Positron Annihilation Study of Zr-2.5 wt.% Nb alloy Irradiated by Ar$^{9+}$ heavy ions

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Abstract. Zr-2.5 Nb alloy is used as a pressure tube material in pressurized heavy water reactor (PHWR). It is one of the most critical component which decides the lifespan of the reactor. The in-reactor degrading phenomenon of prime concern is dimensional changes caused by irradiation induced creep and growth processes. The present study aims to understand the mechanism of irradiation damage by irradiating the alloy with heavy ion. Such type of irradiation study would facilitate larger damage of material in a shorter time. Zr-2.5Nb alloy samples were irradiated using 315 keV Ar$^{9+}$ ion for different durations. The irradiation doses were varied in the range of 3.1X10$^{15}$ to 4.17X10$^{16}$ Ar$^{9+}$/cm$^2$. SRIM calculation was carried out to evaluate damage profile in the irradiated samples. Beam based Positron Annihilation Spectroscopy (PAS) technique was used for depth profiling to characterize defect distribution in the alloys. The no. of defects generated is seen to increase with the increase in the fluence.

1. Introduction

Zirconium based alloys are used as structural materials in pressurized heavy water reactors (PHWRs) and replaced from Zircaloy-2 due to their low neutron absorption cross-section, good mechanical strength at operating temperature, low irradiation creep rate, high corrosion resistance, irradiation creep resistance and lower hydrogen absorption rates [1-3]. The pressure tube carries the nuclear fuel and the high temperature, high pressure (typically 573 K and 10 MPa, respectively) water coolant, and it is subjected to fast neutron irradiation (typical neutron flux of 3.0 X 10$^{17}$ n/m$^2$.s, E > 1 MeV neutrons) [4,5]. Under this critical operating environment, the pressure tube material undergoes irradiation enhanced deformation and change in microstructure properties over a period of time. The nature of irradiation damage in Zr-2.5Nb is affected by the type of ion, irradiation dose and impurity content [6]. In case of heavy charged particle irradiation, having moderate energy, a significant amount of line defects in form of dislocations are also formed along with considerable amount of point defects [7]. Ion irradiation is not only an interesting method to qualify reactor materials but also to simulate the in-reactor damage by neutron irradiation [8]. There exist similarities and correlation between the damage or defects in materials generated by ion irradiation and neutron irradiation. Irradiation by heavy ion provides many advantages such as: (1) higher displacement rate which leads
to shorter irradiation time, (2) lesser nuclear reactions, (3) controlled bombardment conditions and (4) lower irradiation cost compare to neutron irradiation experiments [9,10]. Heavily charged Ar\(^{9+}\) ions have been used in present study as it leads to dense cascade similar to those observed in neutron beam damage [11].

Positron annihilation spectroscopy (PAS) is a powerful technique for characterizing the vacancy-type defects such as micro-voids, open volume defects in solids materials [12]. The slow positron technique, Doppler broadening spectroscopy (DBS) using mono-energetic or variable energy positron allow to measure the defect profiles along the depth in solids, and it is most suitable for analyzing the surface and near-surface defects in ion-irradiated materials [13,14].

The focus of this work has been to characterize the irradiation damage of Zr-2.5Nb alloy following irradiation by 315 keV energy Ar\(^{9+}\) ions in the fluence range of \(10^{15} - 10^{16}\) Ar\(^{9+}\) /cm\(^2\). The formation of vacancy-like defects due to irradiation was investigated by PAS technique. Analytical calculations using the SRIM-2013 Monte Carlo Code were carried out for ascertaining the dpa (displacement per atom) level at different fluences of ion irradiation. The findings of the slow positron DBS measurements are correlated with SRIM-2013 [15] simulation results.

2. Experimental methods
2.1. Material and sample preparation
Zr-2.5Nb pressure tube material was received from Nuclear Fuel Complex, Hyderabad, India. Samples of approximately 1 cm X 1 cm X 0.5 cm size were machined out and the surfaces were mechanically prepared following standard metallographic practice. The sample surfaces were finally electrochemically polished using an electrolyte consisting of 20% v/v Perchloric acid in Methanol at a temperature of -48 °C and voltage of 20 V to remove any stresses introduced during sample preparation.

