Irradiation induced damage of the reactor pressure vessel steels studied by positron annihilation lifetime techniques

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Abstract
This paper presents a comparison of commercially used German and Russian reactor pressure vessel steels from the positron annihilation spectroscopy (PAS) point of view, having in mind knowledge obtained also from other techniques from the last decades. The second generation of Russian RPV steels seems to be fully comparable with German steels and their quality allows prolongation of NPP operating lifetime over projected 40 years. The embrittlement of CrMoV steels is relatively low due to effect of higher temperatures which implies partial in-situ annealing of primary microstructural point defects and therefore delays the degradation processes caused by neutron irradiation. PAS techniques can be effectively applied for evaluation of microstructural changes caused by extreme external loads (characterized by high dpa values) by proton implantation, with aim to simulate irradiation and for the evaluation of the effectiveness of post-irradiation thermal treatments. We used our actual and previous results, collected during last 20 years from measurements of different RPV-steels in “as received”, irradiated and post-irradiation annealed state and compare them with the aim to contribute to general knowledge based on experimental PAS data. Actual results from irradiated German and Russian steels confirmed that no large voids or vacancy clusters were formed at defined irradiation conditions stated according to the real operational conditions at nuclear power plants. This indicate the fact that vacancy type defects bear hardly any responsibility for radiation-induced hardening and embrittlement of reactor pressure vessel steels and does not affect significantly the long-term operation of nuclear power plants from safety point of view.

Keywords: nuclear safety, reactor pressure vessel steels, positron annihilation spectroscopy, atomic force microscopy
1. INTRODUCTION

The nuclear reactor pressure vessel (RPV) is a key component if considering the safety of the nuclear power plant (NPP) operation and possible lifetime prolongation. It is necessary to ensure the integrity of the reactor pressure vessel during normal and abnormal operating conditions. The ability of RPV to resist brittle fracture is of particular importance, especially under the loss of coolant accident (LOCA) conditions. The degradation of RPV steel is a complicated process depending on many factors (thermal and radiation treatment, chemical composition, manufacturing conditions, ageing, microstructure of the RPV material, operational history, etc.). These topics were studied in many comprehensive works [1-7].

In this paper we focus on the comparison of German and Russian RPV-steels from the positron annihilation spectroscopy (PAS) point of view, having in mind knowledge obtained from other techniques from the past.

Undoubtedly, the neutron embrittlement of RPV steels was a serious problem in Russian types of nuclear reactors (WWER-440, first generation V-230). It was caused mostly due to the narrower gap between the outside surface of the core barrel and the inside surface of the RPV as compared to Western RPV’s. The relatively small diameter (Φ_{in} = 3542 mm in the case of WWER-440/V-230 type) facilitated transport and installation of the RPV, but, on the other hand, the neutron fluxes and consequently neutron fluencies on the RPV wall were generally several times higher than in other equivalent types in western Europe. This influence of neutron flux (even neutrons of energy over 0.5 MeV) on RPV embrittlement is much more impressive than contributions from a coolant temperature or an operational pressure in the primary circuit.

According to previous works [1-6] it seems to be generally accepted that (even in those Western types of RPV steels containing more than 0.1 wt. % of Cu) Cu-rich and, depending on P content, P-rich precipitates play a dominant role in radiation induced embrittlement. In the case of WWER-type RPV steels, several studies [2,7,11,13,14] have suggested that carbide formation is an important additional microstructural mechanism.

Due to long-term ageing and external loads including irradiation, the development of the fine scale defects occurs, which impede dislocation motion under applied stress. This process is the driving force for irradiation embrittlement. It leads to mechanical properties degradation which can result into the partial loss of plasticity and increase of the probability of brittle fracture [2,5,6]. Defects are formed from vacancies and interstitials created in collision cascaded processes. Those point defects surviving the cascades, migrate freely through the crystal lattice, interact with each other and with solute atoms in the matrix and also with dislocation substructure and precipitates. These irradiation-induced diffusion processes result into the formation of point defect clusters; dislocation loops and precipitates [8]. Under the influence of temperature, the initial state of damage changes as a result of thermally activated migration of point defects, which is accompanied by their mutual recombination, annihilation on sinks and formation or dissociation of pile-ups [9-11].

