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The study of microstructural defects and mechanical properties in proton-irradiated Zr–1.0%Nb–1.0%Sn–0.1%Fe

P. Mukherjee [a,*], P.M.G. Nambissan [b], P. Barat [a], Pintu Sen [a], S.K. Bandyopadhyay [a], J.K. Chakravartty [c], S.L. Wadekar [c], S. Banerjee [c], S.K. Chattopadhyay [d], S.K. Chatterjee [d], M.K. Mitra [e]

[a] *Variable Energy Cyclotron Centre, 1/AF Bidhannagar, Calcutta 700 064, India*
[b] *Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta 700 064, India*
[c] *Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
[d] *Regional Engineering College, Durgapur 713 209, India*
[e] *Department of Metallurgy, Jadavpur University, Calcutta 700 032, India*

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Abstract

We had earlier analysed point defects in irradiated Zr–1.0%Nb–1.0% Sn–0.1%Fe samples by positron annihilation lifetime spectroscopy (PALS). The studies revealed the generation of irradiation induced di- and tri-vacancy clusters. In the present work, we have carried out X-ray diffraction line profile analysis (XRDLPA) and studies of mechanical properties like ultimate tensile strength (UTS), yield strength (YS) and percentage elongation (%E) on the same irradiated samples at different doses. XRDLPA reveals that order of dislocation density remains almost unchanged up to the experimental limit of irradiation dose. Attempts have also been made to correlate the changes in mechanical properties with irradiation-induced defects. YS of the alloy increases with irradiation due to locking, or pinning of dislocations with vacancy clusters. However, there is an anomaly in YS at a dose of 5×10^{20} protons/m^2 which has been explained in the light of interaction of vacancies with solute atoms. Percentage elongation on the other hand, shows a monotonic fall with increasing dose.

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1. Introduction

The microstructural changes during irradiation and its effects on mechanical properties of pure zirconium (Zr) and its alloys like Zircaloy and Zr–2.5%Nb have been widely studied. The reviews [1–4] are mainly based on neutron and electron irradiation on pure Zr and zircaloys. The nature of radiation damage in zirconium alloys is affected by the type of ion, dose of irradiation, alloying elements and impurity variations [1]. Studies on microstructural evolution on proton irradiation [5,6] in zirconium alloys have also been reported. However, there is little work on the effects of irradiation on mechanical properties of Zr–1%Sn–1%Nb–0.1%Fe, a promising candidate material for the nuclear fuel cladding tube [7]. The irradiation-induced point defects play a significant role on the changes in mechanical properties. We had earlier characterised the irradiation-induced defects and their significant interactions with the substitutional and interstitial solutes of proton-irradiated Zr–1%Sn–1%Nb–0.1%Fe samples at different doses by positron annihilation lifetime spectroscopy (PALS) and Doppler broadening measurements [7].

In the present work, we report studies of X-ray diffraction line profile analysis (XRDLPA) by modified Rietveld technique [8] on the same irradiated samples. XRDLPA has been widely applied for the evaluation of microstructural parameters such as coherently scattered domain size, microstrains within the domains and dis-

* Corresponding author. Tel.: +91-33 337 1230 ext. 2409; fax: +91-33 334 6871.
E-mail address: paramita@veccal.ernet.in (P. Mukherjee).

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location densities of the defect state of materials [9,10]. In this work, modified Rietveld technique has been applied on unirradiated samples as well as samples irradiated at different doses in order to ascertain any change in density of dislocations due to irradiation. Variations of mechanical properties like ultimate tensile strength (UTS), yield strength (YS) and percentage elongation (%E) with doses of irradiation have also been studied and correlated with microstructural defects generated during irradiation.

2. Experimental

Ingot of this alloy was prepared in the Nuclear Fuel Complex, Hyderabad, by the double vacuum arc melting technique. It was then β-quenched, followed by hot extrusion and cold pilgering for producing a tube of 0.4 mm wall thickness.

