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Xe Bubbles Formation in Materials for use in Nuclear Reactors Studied by Slow Positrons*

N. Djourelov, H. Marinov

Institute of Nuclear Research and Nuclear Energy, Bulg. Acad. Sci.,
72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

Abstract. Materials (UO_2 and ZrC) for use in nuclear reactors implanted with 800-keV Xe-ions were studied by means of slow positron beam (SPB) spectroscopy. Doppler broadening of annihilation gamma-line technique was used to measure the momentum density distribution (MDD) of annihilating positron-electron pairs in two sets of samples implantated at fluences of 1×10^{16} Xe cm^{-2}. The sensitivity of the MDD shape parameter S to discriminate single Xe atoms and Xe bubbles was discussed. Common trends in Xe bubbles formation as a result of the Xe fluence and/or post-implantation annealing in both materials were described. Positron spectroscopy on SPB was demonstrated to be an excellent complementary technique to secondary ion mass spectroscopy for studying the formation and evolution of Xe-bubbles, and Xe retention.

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1 Introduction

The accumulation of gaseous fission products in materials such as UO_2 and ZrC used in nuclear reactors is of great importance of their performance. Xenon makes up to 90% of the gaseous fission products. Due to its low solubility Xe segregates and forms bubbles [1]. Different experimental methods, such as EPMA, RBS, secondary ion mass spectroscopy (SIMS), X-ray absorption spectroscopy, and TEM, are applied to study nucleation and diffusion of Xe bubbles. Ion implantation is widely used to simulate the accumulation of fission products, however, the implantation is accompained by simultaneous formation of near surface defects. Positrons spectroscopy detects defects (vacancies, pores, gas bubbles) [2] with possibility for depth profiling by slow positron beam (SPB) [3]. In our previos works on UO_2 and zirconium oxycarbide the effects of post-polishing annealing, Xe-implantation, and post-implantation annealing by means of Doppler broadening of the annihilation gamma-line (DBAL) combined with SPB were reported [4, 5]. In the present work common trends considering

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the Xe bubbles formation in these materials by means of DBAL on SPB are summurized.

2 Experimental

$ZrC_{0.95}O_{0.05}$ powders were sintered in the form of pellets at 2225K under vacuum using spark plasma sintering. Depleted (0.3 at.% ^{235}U) UO_2 pellets were sintered at 1973K. Then the pellets were polished and annealed. These samples are used as references. Samples were implanted with 800-keV $^{136}Xe^{2+}$ to fluence of 1×10^{16} Xe cm^{-2} at INPL. SRIM [8] calculates the creation of 70 dpa (displacements per atom) with a distribution peaking at $R_d = 80$ nm. The maximum Xe concentration was calculated as being 1 at.% at projected range $R_{\mathrm{Xe}} = 148$ nm. Post-Xe-implantation annealing was also performed (Table 1).

Table 1. Post-Xe-implantation annealing conditions. Depth position Z_d and fwhm Z_w of the damaged region, S_d/S_{bulk} and L_{bulk} as obtained by VEPFIT.

label	material	post-Xe-impl. annealing	Z_d (nm)	Z_w (nm)	S_d/S_{bulk}	L_{bulk} (nm)
UI	UO_2	no	41 ± 6	68 ± 10	1.055	193 ± 26
UA	UO_2	16h 1673K	42 ± 2	56 ± 2	1.143	206 ± 13
ZI	$ZrC_{0.95}O_{0.05}$	no	55 ± 7	56 ± 4	1.084	112 ± 10
ZA	$ZrC_{0.95}O_{0.05}$	16h 2075K	27 ± 2	40 ± 6	1.172	130 ± 23

The $S(E_+)$ profiles were fitted by the VEPFIT program [6]. The samples were analyzed with a 3-contribution model: surface, bulk and damaged layer (the defect concentration of it is assumed to follow a Gaussian depth distribution, surface side truncated if neccesary). The third contribution was not used for the reference samples. The fit parameters are: the centroid, Z_d, and Z_w -the fwhm of the defects concentration depth profile, the S_d characteristic parameter for the defects, S_{bulk} and L_{bulk} (effective e^+ diffusion length in nm) for the bulk material. The mean e^+ depth was calculated from E_+ according to $z_m = (36/\rho)E_+^{1.62}$ nm, where ρ is the density in g.cm^{-3}.

3 Results and Discussion

The normalized parameter S/S_{bulk} depth profiles for reference, as-Xe-implanted and post-implantation annealed samples are shown in Figure 1 (a) and (b) respectively for $ZrC_{0.95}O_{0.05}$ and UO_2. It is seen that the well-annealed references profiles follow fairly well the unit line which indicates that these samples are close to defect free state, which is also supported by the long L_{bulk} (Table 1). The enhenced S/S_{bulk} at very low E_+ for UO_2 is typical for materials in which

