STUDIES OF NUCLEAR REACTOR CORE MATERIALS BY POSITRON SPECTROSCOPY

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Abstract
The behavior of the materials used for designing nuclear reactor cores is necessary to be predicted under severe irradiation and high-temperature regimes with high accuracy. The accumulation of gaseous fission products is of great importance for the performance of the materials. The results were obtained by Doppler Broadening of the Annihilation Line (DBAL) technique using a Slow Positron Beam (SPB) of UO$_2$ and ZrC implanted by Xe-ions, in order to simulate in core conditions, at different fluences up to $1\times10^{16}$ Xe cm$^{-2}$. The sensitivity of the DBAL to discriminate single Xe atoms and Xe bubbles is discussed. Common trends in the formation of Xe bubbles as a result of the Xe fluence and/or post-implantation annealing of the studied materials were found. DBAL results on structural modification by ion irradiation in B$_4$C were also reported. The DBAL spectroscopy using an SPB is demonstrated to be an excellent complementary technique to SIMS, RBS, and TEM. A project to build an SPB laboratory at the Extreme Light Infrastructure - Nuclear Physics (ELI-NP) in Magurele (Ilfov, Romania) is presented. The Gamma Beam System at ELI-NP is a unique machine which will produce a brilliant gamma beam, with energy up to 19 MeV, by Compton backscattering of laser photons on electrons from a warm LINAC. Part of the time, the gamma beam will be used for pair production in a tungsten converter and, after moderation, slow positrons of high intensity ($>10^5$ s$^{-1}$) will be extracted to form an SPB. As a user dedicated facility, ELI-NP will provide access to scientists interested in condensed matter studies by slow positrons.

Keywords: slow positron, implantation, xenon, irradiation, nuclear reactor materials

Introduction
An important aim of the designing process of a nuclear reactor power plant is to ensure its safe operation. The core of any nuclear reactor is subjected to high irradiation due to the nuclear fission processes. The materials involved in the construction of a nuclear reactor core (e.g. pressure vessel, fuel cladding, and fuel pellets) are subjected to strong irradiation and work at a designed high temperature, usually few hundred degrees centigrade depending on the reactor type. In thermal transient regimes or accidental situations, their temperature can be significantly increased. The behaviour of the materials under these severe irradiation conditions and high-temperature regimes is necessary to be predicted with high accuracy.

Some of the fission products are gaseous (Xenon makes up to 90%) and along the fuel burnup process, they are accumulated in reactor core materials. An uncontrollable release of volatile fission products is undesirable. That is why, the processes of accumulation, segregation, diffusion and release of the gaseous fission products as a function of the thermal and irradiation conditions are comprehensively studied both theoretically and experimentally.

Along with the universal experimental methods - e.g. electron microscopy (TEM and SEM), Rutherford Backscattering Spectrometry (RBS), Secondary Ion Mass Spectroscopy (SIMS), and X-ray Absorption Spectroscopy (XAS) - the Positron Annihilation Spectroscopy (PAS) is able to provide valuable information on the structure of the studied samples.

Due to research laboratory restrictions and/or difficulties of accessing in-core irradiated samples, the ion implantation is widely used to simulate strong irradiation conditions and accumulation of fission products.

The results were obtained by Doppler Broadening of the Annihilation Line (DBAL), which is one of the PAS techniques, using a Slow Positron Beam (SPB) of UO$_2$ and ZrC implanted by Xe-ions at different fluences and subjected to thermal treatment. UO$_2$ is the usual fuel used in pressurized water nuclear reactors (PHWR) and ZrC is a candidate for fuel shielding material in the gas cooled fast reactors. The study also displays DBAL results on structural modifications by ion (C, Ar, and I) irradiation of B$_4$C, ceramics used as a neutron absorber in PHWRs and foreseen as material for the sodium-cooled fast reactor.
The paper also presents a project to build a PAS laboratory at the Extreme Light Infrastructure – Nuclear Physics (ELI-NP), as a user-dedicated facility, where some PAS instruments will be available for material study experiments.

**Experimental**

The materials under study UO$_2$, ZrC (ZrC$_{0.95}$O$_{0.05}$), and B$_4$C were prepared in a form of pellets by sintering under vacuum at a controllable high temperature. The samples were polished on one-side and then annealed prior further treatment. The ion implantations were performed by 0.8-MeV $^{136}$Xe$^{2+}$ on UO$_2$ and ZrC and by 0.6-MeV C$^+$ and 0.8-MeV Ar$^+$ on B$_4$C, and B$_4$C samples were irradiated by 100-MeV $^9$I. The maximum fluence in all cases was $\sim 10^{16}$cm$^{-2}$. Details on the preparation and treatment of the samples can be found in [1-3].

