Journal of Nuclear Materials 384 (2009) 245–248

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Defect recovery in proton irradiated Ti-modified stainless steel probed by positron annihilation

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ARTICLE INFO

Article history:
Received 22 July 2008
Accepted 19 November 2008

ABSTRACT

The defect recovery in proton irradiated Ti-modified D9 steel has been studied by positron annihilation isochronal and isothermal annealing measurements. D9 samples have been irradiated with 3 MeV protons followed by isochronal annealing at various temperatures in the range of 323 to 1273 K. The dramatic decrease in positron annihilation parameters, viz. positron lifetime and Doppler S-parameter, around 500 K indicates the recovery of vacancy-defects. A clear difference in the recovery beyond 700 K is observed between solution annealed and cold worked state of D9 steel due to the precipitation of TiC in the latter. Isothermal annealing studies have been carried out at the temperature wherein vacancies distinctly migrate. Assuming a singly activated process for defect annealing, the effective activation energy for vacancy migration is estimated to be 1.13 ± 0.08 eV.

1. Introduction

Ti-modified D9 steel is identified as a potential candidate for use in nuclear core components of prototype fast breeder reactor (PFBR) programme in India [1]. Intense neutron flux in the nuclear reactor causes void swelling in structural components. To improve the resistance to void swelling, the material is suitably modified by adjusting alloying elements and by subjecting it to thermo-mechanical treatments. Effects of minor alloying components [2–4] on the swelling properties of the steel and also the effect of cold working [5,6] had been investigated earlier. The basic understanding of defect production due to irradiation and their thermal stability would pave the way to gain better insight into macroscopic dimensional changes in the material.

The study of defect recovery during annealing of irradiated samples yields information regarding the occurrence of defects, migration, clustering, growth and annealing of various defect species. Though the defect recovery has been studied in detail in pure metals, such studies are lacking in complex alloys and steels. The objective of this work is to investigate the vacancy-defect recovery processes in irradiated D9 steel through positron annihilation spectroscopy. Though proton irradiation produces both vacancies and interstitials in the material, interstitials which are mobile at the temperature of irradiation will annihilate, and the defects which accumulate after irradiation will be predominantly vacancies and their clusters. Positrons get trapped preferentially at vacancies and are used as sensitive probes to investigate vacancy-type defects in metals and alloys [7–9]. So, positron annihilation spectroscopy is a powerful tool to investigate the migration of such vacancy-defects, their clustering as well as annealing. In the present paper, positron annihilation studies have been carried out on proton-irradiated D9 steel to identify the annealing stages due to defect recovery, while isothermal studies have been carried out to investigate the migration kinetics of vacancy-defects.

2. Experimental details

The chemical composition (in wt%) of the material is used in the present work is given in Table 1. D9 samples of dimensions 10 × 10 × 1 mm thick were subjected to solution annealing treatment by heating it in a vacuum of 1×10^{-6} mbar at 1343 K for 30 min, subsequently at 1373 K for 5 min and then furnace cooled.

The solution annealed and 20% cold-worked D9 were irradiated at room temperature by 3 MeV protons using 1.7 MV Tandetron accelerator. The irradiation doses were 1×10^{15}, 1×10^{16}, 5×10^{16} and 1×10^{17} protons/cm^2 with a beam diameter of 10 mm. TRIM [10] calculations indicated that the radiation damage starts from the surface and extends to a depth of 40 µm with a peak damage around 35 µm. This damage depth is well within the penetration depth of fast positrons emanating from radioactive ^{22}Na source. Isochronal annealing was performed in steps of 50 K ranging from 323 to 1323 K for a period of 30 min each. For isothermal studies, temperature was chosen in the region wherein the sample recovers from the damage, viz. 623 K, with a time scale ranging from 5 min to few hours in a vacuum of 1×10^{-6} mbar.

Positron lifetime measurements were performed at room temperature on identical set of samples, in the standard sample-source sandwich geometry using ^{22}Na positron source of 10 µCi activity. A fast–fast coincidence system coupled with a pair of BaF$_2$ detectors

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doi:10.1016/j.jnucmat.2008.11.014

Table 1
D9 composition (in wt%).