Subsize tensile samples of 12 mm gauge length and 0.4 mm thickness were prepared from these tubes. Another six samples of 5 mm × 5 mm were taken for XRD. All the samples were annealed at 1023 K for 4 h. The samples were irradiated with 15 MeV protons using the beam from the Variable Energy Cyclotron Centre (VECC), Calcutta, at doses of 1×10^{20}, 3×10^{20}, 5×10^{20}, 1×10^{21}, 3×10^{21} and 5×10^{21} protons/m^2. The samples for irradiation were mounted in a target holder flange, made of aluminium. The dose accumulating to the target material (sample) was measured from the total charge of projectile particles i.e. protons falling on the sample. Water is allowed to flow through the target flange to minimise the heat generated during irradiation. The temperature did not rise above 313 K, as monitored by a thermocouple sensor placed inside a groove of the flange in close proximity to the sample. The displacement per atom (dpa) was obtained by Monte-Carlo simulation technique using the code TRIM 95 [11]. XRD patterns were obtained from a Philips PW 1710 X-ray diffractometer using CuK_α radiation with 2θ ranging from 10° to 100° and a step scan of 0.02°. XRDLPA was done with the help of the modified Rietveld technique using program LS1 [8] for determining average domain size (D_{av}) and root mean squared (r.m.s.) strain ($\langle \epsilon_1^2 \rangle^{1/2}$), from which dislocation densities were calculated. Tensile samples were tested in a universal testing machine (Instron) at a strain rate of 2×10^{-4}/s.

3. Results and discussion

The range of the 15 MeV proton in the alloy obtained by TRIM 95 calculation was found to be 720 μm, which is more than the thickness of the sample. Hence, the proton completely penetrates the sample and therefore the damage produced in the samples is believed to be a bulk phenomenon.

The radiation damage is generally assayed by the damage energy deposited causing displacements of atoms and it is measured by the number of dpa. Therefore, dpa is proportional to the dose of irradiation. In these samples, dpa ranges from 0.88×10^{-4} to 4.38×10^{-3}.

In our earlier investigation [7], the lifetime of positrons in the bulk and defect state was analysed using the conventional two-state trapping model [12]. In this model, there are two lifetimes, τ_1 and τ_2, where τ_1 represents the lifetime for combined effects of positrons annihilating in the bulk and those with free Bloch state residence time and τ_2 is the lifetime of trapped positrons in vacancy-type defects.

The analysis of τ_2 for all the irradiated samples except at 5×10^{20} protons/m^2 showed values in the range of 244–292 ps [7]. These values correspond to the vacancy cluster size of 2–3 atoms [13]. Interestingly, τ_2 falls at a dose of 5×10^{20} protons/m^2 to a value of 244 ps, which corresponds to a size of mono-vacancy. We have explained this suppression of vacancy agglomeration by the formation of solute atom–vacancy complex either by interstitial oxygen or by substitutional solutes like Sn, Nb [14,15] at this critical dose. Thus, PAS studies did not reveal any agglomeration beyond tri-vacancy clustering (3 atoms size) even up to the highest dose.

The diffraction profile of the sample irradiated at the highest dose, 5×10^{21} protons/m^2, is shown in Fig. 1 as a typical representation. The XRD patterns revealed a primarily phase α. The β phase, whatever little may be

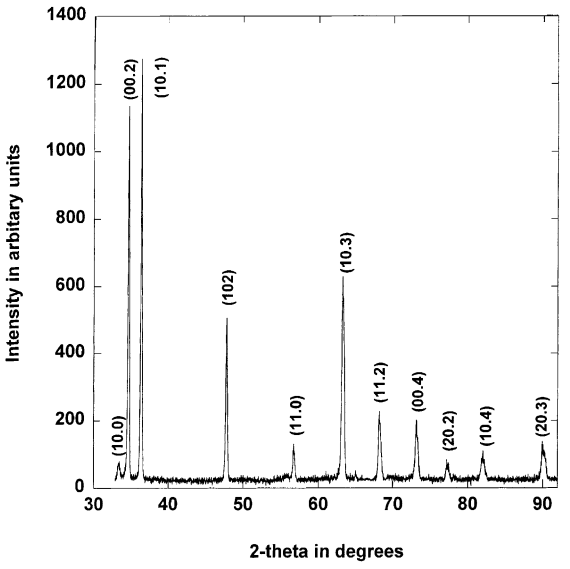

Fig. 1. X-ray diffraction profile of the sample irradiated at 5×10^{21} protons/m^2.