The DBAL spectroscopy is one of the PAS techniques. It is based on the fact that the positron injected into condensed matter quickly thermalizes before annihilation with an electron. That is why momentum of annihilating pair is dominated by the momentum of electron.

The longitudinal component of the momentum is transferred as energy shifts to the energy of the annihilation gamma rays. These shifts cause Doppler broadening of the annihilation gamma line. The energy spectrum of the gamma rays is registered by an HPGe detector.

The Doppler-broadened 511-keV peak, after subtraction of the stepwise background, can be characterized by shape parameters. The sharpness parameter, $S$, is defined as the ratio of the central region counts (|$\Delta | < E_s$, where $\Delta$ is the shift from 511 keV) over the integrated counts in the peak. The wings parameter, $W$, is defined as the ratio of the peak wings counts ($E_{in} < |\Delta | < E_{out}$) over the peak counts which is illustrated in Fig.1.

The choice of $E_s$, $E_{in}$ and $E_{out}$ (0.9, 3 and 8 keV, respectively, in this study) has some freedom which affects the absolute values for $S$ and $W$. In order to minimize the influence of this freedom, often the changes in the shape are presented as a ratio of the $S$ and $W$ parameters to $S_{bulk}$ and $W_{bulk}$ which are characteristic constants for the bulk of a reference sample. Due to the contribution of the electrons with low momentum, the $S$ parameter is sensitive to the number density of defects and also to the self-annihilation of positronium (Ps).

Positrons can be obtained from $\beta^+$ decay radioactive isotopes, pair production by gamma rays from nuclear reactions, or bremsstrahlung of high energy particles. The energy of these positrons ranges from a few hundred keV to a few ten MeV.

The SPB technique is based on moderation of a small fraction of the energetic positrons to a few eV [4]. The moderated positrons are separated from the energetic ones by an energy filter and electrostatically or magnetically guided to a target. Just before the implantation into the target, the moderated positrons are accelerated to a controllable desired energy, $E_+$, typically up to 30 keV.

The positron penetration is described by the probability density function $P(z,E_+) = 2(z/z_0)^2 \exp\left[-(z/z_0)^2\right]$, where $z_0 = 2 z_n / \sqrt{\pi}$ and $z_n = (36/\rho) E^{1/2}_+$ is the mean penetration depth, $E_+$ being expressed in keV and $\rho$ in g/cm$^3$ [5]. By controlling the energy of the slow positrons incident on the target and recording the energy of the annihilation gamma rays, the depth profiles, $S(E_+)$ and $W(E_+)$, can be obtained.

The DBAL measurements were performed on the direct current magnetically guided slow positron beam at INRNE-BAS, Sofia, with a Canberra high purity Ge detector (HPGe) with a resolution of 1.17 keV (fwhm) at the 514 keV line of $^{85}$Sr.

The VEPFIT program was used to fit the profiles of $S$ as a function of $E_+$ by a model function which describes the implantation and diffusion of positrons [6]. The chosen model function comprises 3 contributions: surface, bulk, and defects layer (of a Gaussian depth distribution, truncated on the surface side if necessary). The fit parameters are the centroid, $Z_d$, and $Z_m$ – the fwhm of the defects concentration depth profile, the $S_d$ characteristic parameter for the defects, $S_{bulk}$ and $L_{bulk}$ (effective positron diffusion length, in nm) for the material bulk.
Results and discussion

The preparation of reference samples includes polishing, which leads to creation of near surface defects such as vacancies and dislocations [7]. The annealing of the samples was proved to drastically decrease the content of the defects [1, 8].

Fig. 2 shows the normalized parameter $S/S_{\text{bulk}}$ depth profiles for polished and post-polishing annealed (from this point forward they will be listed as “reference”) UO$_2$ and ZrC samples. The post-polishing annealing was performed in vacuum conditions for 10h at 1000°C for UO$_2$, and for 10h at 1000°C plus 3h at 1400°C for ZrC. The reference profiles satisfactorily correspond with the unit line showing good depth structural uniformity. The long positron diffusion lengths $L_{\text{bulk}} \sim$ 200 and 120 nm (respectively for UO$_2$ and ZrC), obtained by the VEPFIT analysis, indicate that the defects created by the polishing are annealed. The high $S/S_{\text{bulk}}$ value for UO$_2$ (see Fig. 2b) at very low $E_+ < 2 \text{ keV}$ is due to Ps formation by surface electron capture, a process that does not occur for ZrC.