2.2. Argon ion irradiation
A set of five samples were irradiated at room by 315 keV Ar\(^{9+}\) ion with the fluence of \(3.1 \times 10^{15}\), \(6.25 \times 10^{15}\), \(9.3 \times 10^{15}\), \(2.08 \times 10^{16}\), and \(4.17 \times 10^{16}\) Ar\(^{9+}\) ion/cm\(^2\) at Variable Energy Cyclotron Centre, Kolkata, India. All the irradiations were carried out at room temperature. SRIM-2013 simulation software has been used to evaluate the depth profile of Ar\(^{9+}\) ions and damage distribution in terms of displacement per atom (dpa). The dpa was calculated from Norgett-Robinson-Torrens (NRT) formula [16]:

\[
dpa = \frac{0.8}{2E_d} \times \left( \frac{dE}{dX} \right) \times 10^8 \times \frac{\phi}{N}
\]

where \(E_d = 40\) eV [17] is the threshold displacement energy, \(\phi\) is the fluence in Ar\(^{9+}\)/cm\(^2\), \(N\) is the atomic density (\(4.316 \times 10^{22}\) atom/cm\(^3\)) and \(dE/dX\) in eV/Å is the linear energy transfer to the target material in nuclear process. \(dE/dX\) was calculated from SRIM-2013, which is equal to the sum of the phonon and binding energy distribution profile.

2.3. Doppler broadening spectroscopy (DBS) measurement
The DBS experiments were carried out at room temperature using slow positron beam with implantation energy ranging from 0.2-20 keV. Positron from a 50 mCi \(^{25}\)Na source was moderated by a 1 μm tungsten foil and guided to the target chamber with the help of electric and magnetic field. A high purity germanium detector (HPGe) with a resolution of 2.0 keV at 1332 keV photopeak of \(^{60}\)Co is used for Doppler broadening measurements. Doppler broadened annihilation \(\gamma\)-radiation characterized by the line shape \(S\)-parameter which is defined as the ratio of integral counts within ~2.0 keV energy window centered at 511 keV to the total photo peak area is evaluated as a function of positron implantation energy. The implantation depth of positron is related to incident energy by the relation, \(z_0 = AE^2/\rho\), where, \(z_0\) is expressed in nm, \(E\) is positron energy in keV, \(\rho\) is density of the
medium in g/cc, $n = 1.6$ for positron incident on most of the materials and $A$ is a material dependent constant.

3. Results and discussion

In this section the SRIM simulation and PAS results of the irradiated Zr-2.5Nb alloy samples are presented and discussed. The purpose of this irradiation study was to understand the irradiation degradation mechanism for the assessment of pressure tube behavior during in-service operation. Figure 1 shows the distribution of 315 keV Ar$^{9+}$ ions in Zr-2.5Nb binary alloy. The mean implantation depth and maximum range of penetration of 315 keV Ar$^{9+}$ ions in this alloy was found to be around 100-200 nm and 450 nm, respectively. The energy of Ar$^{9+}$ ion decides the extent of damage in the form of number of displacement of atoms. Figure 2 shows the damage profile of Zr-2.5Nb alloy indicated by total number of target atoms displaced in the collision events. The peak damage was found to occur at a depth of around 100-200 nm (Figure 2) as indicated by the maximum number of dpa at this depth. This indicates an inhomogeneous distribution of the ion energy along the path traversed by the Ar$^{9+}$ ions, which is inherent characteristic of damage caused by heavy ions in a medium and results into a distribution of defects generated across the depth of the samples. Figure 3 represents the damage depth profile for the samples irradiated with different fluences indicating the number of dpa as a function of depth in the sample. It is seen that number of dpa increases rapidly with the increase in the fluence. The increase is seen to be highest at the mean implantation depth of the ions in the alloy indicating maximum number of defects generated in this region. The inset in Figure 3 shows the number of dpa as a function of Ar$^{9+}$ ion fluence indicating the increase in the defect concentration with the increase in the fluence.