Element	wt%	Element	wt%
Cr	14.0 ± 0.5	Ni	15.0 ± 0.5
Mo	2.20 ± 0.05	Mn	1.90 ± 0.05
Si	0.75 ± 0.05	Ti	0.25 ± 0.005
C	0.037 ± 0.005	V	0.05 ± 0.003
Co	0.020 ± 0.005	Cu	<0.05
Al	<0.05	S	<0.005
P	<0.014	Nb	<0.016
Ta	<0.02	N	<0.005
As	<0.034	B	10–20 ppm
Fe	Balance	–	–

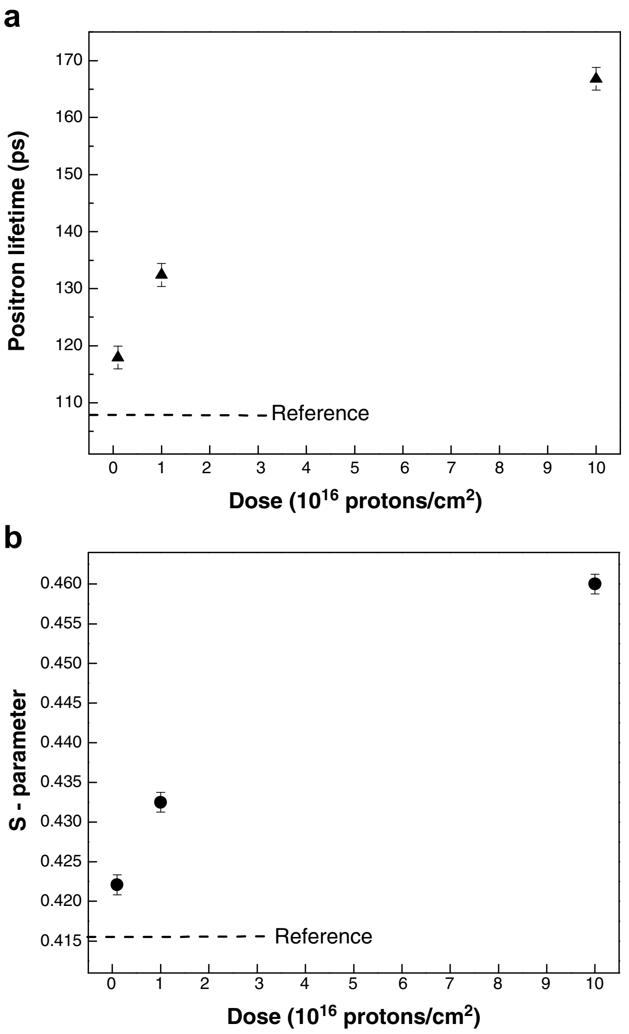

Fig. 1. Comparison of positron lifetime (a) and S-parameter (b) for different doses of proton irradiation on well annealed D9.

having a time resolution of 260 ps was used. A total of about 10^6 counts were accumulated for each spectrum. For the analysis of positron lifetime spectrum, LT program was used [11]. Instrumental time resolution and source correction terms were subtracted from the measured lifetime distribution. Analysing the lifetime spectra of samples in terms of multi-component lifetimes did not yield satisfactory variance values. The spectra could be fitted only to a single lifetime component with a fitting variance close to unity. To complement the lifetime results, Doppler broadening measurements were carried out using a HPGe detector having 1.3 keV energy resolution for 662 keV γ-line of ^{137}Cs source. From these measurements, a defect-sensitive lineshape S-parameter was deduced to monitor the annealing stages occurring at different temperatures.

3. Results and discussion

The variation of positron lifetime and S-parameter as a function of irradiation dose in annealed D9 is shown in Fig. 1. The defect-free lifetime of the solution annealed D9 is 108 ps. Upon irradiation, the positron lifetime increases indicating the presence of radiation-induced vacancy-type defects. As the dose of protons is increased from 0.1 to 10 of the order of 10^{16} protons/cm^2, there is a significant increase in positron lifetime. This observation is also supported by the behaviour of defect-sensitive lineshape S-parameter, which exhibits similar tendency (Fig. 1). Based on the consistent variation seen in both positron lifetime and S-parameter, the observed increase is due to the increase in the concentration of vacancy-defects at higher irradiation doses.

