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Letter to the Editors

Proton irradiation effects in Zr–1.0 Nb–1.0 Sn–0.1 Fe probed by positron annihilation [1]

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Abstract

Samples of a new zirconium-based alloy (zirlo) were proton-irradiated and the structural defects were characterised by positron annihilation. The lifetimes of positrons trapped in the defects generated at different doses of irradiation appeared to suggest significant interaction of the defects with the substitutional solute atoms. The isochronal recovery of the sample irradiated at the highest dose showed three distinct stages. The initial annealing of free vacancy clusters was followed by a solute atom-vacancy dissociation stage above 673 K. The vacancies thus released annealed out at 973 K.

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1. Introduction

Extensive studies in recent years on the response to high energy particle irradiation and consequent defect production and evolution in zirconium-based alloys have emphasized the influence of solute elements on the defect migration and recovery aspects [1–3]. There exist conflicting views rather than general agreement on this subject. While the general view regarding the effects of solute atoms on irradiation damage was related to slowing down the diffusion of vacancies and self-interstitial atoms [3], the iron atoms, for instance, were shown to form highly mobile Fe/vacancy defects, which accelerate and control vacancy migration [4]. The substitutional alloying elements such as Nb, Sn, Fe, Cr and Ni have significant roles in the initial phase structure of the alloy and will have strong bearing on the defect recovery processes. Hence there is a need for independent investigations on new alloys in view of their increasing utility in reactor technology.

A new zirconium-based alloy, popularly known as zirlo is gaining importance as a potential candidate material for fuel cladding tubes. The most promising features of this alloy are its low corrosion rate, better irradiation creep and growth resistance and ability to withstand higher burn-up. In this alloy Nb, Sn and Fe are present as substitutional elements in respective strengths (by weight) of 1.0 ± 0.1%, 1.0 ± 0.1% and 0.10 ± 0.01%. These elements in solid solutions can lead to the formation of intermetallic compounds on cooling from high temperatures [2,5,6]. A study of particle irradiation damage in this alloy is useful in understanding the interaction of the solute elements with the defects. Positron annihilation spectroscopy (PAS) studies are highly promising in this context by virtue of the sensitivity of positrons to vacancy-type defects on the atomic scale [7].

2. Experimental

The samples used in this study were in the form of tubes with a thickness about 0.4 mm. Specimens of

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dimensions 5 mm × 5 mm were cut and flattened by giving slight mechanical pressure. This may generate a small density of dislocations and hence they were thermally annealed at 1023 K for 4 h in high vacuum and slowly cooled before further experiments. The 15 MeV proton-irradiation on six pairs of samples was done using the beam from the variable energy cyclotron at Calcutta. Each pair was irradiated to a different dose, the doses being 1×10^{20}, 3×10^{20}, 5×10^{20}, 1×10^{21}, 1.8×10^{21} and 5×10^{21} protons/m^2. During the irradiation, the temperature of the specimens did not rise above 313 K. PAS studies were started only after the induced radioactivity in the specimens died out so that there were no interference effects in the measurements.

PAS measurements at room temperature were performed using a ^{22}Na source of strength ~1 μ Ci deposited over and covered by a nickel foil of ~2 μm thickness. For positron lifetime measurements, a fast–fast gamma–gamma coincidence set-up with time resolution 260 ps for ^{60}Co gamma rays was used [8]. Doppler broadening measurements [8] were done using a high pure germanium detector of resolution 1.10 keV for 475 keV gamma rays from ^{102}Rh. The positron lifetime spectra were analysed using RESOLUTION and POSITRONFIT [9]. The observations from Doppler broadening measurements were quantified in terms of the S parameter, computed as the area under the energy window of 510.4–511.6 keV normalised by the area under the lineshape extending from 503.3 keV to 518.7 keV. Similar measurements were carried out after isochronal (1 h) annealing of the pair of specimens with the highest dose of irradiation at different temperatures of regular intervals from 373 K to 1023 K in vacuum of $\sim 10^{-3}$ Pa.