The $S/S_{\text{bulk}}$ depth profiles for the reference, as-implanted and post-implantation annealed ZrC and UO$_2$ are shown in Fig. 3. It can be seen that the Xe-implantation causes enhancement in $S/S_{\text{bulk}}$. This can be interpreted as a result of the creation of defects (voids and interstitials) due to the implantation.

The VEPFIT model reveals a defect layer which is represented by a Gaussian in Fig. 4 with $S_d/S_{\text{bulk}}=1.055$ and 1.084 for the as-implanted UO$_2$ and ZrC, respectively. The $S$ parameter for annihilation line of a positron trapped at defects decorated, or, lacking the presence of Xe, has been computed by the theoretical DFT calculation of the positron wave function [8]. It has been concluded that $S$ parameter due to positron annihilation is sensitive only to the open volume defects, but not to interstitial or substitutional Xe defects or voids filled with Xe (Xe bubbles). The last is confirmed by the relatively low $S_d/S_{\text{bulk}}=1.055$ and 1.084 values for the as-implanted samples.

The post-implantation annealing was performed in vacuum conditions for 16h at 1400°C and 1800°C for UO$_2$ and ZrC, respectively. As it can be seen in Fig. 3, $S/S_{\text{bulk}}$ increases as a result of the post-implantation annealing which seems to contradict the already discussed effect of the post-polishing annealing. The VEPFIT analysis of the experimental data of the post-implantation annealed UO$_2$ and ZrC has shown high values of $S_d/S_{\text{bulk}}$, respectively 1.143 and 1.172. It was strongly argued in our previous studies that the only possible explanation is the annihilation of Ps [8, 9]. The Xe determines the difference between the post-polishing and post-implanted annealing. Due to the high defect and Xe mobility at high temperature, the post-implantation annealing leads to formation of Xe bubbles which has been confirmed by TEM [10]. Positronium is formed in Xe bubbles and the Ps...
self-annihilation leads to high $S$ parameter. The self-annihilation probability is increased by the conversion of ortho-Ps into para-Ps, leading to further increase of $S$ [11]. In other words, the higher the Xe concentration in bubbles, the higher the conversion rate and more Ps annihilation from its para-state via self-annihilation ($e^- + e^+$ which comprise Ps annihilate with each other). Localized in bubble, Ps has a low momentum contributing to high $S$.

SRIM simulates the ion interaction with matter [12]. The depth profiles of the displacements (dpa) and Xe content, as obtained by SRIM, for UO$_2$ and ZrC implanted to fluence 10$^{16}$ cm$^{-2}$ by 800-keV $^{136}$Xe$^{2+}$ are shown in Fig. 4.

The defects depth profile found by VEPFIT are closer to the surface than the dpa and Xe distributions. The first reason is the insensitivity of $S$ to annihilation of positron trapped at Xe defects. The second reason is most likely the incomplete cancellation of interstitials by vacancies, known as the "R$_{p/2}$" effect [13, 14].

The distribution of implanted Xe in a sample can be obtained by RBS and/or SIMS [1, 2, 8,9]. This information can shed light on the processes of the release of Xe out of the studied samples due to diffusion; however, the processes of Xe bubble formation are intangible. Information on bubble size and density can be obtained by TEM [10, 15]. The influence of the temperature and the duration of annealing, grain size, stoichiometry, impurities on Xe bubbles formation and Xe retention have been extensively studied [1, 2, 8]. The DBAL on SPB appears to be complementary to RBS, SIMS and TEM techniques by which the processes of Xe bubble formation and dissolution can be monitored because positrons via formation of Ps are very sensitive to Xe caught in bubbles.

Fig. 4. Concentration of Xe and displacement per atom as a function of the depth for ZrC and UO$_2$ implanted with $^{136}$Xe$^{2+}$ at fluence of 10$^{16}$ Xe/cm$^2$ computed by SRIM.

The $S$ parameter profiles for a reference B$_4$C and B$_4$C after implantation by C$^+$, Ar$^+$ and I$^+$ are shown in Fig. 5a. The post-polishing annealing was performed in vacuum conditions for 10h at 1000°C plus 3h at 1400°C [3]. It has to be underlined that bulk properties of the B$_4$C samples as seen by positrons are very sensitive to the annealing conditions. This observation was found by a preliminary study (not published) of non-irradiated samples with different annealing history.

For a homogenous sample, the behavior of $S(E_\text{f})$ profile should resemble that of ZrC or UO$_2$ shown in Fig. 2, i.e. to start at $E_\text{f} = 0$ keV at some characteristic for the surface point and then around 4-6 keV levels off at the $S_{\text{bulk}}$ for the higher $E_\text{f}$. Obviously, the situation seen in Fig. 5a is different from the one described above. Consequently, the bulk structure of the studied B$_4$C samples is not homogeneous. Most likely, this is due to a small amount of structural oxygen. The closer it is to the surface, the higher the content of structural oxygen. The oxygen in B-C-O structures is partly negatively charged. It traps positrons and this trapping center possesses a higher specific $S$ parameter compared to a defect free B$_4$C.