3.1. Isochronal annealing of irradiated D9

3.1.1. Annealed D9 – effect of proton irradiation

Annealed D9 irradiated to a dose of 1×10^{17} ions/cm^2 was subjected to isochronal annealing (Fig. 2). The variation of positron lifetime and S-parameter, while annealing, indicates the changes in the size as well as in the concentration of the defects. During the initial annealing temperatures, there is not much change in the lifetime but beyond 500 K the lifetime exhibits steep reduction, attaining defect-free values beyond 700 K. In the temperature range of 500 to 700 K, vacancies are highly mobile, they get rapidly annealed out due to migration to sinks and finally they disappear beyond 700 K. Positron lifetime is found to attain the defect-free value above 700 K annealing temperatures. This stage indicates the complete recovery of steel from radiation-induced vacancy-defects. As can be seen, S-parameter also shows similar variation (Fig. 2(b)).

3.1.2. Cold-worked D9 – effect of proton irradiation

Isochronal annealing studies on cold-worked D9 irradiated to a dose of 10^{17} ions/cm^2 were also carried out (Fig. 3). It is known that cold working produces both dislocations as well as vacancies. Since positron trapping at vacancies is stronger and dominant as compared to that of dislocations, the observed lifetime of 165 ps is ascribed to vacancies. The irradiation did not produce much increase in the lifetime and S-parameter values as compared to non-irradiated cold-worked D9. This is understandable as the cold-worked sample itself contains a large concentration of defects before irradiation. The annealing behaviour of isochronal recovery curves for both irradiated and non-irradiated cold-worked D9 is almost comparable.

In the temperature region up to 700 K, the cold-worked D9 shows similar recovery behaviour as observed in the annealed D9 irradiated by protons. The large decrease of the positron lifetime and S-parameter with temperature from 500 to 700 K clearly demonstrates the annealing of vacancy-type defects. It should be noted that the lifetime has not reached the defect-free value of 108 ps. This clearly indicates that there is yet another competing process taking place. Above 800 K, both irradiated and non-irradiated samples show increase in lifetime and S-parameter due to the creation of carbide precipitates, mainly TiC at these temperatures. These carbide precipitates have a large lattice mismatch with the austenite matrix, and are associated with misfit dislocations [12–14]. These interfacial defects acts as excellent traps for positrons, and hence the observed variation of life time and S-parameter is attrib-

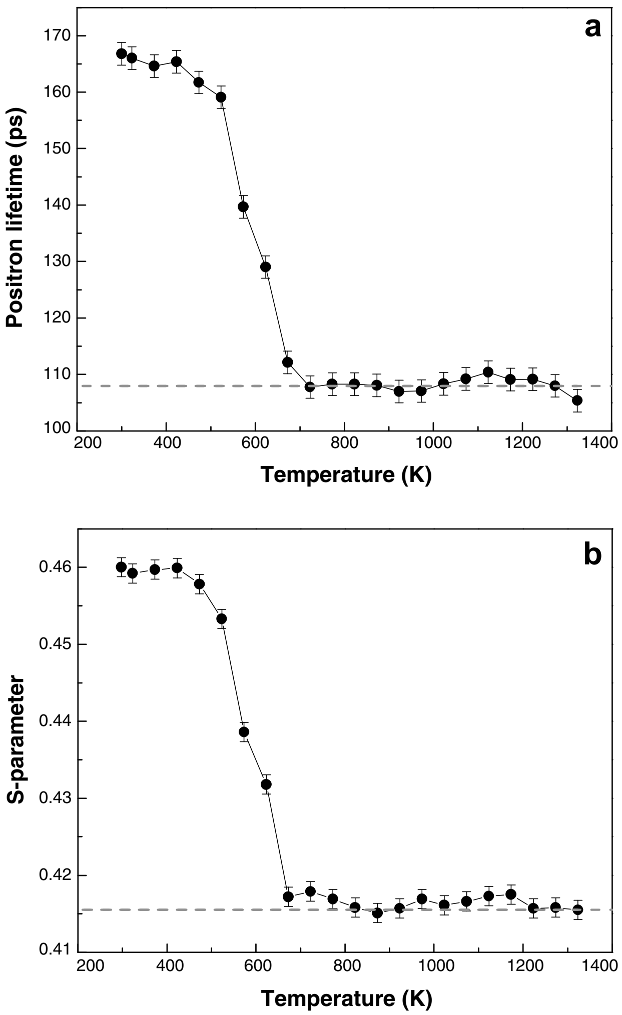

Fig. 2. Variation of lifetime (a) and S-parameter (b) as a function of post-irradiation annealing temperature observed in proton irradiated on solution annealed D9. The solid line through the points is a guide to the eye. The dashed line corresponds to defect-free value.