3. Results and discussion

The samples, originally in the form of tubes, had undergone repeated thermo-mechanical treatments during fabrication which would produce high residual stresses. Due to the anisotropies in the elastic and thermal properties, these stresses would influence the subsequent defect interaction stages. Initial annealing at 1023 K for 4 h did not fully remove these stresses. This was evident from the positron lifetime spectrum of these samples with a second lifetime of 240 ps with ~2% intensity. The restriction on the choice of the annealing temperature was made in view of the structural phase transition (hcp $\alpha \rightarrow$ bcc β) in zirconium alloys above 1073 K [2,6]. That the positron annihilation parameters are sensitive to this transition was earlier verified separately [10].

To estimate the lifetime of positrons not trapped in these defects prior to their annihilation, we used the conventional two-state trapping model [11]. It is assumed in this model that the positrons can annihilate either in the free state in the bulk with a rate λ_b or after being trapped into a vacancy-type defect where they will have a reduced annihilation rate λ_t. At a given instant of time t, if n_b and n_t are the number of positrons in the bulk and the defects respectively, the two rate equations governing the annihilation process can be written as

$$dn_b/dt = -n_b\lambda_b - n_b\kappa_t \tag{1a}$$

and

$$dn_t/dt = -n_t\lambda_t + n_b\kappa_t, \tag{1b}$$

where κ_t is the rate of positron trapping by the defects. Assuming that the positrons are initially released into the bulk and the number of trapped positrons $n_t = 0$ at $t = 0$, these equations can be solved to represent the measured positron lifetime spectrum as

$$N(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2), \tag{2}$$

where $\tau_1 = (\lambda_b + \kappa_t)^{-1}$ and $\tau_2 = \lambda_t^{-1}$ are the two measured positron lifetimes and $I_1 + I_2 = 100\%$. The relative intensity $I_2 = \kappa_t/(\lambda_b - \lambda_t + \kappa_t)$ from which κ_t can be calculated.

The positron lifetime τ_b for the annealed samples as estimated from this analysis is 164 ps, which is in agreement with the mean lifetime of positrons in zirconium (166 ps), niobium (120 ps), tin (202 ps) and iron (160 ps) with the intensities chosen in the same ratio of their percentage composition in the alloy. The positron lifetimes and intensities (shown in Table 1) in the as-irradiated specimens indicated the need to interpret the data using the three state trapping model [11] to account for the observed anomalies in the intermediate dose range. The effect of an additional positron trapping site,

Table 1
Positron lifetime parameters in the samples irradiated by different doses of 15 MeV protons. (χ^2/ν is the variance of the fit in the positron lifetime data analysis using ν degrees of freedom [9])

Dose (protons/m^2)	χ^2/ν	τ_1 (ps)	τ_2 (ps)	I_2 (%)
1×10^{20}	0.90	173 ± 2	290 ± 7	13.4 ± 1.3
3×10^{20}	1.00	162 ± 1	284 ± 5	10.1 ± 0.8
5×10^{20}	1.14	166 ± 1	244 ± 8	5.4 ± 0.9
1×10^{21}	1.21	168 ± 1	277 ± 7	5.8 ± 0.8
1.8×10^{21}	1.13	175 ± 2	281 ± 7	11.7 ± 1.3
5×10^{21}	1.18	164 ± 1	292 ± 6	11.1 ± 1.0

possibly the oxygen environment near dislocations (see below), would modify the shorter lifetime τ_1 to a value determined together by both the trapping rates κ_{t1} and κ_{t2} by the relation

$$\tau_1 = \frac{1 + (\kappa_{t1}/\lambda_{t1})[1 + \kappa_{t2}/(\lambda_b - \lambda_{t2} + \kappa_{t1})]}{\lambda_b + \kappa_{t1} + \kappa_{t2}}, \quad (3)$$

where the two trapping rates could be calculated from the following expressions:

$$\kappa_{t1} = \frac{\tau_1(\lambda_b - I_2\lambda_{t2}) - I_1}{\tau_{t1} - \tau_1} \quad (4a)$$

and

$$\kappa_{t2} = \frac{I_2}{I_1}(\lambda_b - \lambda_{t2} + \kappa_{t1}). \quad (4b)$$

The saturation lifetime τ_{t1} in weak traps is taken as the positron lifetime in monovacancies (about 240 ps).