The inhomogeneity in the reference makes the VEPFIT analysis of the B$_4$C samples very complicated.

Fig. 5. (a) $S$ as a function of the incident positron energy, $E_\text{f}$, for B$_4$C samples. The errors are of the order of the marker sizes. The lines are fits obtained by VEPFIT (b) difference $S(E_\text{f}) - S_{\text{ref}}(E_\text{f})$ for B$_4$C samples. The legend shows the type of the applied implantation. The secondary x-axis shows the correspondence to the mean positron implantation depth, $z_{\text{m}}$. 

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One way of performing a qualitative analysis is to check the differences in \( S \) parameters from the reference sample as shown in Fig. 5b. The plotted data carry information on the defects (created or annealed) during the implantation, irradiation and annealing treatments.

Further quantitative analysis of this data by VEPFIT is not possible due to the subtraction of \( S_{\text{ref}} \) thus masking the positron diffusion lengths. However, a rough estimation of the defects profile was still possible [3]. The estimated defects profiles for the implanted by \( \text{Ar}^+ \) and \( \text{C}^+ \) samples obtained by analysis of the data plotted in Fig. 5b, confirmed that positrons are not sensitive to interstitial defects if these defects are neutral or positively charged. For \( \text{C} \) implanted sample defects at the projection range of the implanted \( \text{C} \) were not detected. This was interpreted due to the fact that \( \text{C} \) is a structural element of \( \text{B}_4\text{C} \). The dpa results in a creation of vacancies. However, these vacancies are efficiently compensated by implanted \( \text{C} \) and solely vacancies close to the surface survive.

The 100-MeV \( \text{I}^{9+} \) penetrate much more deeply (11 \( \mu \)m) than the 30-keV positrons. The positrons probe a sample layer of \( \sim 2 \) \( \mu \)m. As seen from the data shown in Fig. 5b, the RT irradiation resulted in higher \( S \) parameter compared to the reference. This means that positron traps are created and these traps are most likely to be vacancies. By maintaining the sample temperature during 1-irradiation at 800°C, the vacancies created by the irradiation are successfully annealed.

The heat-treatment also functions by improving the bulk structure of the sample, as seen from the negative difference with the reference sample.

One of the advanced machines at ELI-NP will be the Gamma Beam System (GBS). The GBS will provide a brilliant gamma beam by Compton backscattering of laser photons on electrons from a warm LINAC. Fast positrons can be produced by the interaction of the gammas with a special Converter/Moderator Assembly (CMA) made of thin tungsten foils. The fast positrons will be moderated and then slow positrons will be guided to PAS spectrometers. The simulations, based on the expected gammas intensity \( (2.4\times10^{10} \text{ s}^{-1}) \) of low-energy beam (up to 3.5 MeV), showed that the slow positron intensity of \( 1\times10^6 \text{ s}^{-1} \) is achievable when the CMA foils are used as moderators [16]. It was also found that the moderation technique by neon, frozen directly on the CMA foils, is applicable [17]. Due to high moderation efficiency of this technique, the slow positron intensity can reach \( 10^7 \text{ s}^{-1} \).

The planned layout of the PAS laboratory is shown in Fig. 6. Some details on the techniques, namely: Positron Annihilation Lifetime Spectroscopy (PALS), Coincidence Doppler Broadening Spectroscopy (CDBS, note that this is a modification of DBAL), and Positron annihilation initiated Auger Electron Spectroscopy (PAES), can be found in [16]. At ELI-NP as a user-dedicated facility, these few PAS instruments will be available for material study experiments.

**Conclusions**

The DBAL technique and the depth profiling by SPB have been introduced. The paper summarized DBAL coupled with SPB studies on \( \text{ZrC} \), \( \text{UO}_2 \) and \( \text{B}_4\text{C} \) ion-implanted to high fluence in order to simulate strong irradiation conditions at nuclear reactor cores.

The high sensitivity of the positrons to defects has been demonstrated. The formation of \( \text{Ps} \) in bubbles allows for the monitoring of bubble evolution as a function of thermal and irradiation treatments. The valuable structural information, which can be obtained by slow positrons, makes PAS an excellent complementary technique to SIMS, RBS, and TEM.

The planned SPB laboratory at ELI-NP will provide a new opportunity for experiments in material science by the planned PAS instruments.

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