present, remained undetectable. The profile (Fig. 1) showed preferred orientations [16] on certain crystallographic planes like (0 0 2), (1 1 2), (1 0 1), (1 0 3). The grain orientations are believed to have resulted from the repeated thermo-mechanical treatments during fabrications of the tubes. We did not observe any additional peak in XRD profile during irradiation. We expect that no major phase change had occurred even up to the highest dose of irradiation.

Broadening of diffraction peaks contains information about microstructural parameters, particularly lattice microstrains due to irradiation and the sizes of incoherently diffracted domains. The X-ray diffraction patterns are fitted with the pseudo-Voigt (pV) function, which is basically a linear combination of the Gaussian and Lorentzian function. Instrumental broadening correction is done using a standard defect-free Si crystal. The refinement of the profile is done by the programme LS1 [8], which includes simultaneous refinement of the crystal structure (lattice parameters) and the microstructural parameters like domain size (D_{av}) and microstrains ($\langle\epsilon_l^2\rangle^{1/2}$). The domain size and microstrain are incorporated in the programme as fitting parameters. The programme also incorporates correction for preferred orientations by proper mathematical modelling with preferred orientation function [17–19]. Average domain size (D_{av}) and r.m.s. strain $\langle\epsilon_l^2\rangle^{1/2}$ are determined for unirradiated and irradiated samples at doses 1×10^{20}, 5×10^{20} and 5×10^{21} protons/m^2 and have been listed in Table 1.

The dislocation densities ρ [20] have been measured from the relation $\rho=(\rho_D\rho_S)^{1/2}$, where $\rho_D=3/D_{av}^2$ (dislocation density due to domain size) and $\rho_S=k\langle\epsilon_l\rangle^2/b^2$ (dislocation density due to strain), k is a material constant and $\bar{b}$ is the modulus of Burger's vector, 1/3[1 1 $\bar{2}$ 0], and are listed in Table 1. It has been observed that the order of dislocation density of the irradiated samples does not change as compared to the unirradiated ones even up to the highest dose. This clearly depicts that proton irradiation at this level did not generate additional dislocation loops through collapse of point defects. Since point defects do not cause broadening till they form dislocations, the XRD profiles of the irradiated samples did not exhibit any broadening compared to the unirradiated one.

Table 1
Variation of average domain size (D_{av}), root mean square strain $\langle\epsilon_l^2\rangle^{1/2}$ and dislocation density ρ (10^{-14}/m^2) with dose

Dose (protons/m^2)	D_{av} (Å)	$\langle\epsilon_l^2\rangle^{1/2}$ (10^{-4})	ρ (10^{-14}/m^2)
Unirradiated	1071 ± 70	6.75	1.5
1×10^{20}	998 ± 62	7.17	1.7
5×10^{20}	1008 ± 60	5.79	1.4
5×10^{21}	1090 ± 70	9.37	2.0

The variation of tensile properties like UTS, YS and %E of the unirradiated and irradiated samples with dose have been shown in Fig. 2.

It is observed that variation of UTS is quite irregular with dose. On the other hand, YS increases with dose because the elastic interactions between the vacancies created during irradiation and the dislocations present in the material result in the locking or pinning of these dislocations by point defects. Moreover, it is interesting to note (Fig. 2) that the increase in YS is not monotonic with dose. Rather, a significant fall in YS at a dose of 5×10^{20} protons/m^2 is observed. The anomaly in the variation of YS can be explained as follows. In the alloy, 900–1300 ppm oxygen is present as interstitial solute element. During irradiation, Zr vacancies are mostly created and agglomerated in the matrix (containing ~98% Zr). At the same time, the loosely bound oxygen from the interstitial position tends to occupy the vacancy sites and suppress the agglomeration of vacancies. This argument supports the observation by PAS that the agglomeration of the zirconium vacancies was rather restricted up to the formation of di-vacancies and trivacancies and no fully grown voids or vacancy loops were present in the irradiated sample. This suppression