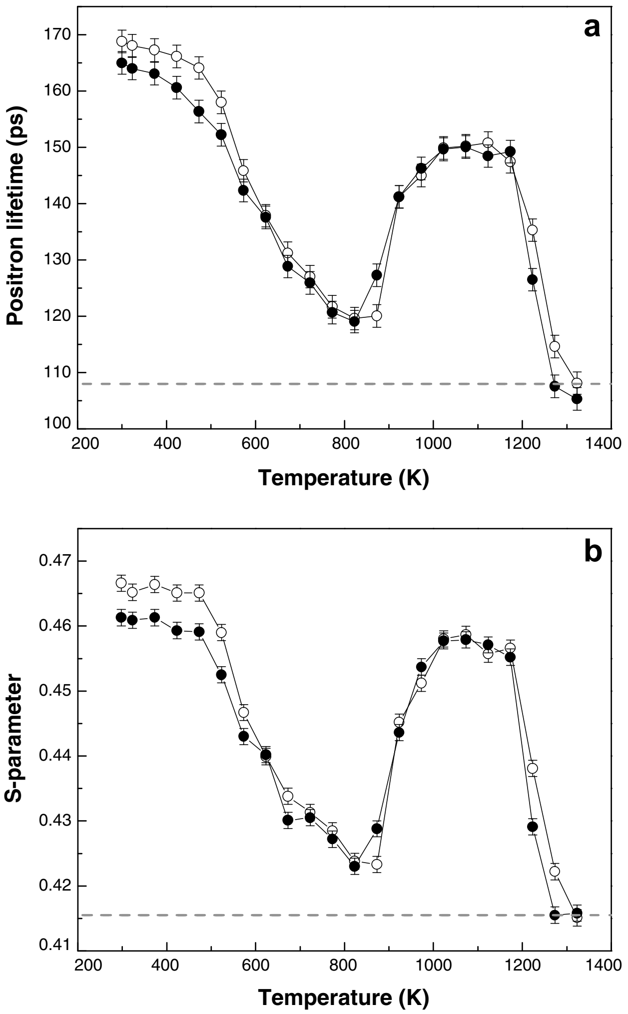

Fig. 3. Variation of positron lifetime (a) and S-parameter (b) as a function of post-irradiation annealing temperature observed in cold-worked D9 with proton irradiated (○) and non-irradiated (●). The solid line through the points is a guide to the eye. The dashed line corresponds to defect-free value.

uted to change in TiC precipitate concentration [15,16]. Further above 1100 K, the decrease in lifetime and S-parameter is attributed to coarsening of the precipitates [15–17]. By comparing Figs. 2 and 3, it is clear that the proton irradiation in well annealed D9 could not produce dislocations, which otherwise would have aided in the nucleation and growth of secondary TiC precipitates as observed in the case of 20% cold-worked D9.

3.2. Isothermal annealing of irradiated D9

Since the proton irradiation on annealed D9 has produced vacancy-defects as identified by positron annihilation, isothermal annealing was carried out to study the kinetics and to deduce the effective activation energy for vacancy migration. Annealed D9 samples were irradiated to a dose of 1×10^{17} protons/cm^2 under identical conditions, so that the initial defect concentration remains the same as that of as-irradiated samples for which isochronal annealing curve was carried out. Irradiated samples were isothermally annealed at 623 K until the asymptote appears at this temperature.

An exponential decay of the positron lifetime as a function of annealing time is observed in the isothermal recovery curve (Fig. 4). Assuming a single-activated process, the rate of change of positron lifetime $\bar{\tau}$ can be written as

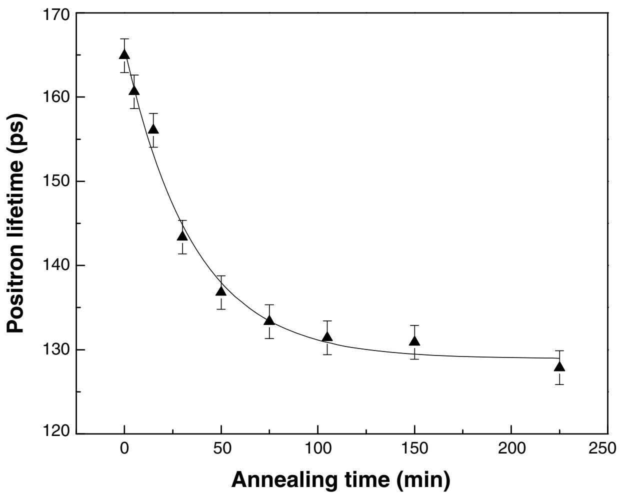

Fig. 4. Isothermal annealing curve for the proton-irradiated D9 at 623 K.