These changes in the microstructure can be basically studied using several methods. Material properties of the steels and influence of thermal and neutron treatment on these properties are routinely investigated by macroscopic methods such as Charpy V-notch and tensile tests [1,2,4,5,11]. A number of semi-empirical laws, based on macroscopic data, have been established, but, unfortunately, these laws are not completely consistent with all measured data and do not provide the desired accuracy. Therefore, many
additional test methods, summarised in [12] have been developed to unravel the complex microscopic mechanisms responsible for RPV steel embrittlement. The possible contribution of techniques as Mössbauer spectroscopy (MS), positron annihilation spectroscopy (PAS) and transmission electron microscopy (TEM) were analysed in [13-17].
2. EXPERIMENTAL

2.1. Specimens materials

The high quality of RPV-steels is the basic precondition for safe use of nuclear reactors. The operation conditions of WWERs are generally characterized by the following parameters [18]:

- no less than 40 years of service life or $2.10^5$ h of operation at normal power,
- up to 30 planned shutdowns,
- coolant working pressure at the core outlet of 10-16 MPa,
- coolant temperature at steady operation of 250 to 289°C at the inlet and 269 to 324°C at the outlet,
- pressure vessel temperature (considering heating due to $\gamma$ radiation) up to 300°C,
- a maximum neutron flux density at the level of the core center of around $10^{11}\text{n/(s cm}^2\text{)}$ with respect to neutrons with energy greater than 0.5 MeV.

Our PAS studies were focused on Russian VVER-440 steels. Content of impurities and alloying elements for studied RPV steels from V-230 reactor base and weld metals is shown in Table 1. These specimens were later irradiated (1995-1998) in the framework of the Slovak surveillance specimens program in the NPP Jaslovské Bohunice. Neutron doses are shown in Table 2.

<table>
<thead>
<tr>
<th>Code</th>
<th>Type of steel</th>
<th>Contents of alloying elements in RPV specimens (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C   Si  Mn  Mo  Ni  Cr  Cu  P  S  V  Co  Total</td>
</tr>
<tr>
<td>ZM</td>
<td>Base metal WWER-440</td>
<td>15Kh2MFA</td>
</tr>
<tr>
<td>ZK</td>
<td>Weld metal WWER-440</td>
<td>Sv10KhMFT</td>
</tr>
</tbody>
</table>

Table 1 – The chemical composition of the studied RPV-steel specimens.

<table>
<thead>
<tr>
<th>Material</th>
<th>Code of specimen</th>
<th>Time of irradi. [eff. days]</th>
<th>Neutron Fluency [m$^{-2}$]</th>
<th>Total activity [kBq]</th>
<th>Thickness of specimen [$\mu$m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Base material – non-irradiated</td>
<td>ZAE-ZM</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>2 Base material – 1 year irradiated</td>
<td>ZM1Y</td>
<td>280.8</td>
<td>7.81E23</td>
<td>62</td>
<td>50</td>
</tr>
<tr>
<td>3 Base material – 2 year irradiated</td>
<td>ZM2Y</td>
<td>578.5</td>
<td>1.64E24</td>
<td>109</td>
<td>40</td>
</tr>
<tr>
<td>4 Base material – 3 year irradiated</td>
<td>ZM3Y</td>
<td>894.3</td>
<td>2.54E24</td>
<td>89</td>
<td>30</td>
</tr>
<tr>
<td>5 Weld – non-irradiated</td>
<td>ZBG-ZK</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>55</td>
</tr>
<tr>
<td>6 Weld – 1 year irradiated</td>
<td>ZK1Y</td>
<td>280.8</td>
<td>7.81E23</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>7 Weld – 2 years irradiated</td>
<td>ZK2Y</td>
<td>578.5</td>
<td>1.64E24</td>
<td>48</td>
<td>25</td>
</tr>
<tr>
<td>8 Weld – 3 years irradiated</td>
<td>ZK3Y</td>
<td>894.3</td>
<td>2.54E24</td>
<td>110</td>
<td>47</td>
</tr>
</tbody>
</table>