The defect depth profiling using Doppler broadening has been carried out to corroborate the damage profile obtained through simulation. It is seen that S-parameter for irradiated samples is higher as compared to unirradiated one upto ~ 15 keV positron implantation energy (depth ~ 450 nm). The high S-parameter indicates presence of defects in the alloys which are generated due to ion irradiation. At higher positron implantation energies (E> 15 keV), the S-parameter for irradiated samples approaches to the value corresponding to bulk of the unirradiated sample. This shows that irradiation by 315 keV Ar$^{9+}$ ion results in the generation of defects from the surface to ~ 450 nm depth of the sample. The S-parameter shows maximum at the depth ~ 100-200 nm indicating the region with maximum number of defects. This defect distribution is consistent with that obtained from SRIM simulations. Heavy ion irradiation leads to generation of different vacancy type defects viz. monovacancies, divacancies, vacancy clusters, vacancy loops etc. The trapping of positron in these defects results in increase in S-parameter compared to its value in defect free materials [18]. In addition to high value of S-parameter in irradiated samples, the S-parameter is seen to increase with the increase in fluence of the ions. The S-parameter profile at the lowest and highest fluencies is shown in Figure 4. The S-
parameter profiles for other fluences are seen to lie between these two extremes and are not shown here. The large increase in S-parameter for the sample irradiated at the lowest fluence compared to unirradiated one indicates the generation of large number of defects even at this fluence. On further increasing the fluence the increase in defect concentration is not so pronounced.

4. Conclusions

The defect depth profiling has been carried out in Zr-2.5Nb alloys irradiated by 315 keV Ar$^{9+}$ ions at different fluences using slow positron beam. The S-parameter profiles indicated the generation of defects from the surface to ~ 450 nm depth of the alloy. This region corresponds to the implantation depth of 315 keV Ar$^{9+}$ ions as calculated using SRIM simulation. The study has shown the increase in the number of defects with the increase in the fluence. The maximum damage due to irradiation is seen to be at a depth of 100-200 nm as shown by the maximum in S-parameter profile and consistent with the mean implantation of 315 keV Ar ions calculated using SRIM. The S-parameter profiles indicated the presence of large number of defects even in the sample irradiated at the lowest fluence.

References

[1] Mihalache M, Ionescu V, Meleg T and Pavelescu M, 2011 Rom. J. Phys. 56 952-962.
[2] Chowdhury P S, Mukherjee P, Gayathri N, Bhattacharya M, Chatterjee A, Bhrat P and Nambssan P M G, 2011 Indian Academy of Sci. 34 507–513.
[3] Mihalache M, Radu V, Ohai D and Palelescu, 2010 U.P.B. Sci. Bull., Series B 72.
[4] Nanker P P, Mangsulikar M D, Cleveland J and Shah B K, 2006 Asia-Pacific Conference on NDT. Auckland, New Zealand.
[5] Sinha R K, Sinha S K and Madhusoodanan K, 2008 J. Nucl. Mater 383 14-21.
[6] Jin H J and Kim T K, 2014 Annals of Nuclear Energy, 75 309–315.
[7] Li B S, Du Y Y, Wang Z G, Shen T L, Li Y F, Yao C F, and Sun R J, 2014 Nucl. Instrum. Meth in Physics Research B 337 21–26.
[8] Peng D Q, Bai X D and Pan F, 2007 Physica B 391 72-78.
[9] Peng D Q, Bai X D and Pan F, 2006 Vacuum 81 507-516.
[10] Gordo P M, Liszkay L , Kajcsó Z, Havancsák K, Skuratov V A, Ko'gel G, Sperr P, Egger W,
Lima A P and Marques M F F, 2008 App Surface Sci. 255 254-256.
[11] Was G S, 2007 Fundamentals of Radiation Materials Science: Metal and Alloy., Springer, Verlag Berlin Heidelberg.
[12] Liu X, Wang R, Ren A, Wu Y, Jiang J, Zhang C and Wang X, 2012 Radiation Physics and Chemistry 81 1586-1552.
[13] Qiu J, Ju X, Xin Y, Liu X, and Wang B Y, 2011 J. Nucl. Mater 411 20–24.
[14] Qiu J, Xin Y, Liu S, Wang Y L, Wang H B and Tang D, 2009 Nucl. Instrum. Meth. Phy.Res. B 267 3162–3165.
[15] Ziegler J F and Biersack J P, 2013 Nucl. Instr. And Meth. B 268, 1818-1823.
[16] Wan Q, Shu G, Wang R, Ding H, Peng X, Zhang Q and Lei J, 2012 Nucl. Instrum. Meth Phys. Research B 287 148–152.
[17] Krause-Rehberg R and Leipner H S, 1998 Positron Annihilation in Semiconductors: Defect Studie, Spinger-Verlag Berlin.
[18] Hautojarvi P and Vehanen A, 1979 Analytical Characterization of Aluminum, Steel, and Superalloys Spinger-Verlag Berlin.