distribution inhomogeneity in the cross section of the target in spite of a high mobility of the implanted deuterium under irradiation is one more apparent contradiction. This contradiction may be accounted for by a possible evolution of the defect structure of the radiation-damaged area. The evolution may take place both during and after implantation. It may be reduced to the following. Single vacancies, which are formed during deuterium implantation, are not effective traps. However, vacancy complexes, which efficiently capture the implant atoms, are prone to be formed in the austenitic steel. The number of vacancy complexes, which appear during implantation and subsequent holding, is less than the number of vacancies. Obviously, the probability that a vacancy complex is formed increases both with the implantation dose and the holding time after implantation. As a result of this evolution, the sum capacity of the traps may increase, as was observed in experiment. Moreover, radiation-induced phase transformations may possibly occur in this steel. This may also change the concentration and efficiency of the traps.

The descending section of $\alpha(F)$ at the initial stages of implantation in the austenitic steel may be explained, as in the case of vanadium, by a decrease in the sum capacity of the traps caused by their self-annealing.

Considering all the results obtained in this study on the ion-irradiation-induced segregation of deuterium in the steels and the alloys, it is possible to suggest the following scheme of the behavior of the implanted deuterium in the targets:

(1) The implant is transported from the irradiation zone through both thermal diffusion and radiation-accelerated diffusion by 'radiation defect-deuterium atom' complexes. When the diffusion coefficient in a defect-free matrix is high, the contribution of the former component is negligibly small. If the mobility of the implant atoms in a defect-free matrix is low, the former component makes the decisive contribution. Obviously, the ratio of these components also depends on both the mobility of the hydrogen-containing 'radiation defect-deuterium atom' complexes and the number of these complexes.

(2) The accumulated concentration of the implant in the irradiated volumes of the targets depends not only and not so much on the flux of the implant out of the irradiated zone, as on the sum capacity of the traps formed during the ion bombardment. Large-capacity traps possessing a high binding energy are capable of retaining up to 50% implanted deuterium in the irradiated zone.

(3) The defect structure formed during the ion implantation may change during room temperature holding after implantation. As a consequence, the sum capacity of the hydrogen traps is changed in the absence of irradiation. It is not improbable that the clean-out of the nonequilibrium distribution of the implant and the evolution of the defect structure proceed simultaneously. However, the net result is determined by the contribution of each process to the final picture. Thus, the clearly pronounced evolution of the defect structure, which is observed in the austenitic steel, is probably due to a high mobility of vacancies, a low vacancy-deuterium binding energy, and a fast drain of the implant from the irradiated volume through the radiation-accelerated diffusion. In this case even an insignificant change in the trap capacity can be registered experimentally.

4. Conclusions

The study of the stability of the deuterium segregation induced by irradiation with 700 keV deuterons at room temperature in some steels, vanadium, and vanadium alloys has led to the following conclusions:

1. The concentration of the implanted deuterium in the irradiated areas of the targets rose with increasing dose of the continuous implantation. In vanadium, vanadium alloys, and Fe–16% Cr the dose dependence of the accumulated concentration of the implanted deuterium came to saturation.
2. All the targets under study have been divided into 2 groups in accordance with the behavior of the implanted deuterium after implantation. The first group includes vanadium and the Fe–16% Cr alloy where the deuterium distribution formed during implantation did not change after a many-hour holding without irradiation. A post-implantation holding on the other materials led to a redistribution of the implant between the irradiated areas and the unirradiated bulk. A partial drain of the implant to the volume was observed with time in the vanadium alloys and the two-phase steel, whereas an in-flow of deuterium from the volume to the irradiated areas of the targets occurred in the austenitic steel.
3. The behavior of the implanted deuterium in metal materials cannot be adequately described in terms of a model which allows only for the interaction between the implant atoms and invariable radiation-induced defects. One should consider a possible evolution of the defect structure in the irradiation zone and also possible radiation-induced structural and phase transformations.

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