Table 2 – Specimens irradiated at NPP Bohunice-Slovakia.
The chemical composition of the studied non-irradiated German steels is listed in Table 3. These steels have been comprehensively studied in the research programs CARISMA [19] and CARINA [20]. All specimens belong to commercial reactor pressure vessel steels and vary mostly in the content of Cu, P and Ni.

<table>
<thead>
<tr>
<th>Material</th>
<th>Project</th>
<th>German PWR Generation</th>
<th>Project Code</th>
<th>Cu [wt.%]</th>
<th>P [wt.%]</th>
<th>Ni [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20MnMoNi5-5 JSW</td>
<td>CARISMA</td>
<td>4 (Konvoi)</td>
<td>P141 BM</td>
<td>0.05</td>
<td>0.01</td>
<td>0.79</td>
</tr>
<tr>
<td>22NiMoCr3-7 Klöckner</td>
<td>CARISMA</td>
<td>1-2</td>
<td>P7 BM</td>
<td>0.12</td>
<td>0.02</td>
<td>0.97</td>
</tr>
<tr>
<td>22NiMoCr3-7 JSW</td>
<td>CARISMA</td>
<td>3-4</td>
<td>P147 BM</td>
<td>0.05</td>
<td>0.01</td>
<td>0.84</td>
</tr>
<tr>
<td>S3NiMo1/OP 41 TT UP, GHH</td>
<td>CARISMA</td>
<td>4 (Konvoi)</td>
<td>P141 WM</td>
<td>0.03</td>
<td>0.02</td>
<td>1.01</td>
</tr>
<tr>
<td>NiCrMo1 UP(modified)/LW320, LW330</td>
<td>CARISMA /CARINA</td>
<td>1</td>
<td>P370 WM</td>
<td>0.22</td>
<td>0.02</td>
<td>1.11</td>
</tr>
<tr>
<td>22NiMoCr3-7 JSW</td>
<td>CARINA</td>
<td>3</td>
<td>P150 BM</td>
<td>0.05</td>
<td>0.008</td>
<td>0.83</td>
</tr>
<tr>
<td>22NiMoCr3-7 Klöckner</td>
<td>CARINA</td>
<td>1-2</td>
<td>P151 BM</td>
<td>0.09</td>
<td>0.007</td>
<td>0.97</td>
</tr>
<tr>
<td>Molytherme Electrode Sulzer</td>
<td>CARINA</td>
<td>1</td>
<td>P152 WM</td>
<td>0.03</td>
<td>0.015</td>
<td>0.08</td>
</tr>
</tbody>
</table>

BM – base metal  
WM – weld metal

Neutron irradiated specimens (Tab.4) of western CARINA/CARISMA reactor steels were delivered to our Institute in September 2012. Due to the radioactivity of mentioned neutron irradiated specimen, the special safety requirements for transport of specimens from AREVA NP GmbH Erlangen (Germany) to the Institute of Nuclear and Physical Engineering, FEI STU Bratislava (Slovakia) were needed in form of licensed transport using marked barrel to avoid any influence of activated specimens on outer environment (Fig. 1). Activity of radioisotope $^{60}$Co in irradiated specimens to the date 24.01.2013 is shown in Table 5. Presence of other radioisotopes was not detected.
Specimens were cleaned in an ultrasonic bath and their surface was checked by Atomic Force Microscopy (AFM) analysis. The surface of P370WM specimen is presented in Fig. 2. The size of the scanned area was $10 \times 10 \, \mu m^2$. Larger scratches are about 31 nm deep and 271 nm wide. Smaller scratches are $\sim$10 nm deep and 127 nm wide.