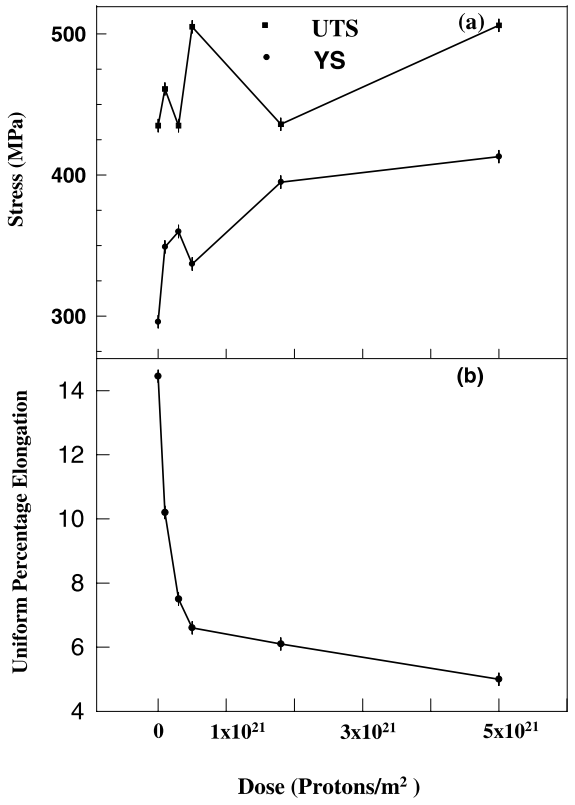

Fig. 2. Variation of mechanical properties as a function of dose.

of agglomeration can also take place by the formation of solute atom–vacancy complex with other substitutional solute atoms like Sn and Nb [14,15]. In these competing processes (the generation of vacancies and their suppression), the latter effect is most dominant at the critical dose of 5×10^{20} protons/m^2. As a result, there is a reduction in effective vacancy concentration with less pinning effect for locking of dislocations indicated by a clear fall in YS. The formation of solute atom–vacancy complex during irradiation was also evident by our earlier PAS studies on samples with highest dose during isochronal annealing. The study revealed generation of additional positron trapping sites (vacancies) at the temperature range of 673–973 K, in contrast to the defect recovery during this stage. This is because of the dissociation of solute atom–vacancy complex releasing vacancies at this range of temperature. At higher doses, the solute atom–vacancy complex formation saturates, and the process of generation of additional vacancies and their agglomeration appear to dominate. As a result, YS again increases after the critical dose.

Percentage elongation in a tensile sample is limited by fracture events. Increasing dose of irradiation enhances release of vacancies, which during deformation are agglomerated resulting in microvoid formation during deformation. Coalescence of such microvoids results in early fracture restricting the elongation prior to plastic instability in samples subjected to uniaxial tension. Percentage elongation thus reveals a monotonically decreasing trend.

4. Conclusions

XRDLPA can be used to assess the microstructural parameters like domain size (D_{av}) and r.m.s. strain $\langle \epsilon_l^2 \rangle^{1/2}$ and dislocation densities ρ of the unirradiated as well as irradiated samples of zirlo. The analysis revealed that there is no change in the order of dislocation density (10^{14} nos./m^2) up to the dose of 5×10^{21} protons/m^2. YS increases with dose of irradiation except at 5×10^{20} protons/m^2. The increase in YS is due to the pinning of dislocations with irradiation-induced point defects. Moreover, there are simultaneous processes of vacancy formation and their recombination with interstitials and substitutional solute atoms (O, Sn, Nb) which saturate at higher dose. The anomaly in YS is the manifestation of this recombination processes dominating over the vacancy formation at 5×10^{20} protons/m^2. Vacancy release during irradiation promotes microvoid formation and subsequent void coalescence, causing decrease in percentage elongation.

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