$$\frac{d\bar{\tau}}{dt} = A\exp\left(\frac{-E_v^m}{kT}\right), \tag{1}$$

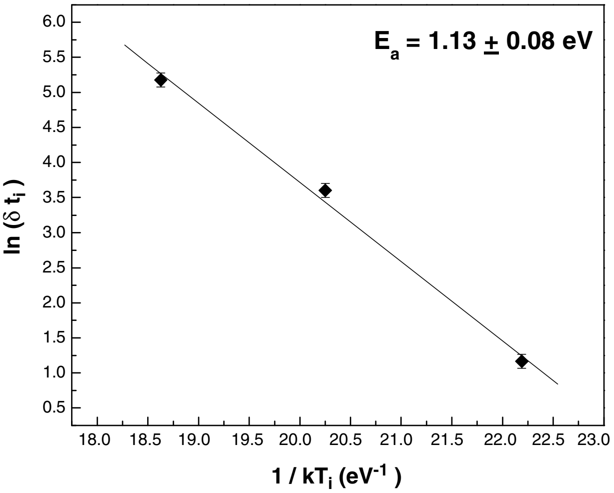

Fig. 5. Determination of effective activation energy for vacancy migration.

Table 2
Experimental values of vacancy migration energy (E_v^m).

Material	E_v^m (eV)	Measurement	Literature
Fe–Cr (8–16 wt%)–25Ni	1.17	Electrical resistivity	[20]
Fe–17Cr–Ni (12–50 wt%)	1.2	Electrical resistivity	[21]
Fe–16Cr–45Ni	1.16	Electrical resistivity	[22]
316L steel	1.4	Electrical resistivity	[21]
316, JPCA steels	1.36	Positron lifetime	[23]
HT9, JFMS steels	1.1	Positron lifetime	[23]
ANSI 321	1.2	Positron S-parameter	[24]
AISI 316L steel	0.9	Positron lifetime	[25]
D9 (14Cr–15Ni–0.25Ti)	1.13	Positron lifetime	Present work

where A is the pre-exponential factor, E_v^m is the activation energy for vacancy migration in eV, k is the Boltzmann constant in eV/K, and T is the annealing temperature in K.

The method of combination of isochronal and isothermal studies [18,19] is applied to extract the activation energy involved in the recovery process. Combining Figs. 2(a) and 4, change in annealing time (δt_i) of isothermal curve corresponds to the change in positron lifetime for each temperature T_i of isochronal annealing.

By plotting ln δt_i vs. $1/kT_i$ (Fig. 5), the slope of the straight line gives the effective activation energy for vacancy migration to be 1.13 ± 0.08 eV.

The vacancy migration energy in Fe–Cr–Ni alloys of various compositions and in different types of steel is listed in Table 2. In Fe–Cr–Ni alloys, vacancy migration energy (E_v^m) has not altered by varying Cr or Ni composition to a great extent [20–22]. In steels, there is a difference of E_v^m due to the presence of different minor alloying elements with varying concentrations [21,23–25]. Adjusting the alloying elements improves the swelling resistance because these minor alloying elements act as fast diffusing impurities and enhance the migration of vacancies to sinks. Also, mechanical treatments in steel provide sufficient sink strength for the vacancies to anneal out. These are reflected in the effective activation energy for vacancy migration in steels. By monitoring the vacancy migration energy, one should be able to identify suitable method to accelerate the diffusion of vacancies to sinks, which can significantly reduce the nucleation of voids and hence swelling in steels.

4. Conclusion

Defect recovery in proton-irradiated D9 has been investigated using the positron annihilation spectroscopy. Isochronal annealing studies reveal that the recovery in irradiated sample of annealed D9 starts around 500 K and complete annealing takes place beyond 700 K, which is attributed to the migration and annihilation of vacancies. In addition to the defect recovery, beyond 700 K, there is nucleation and growth of secondary TiC precipitates found only in cold-worked D9. Isothermal annealing studies gives the effective activation energy for vacancy migration in D9 steel to be 1.13 ± 0.08 eV.

Acknowledgement

Authors would like to thank Dr B.K. Panigrahi for useful discussions.

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