![AFM micrograph of a polished P370WM steel specimen. The size of the scanned area was $10 \times 10 \, \mu m^2$. Higher protrusions that are mapped in white were truncated. Average surface roughness $R_a = 0.006 \, \mu m$.](image)

Fig. 1 – Transportation barrel for neutron irradiated specimens. The German SG in the label of specimen means weld metal (WM) in English.
Table 4 – Chemical composition of RPV steel specimens selected for PAS studies.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturing Type</th>
<th>Place of analysis</th>
<th>C [%]</th>
<th>Si [%]</th>
<th>Mn [%]</th>
<th>P [%]</th>
<th>S [%]</th>
<th>Cr [%]</th>
<th>Mo [%]</th>
<th>Ni [%]</th>
<th>Cu [%]</th>
<th>V [%]</th>
<th>Ta [%]</th>
<th>Co [%]</th>
<th>Al [%]</th>
<th>Sn [%]</th>
<th>As [%]</th>
<th>Sb [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P16 WM</td>
<td>Submerged arc welding</td>
<td>Mean values</td>
<td>0.05</td>
<td>0.15</td>
<td>1.14</td>
<td>0.012</td>
<td>0.007</td>
<td>0.07</td>
<td>0.46</td>
<td>1.69</td>
<td>0.08</td>
<td>0.004</td>
<td>0.002</td>
<td>0.024</td>
<td>0.022</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P370 WM</td>
<td>Submerged arc welding</td>
<td>Mean values</td>
<td>0.08</td>
<td>0.15</td>
<td>1.14</td>
<td>0.015</td>
<td>0.013</td>
<td>0.74</td>
<td>0.60</td>
<td>1.11</td>
<td>0.22</td>
<td>0.010</td>
<td>-</td>
<td>-</td>
<td>0.013</td>
<td>0.013</td>
<td>0.014</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5 – Activities of $^{60}$Co in neutron irradiated specimens to the date of 24.01.2013.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>P370WM-D77</th>
<th>P370WM-D161</th>
<th>P16WM-S103</th>
<th>P16WM-GS67</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity [kBq]</td>
<td>12.85</td>
<td>97.31</td>
<td>40.09</td>
<td>161.46</td>
</tr>
</tbody>
</table>
2.2 Experimental technique

Positron annihilation spectroscopy (PAS) is used in RPV characterization since 80-ties. Its techniques were proved as very valuable to get insight on the population of vacancy-type defects that form under irradiation. The special advantage is that these defects cannot be seen by the electron microscope, so positron annihilation can, in this sense, provide a unique type of information for microstructural studies of selected materials before and after external treatment (irradiation, annealing, ...). Vacancies belong by definition to the class of defects that fall with the general name of “matrix damage”, which is one of the three damage components, commonly considered responsible for radiation-induced embrittlement of RPV steels. Thus, the most obvious use of PAS should be to try to determine quantitatively the main characteristics of the vacancy population after irradiation (density and size of clusters, possible association with specific solute elements, ...), in order to establish whether or not these defects might have a role in neutron embrittlement.

Positron annihilation spectroscopy (PAS) is a non-destructive technique based on positron ($e^+$) implantation from radioactive source. The positron produced by $\beta^+$ decay generally thermalizes (~3 ps) and diffuses (~100 ps) in the specimen. Afterwards $e^+$ is trapped in a defect (vacancy type) and after some time, depending on the defect size and electron density, recombines with an electron and annihilates with emission of two $\gamma$-photons. The positron lifetimes and corresponding intensities are important measured results for the determination of type and size of the vacancy-type defects.

Measurement of neutron irradiated RPV steels by positron annihilation spectroscopy can be influenced by the $^{60}$Co, which was induced in the steels during irradiation. Nucleus of the $^{60}$Co emits two gamma photons with energy of 1174 keV and 1332 keV and these photons can be detected by the start or the stop detector and the false peak can appear.