In the interpretation of the positron lifetimes after the isochronal annealing of the highest-dose-irradiated specimen, we used $\tau_b = 164$ ps to check in reverse the consistency of τ_1 in each spectrum using once again the two-state trapping model. The model was found adequate enough to derive inferences on the annealing behaviour of defects at different temperatures.

The as-irradiated specimens consisted of defects giving a lifetime τ_2 in the range from 244 to 292 ps ($I_2 = 5$–13%) for the trapped positrons. If they are of the vacancy-cluster-type, this value should imply that they essentially consist of 2–3 monovacancies each [12]. It is not possible to rule out the presence of other small order defects since the irradiation-induced displacement cascades ultimately are likely to collapse into dislocation/vacancy loops. Hood et al. has mentioned a temperature range upto 373 K for this process to occur in α-Zr [13]. At ambient temperatures, the oxygen atoms present in the octahedral sites of the hexagonal lattice may diffuse in and segregate near these defects [2]. (Typical oxygen concentration in this alloy is 900–1300 ppm. This segregation process is usually known as Cottrell effect [14].) The positrons annihilating in the oxygen atmosphere near dislocations may account for the deviation of τ_1 of the spectrum of the as-irradiated specimens from the value predicted from the two-state trapping model.

There is another possibility that some of the oxygen atoms, which were present initially in the interstitial sites, would fill a number of vacancies created by the removal of host Zr atoms by the projectile ions. This argument supports the observation that the agglomeration of the Zr vacancies was rather restricted to the formation of divacancies or trivacancies and no fully grown voids or cavities were present in the irradiated alloys.

To account for the apparent anomaly in the variation of τ_2 and I_2 with increasing dose (Table 1), attention is now to be focussed on the solute atoms present in the alloy and their susceptibility to proton-irradiation. In low-temperature irradiated pure Zr samples free of any alloying elements, multiple stages of vacancy agglomeration and recovery had been reported [15]. The extension of this work on Zr containing Sn as substitutional element showed the complete suppression of these stages by these atoms [15]. Hence it is straightforward to argue that the substitutional solute atoms (preferentially iron), due to the relatively weaker binding with the host Zr atoms, may be easily knocked out by the projectile atoms. In the work reported by Eldrup et al. [4] (and supported by electron probe microanalysis studies by Zou et al. [16]), these iron atoms have been shown to form Fe-vacancy defects that would accelerate and control vacancy migration. This is in contrast to the proven role of Nb and Sn which, as substitutional elements, were seen to suppress the vacancy agglomeration considerably [3]. Considering the atomic dimensions of these substitutional elements and also the lattice constants for Zr ($a = 0.323$ nm and $c = 0.515$ nm), it can be argued that Fe atoms are more probable to migrate substitutionally in the c direction while Nb and Sn atoms may do so more likely in the ab plane. In any case, the influence of these elements seems to be important on the subsequent defect evolution. At larger doses of irradiation, the solute atom-vacancy complex formation saturates and the usual effects of increased irradiation like the generation of additional vacancies and partial agglomeration appear to dominate.

The S parameter variation with isochronal annealing temperature (Fig. 1) for the sample irradiated by 5×10^{21} protons/m^2 shows rapid annealing of the irradiation-induced dislocations, vacancies and loops by 673 K. Surprisingly the impurity segregation near disloca-