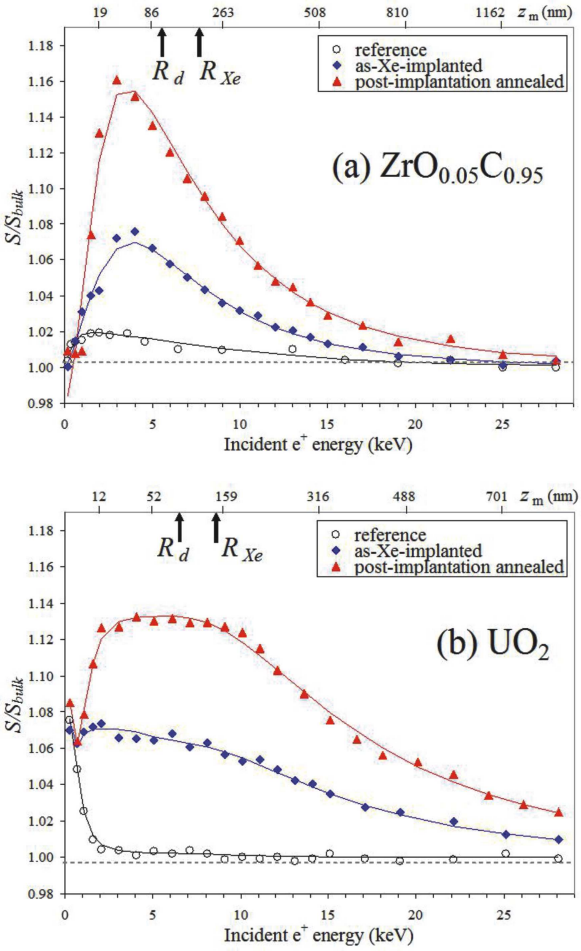

Figure 1. S/S_{bulk} as a function of the incident positron energy, E_+, for reference, as-Xe-implanted and post-implantation annealed samples for (a) $ZrC_{0.95}O_{0.05}$ and (b) UO_2. The curves are the best fits obtained by VEPFIT. The arrows show the simulated R_d and R_{Xe} ranges by SRIM.

positronium (Ps) is formed dominantly by surface electron capture and Ps formation occurs also if voids exist in these materials. For $ZrC_{0.95}O_{0.05}$ such enhencement is missing, indicating than Ps formation does not occur in voids. Electron momentum density distributions at various defects in $ZrC_{0.95}O_{0.05}$ have been computed to extract S changes when e^+ annihilate in defects decorated or not with Xe. The results showed that e^+ annihilation is sensitive only to the open-volume defects, but not to interstitial and substitutional Xe defects, and to va-

cancy clusters filled with Xe (Xe bubbles) [5]. S_d/S_{bulk} increases sharply with the defect open-volume and then saturates [5]. Values of 1.15 are reached for large open-volumes of 1 nm^3, however, such are not observed by SEM. The only way to explain characteristic S_d/S_{bulk} of 1.15 or higher is to suggest positronium (Ps) formation in Xe-bubbles accompanied with ortho-Ps into para-Ps conversion [7]. The mechanism is: the higher the Xe-concentration in the bubbles, the higher the conversion rate and more Ps annihilates from its para state via self annihilation (e^- and e^+ which comprise Ps annihilate with each other). The e^- from Ps is with low momentum contributing to high S values. For both studied materials Z_d is far less than R_{Xe} which is a consequence of the fact that positrons are sensitive only to open-volume defects and it is also less than R_d (see Figure 1 and Table 1). Such a "discrepancy" is observed in several studies mentioned as "$R_p/2$" effect and explained as a result from incomplete cancellation of interstitials by vacancies [9].

For a material with covalent bonds (ZrC) we have shown that positrons sensitivity is negligible to Xe interstitials caused by Xe-implantation [5]. The ionic bonds in UO_2 determine charged defects and e^+ is sensitive to negatively charged defects, i.e. related to uranium vacancies or oxygen interstitials, but not to neutral or positively charged defects. Thus, lack of sensitivity to Xe interstitials in UO_2 is natural to expect. We have shown that defect profiles as seen by e^+ do not differ even if the Xe concentration defers by factor of 10 [4]. The S_d/S_{bulk} values for ZI and UI (Table 1) are in agreement with the characterics values for single vacancies [4, 5]. We came to the conclusion that the implanted Xe remains as single atom precipitates. The post-Xe-implantation annealing (UA and ZA samples) leads to significant change in the profiles and to an increase of S_d/S_{bulk} (Table 1 and Figure 1). Thus the high S_d/S_{bulk} (1.143 and 1.172, respectively for UA and ZA) indicates Ps annihilation which occurs in Xe-bubbles. Therefore, the annealing is responsible for Xe clustering and Xe-bubbles formation. The influence of various factors (annealing temperature and duration, grain size, stoihiometry) on Xe-bubbles formation and retention have been extensively studied [4, 5]. The positrons are very sensitive to Xe caught in bubbles while the other methods like SIMS or RBS can detect the Xe content in the material matrix but do not allow any recognition if it is in form of bubbles.

4 Conclusions

Common features of DBAL on SPB studies of Xe-implanted $ZrC_{0.95}O_{0.05}$ and UO_2 have been discussed. The S parameter depth profiles analysed by VEPFIT comprise valuable information for the Xe state in the matrix. It has been demonstrated that positrons are sensitive to Xe-bubbles and can be used to study Xe-bubbles formation and evolution as result of different sample treatments.

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