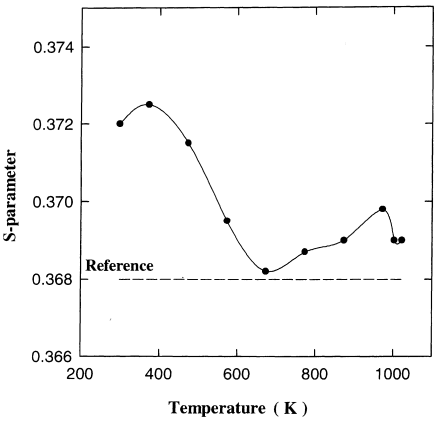

Fig. 1. The variation in S parameter with isochronal annealing temperature of proton-irradiated ZIRLO. (Reference value indicates the state of the sample annealed at 1023 K for 4 h prior to irradiation.)

tions did not hold them stable against thermal annealing. In other words, the interaction of these atoms (mainly oxygen) with the dislocations appears weak and does not seem to act as a barrier against the movements of dislocations. We find further from the behaviour of the lifetime parameters τ_2 and I_2 that the annealing is remarkably sharp and consists of three distinct stages (Fig. 2). Initially both these parameters fall drastically, indicating that there existed a significant number of di or trivacancies in the as-irradiated sample which did not form complexes with the atoms of either the solute elements or the oxygen diffusing out of the octahedral sites. The annealing stage corresponding to the recovery from these defects coincide with that of dislocation/vacancy loops and ends at 673 K. The intermediate stage of defect evolution from 673 K to 973 K involves the release of fresh positron trapping sites into the sample. Earlier when the positron trapping rate κ_t was calculated for using the two-state trapping model discussed, we had observed an increase of κ_t in this temperature range. κ_t depends both on the specific positron trapping efficiency of the kind of defect and its concentration. While the former has a direct bearing on the positron lifetime trapped in it, the latter will be reflected in the measured intensity I_2. Fig. 2 shows a sharper increase in the intensity than in the lifetime, which indicates rather the presence of additional trapping centres than a characteristic defect evolution stage. The release of vacancies at this temperature is possible if the solute atom-vacancy complexes start to dissociate. Earlier observations in deformed and irradiated materials had also indicated the viability of such a process being responsible for similar effects [8,17].

The sharp fall of the parameters above 973 K finally completes the defect recovery processes in the α-phase. A small value (~3%) of I_2 survives the isochronal annealing upto 1023 K, showing that the annealing of defects is still not complete. As the $\alpha \rightarrow \beta$ phase transition was imminent to occur above this temperature, further investigation needs complementary support from alternative experimental studies.

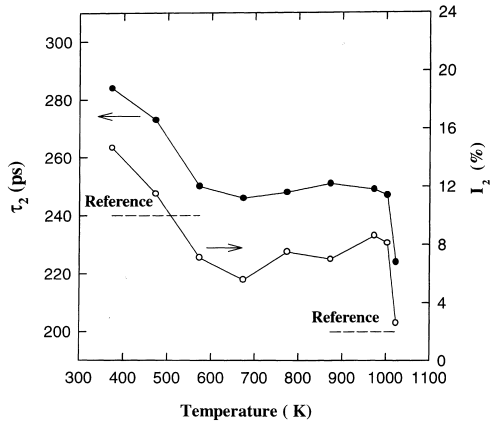

Fig. 2. The lifetime parameter τ_2 and intensity I_2 versus annealing temperature in proton-irradiated zirlo. The values for an annealed reference sample are also shown.

4. Conclusions

The defect microstructures produced in zirlo due to proton-irradiation seem to be instantly modified by the substitutional solute atoms which considerably interact with the irradiation induced vacancies to form solute atom-vacancy complexes. Also the oxygen atoms appear to prevent the remaining vacancies from agglomerating into voids and instead only divacancies and trivacancies are formed. The defect recovery due to isochronal annealing consists of three stages. Initially the impurities segregated around the dislocations move away, leaving the annealing of these defects to proceed. The small vacancy clusters which did not form complexes with the solute atoms or those of oxygen also annealed out in this temperature range. The second recovery stage from 673 to 973 K shows the dissociation of the solute atom-vacancy complexes and additional vacancies are released in the alloy. This results in enhanced positron trapping. Annealing of higher order vacancy clusters begins at 973 K and continues beyond 1023 K, where the $\alpha \rightarrow \beta$ phase transition becomes imminent.

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