Several approaches to tackle the problem of the $^{60}$Co prompt-peak interference with the physical part of the positron lifetime spectra have been considered so far [21]. Besides the pulsed low energy positron systems (PLEPS) application, where the amount of radioactive specimen is drastically reduced to foil of about 30 micrometer [15], the other acceptable solution seems to be a triple-coincidence method using a $^{22}$Na-source [21,22]. In this case three $\gamma$-rays – one with energy of 1274 keV and two with energy of 511 keV – accompany each event of positron annihilation, while only two $\gamma$-rays result from the $^{60}$Co decay. Therefore, three detectors working in triple coincidence mode can assure that one event of positron annihilation is detected with eliminated $^{60}$Co photons influence.

However, compared to conventional two-detector systems, the requirement of the triple coincidence reduces drastically the rate of accumulation of positron lifetime spectra [22] and in comparison, PLEPS reduces the measuring time by a factor of 500 and enables in addition the estimation of the defect concentration [15,21]. However, due to reconstruction of technical systems at FRM-II reactor in Garching, this system was not available in 2012. Therefore, we had to adapt our set-up for requested measurements of radioactive reactor pressure vessel steels to improved 3-detector set-up.

Measurement of positron lifetime was realized in air conditioned unit in order to sustain stability and efficiency of measuring equipment. Measurements of neutron irradiated specimens can be performed only with three detector set-up (Fig.3).
Currently, the “fast-fast” setup is used with decreased number of devices in measuring equipment. This increases accuracy and stability of measurement. Scintillating detectors are of Barium-Fluoride (BaF$_2$) type. A discriminator is used for reduction of noise and forms standard time impulses. A differential discriminator (single channel analyzer - SCA) ensures reception of 1.274 and 0.511 MeV $\gamma$-photons only in particular channel, by setting up corresponding energetic scale for incoming signals [21].

As the source of positrons in positron annihilation lifetime measurements (PALS) was used $^{22}$Na in solution of NaCl instilled between 7 µm kapton foils. These foils are tilled by specimens in so called “sandwich set-up”. Source contribution after reference fit of pure silicon was at level of about 24 %. This includes the annihilation in source, kapton foils and “in-flight” annihilation. Lifetimes of the silicon and kapton foils are well known and were fixed at 222 ps and 382 ps, respectively. Intensity of annihilation in air (in-flight) was at level of 1-2.5 %.

Positron annihilation lifetime spectra were analyzed using software LT version 9 [24]. The software was created in DELPHI development environment and is fully compatible with Windows operating system.
2.3 PALS results from non-irradiated German RPV-steels

Non-irradiated specimens from German RPV-steels in form of slides 10x10x0.2mm (two pieces from each material) were delivered from AREVA NP Erlangen (Germany) and used in this “as received” form for positron annihilation lifetime (PALS) investigations. These specimens were mirror-polished by 1 µm diamond paste and further processed at the Institute of Nuclear and Physical Engineering, Slovak University of Technology (STU) in Bratislava.

The positron annihilation lifetime spectroscopy (PALS) set-up [22] was used for the current (2011-2012) study of reactor steels from the CARINA/CARISMA programs. The results are presented firstly in form of positron mean lifetimes (Fig. 4).

Mean positron lifetimes including all the positron lifetime components were reaching values from about 150 to 170 ps. These values are typical for this type of reactor steels and were confirmed also by several experimental works in the past [11,13,25]. Differences can be assigned to the small variation in chemical composition as well as ageing processes of specimens. After annealing in vacuum at 450 °C these values decrease to about 125-130 ps. The point defects are almost disappearing and the steel microstructure is close to ideal state. For more details and comparison of different annealed reactors steels see [13].

![Fig. 4 - Mean positron lifetimes in studied CARINA/CARISMA steels. Uncertainties of values are less than 2 ps.](image)

The final spectra were later decomposed according to the standard trapping model (STM) [21,26] into three components, where the lifetime $\tau_1$ can be assigned to positron lifetime in bulk; $\tau_2$- positron lifetime in defects (vacancy clusters); $\tau_3$- positron lifetime in air (not in the specimen). Each component has its intensity expressed by $I_1$, $I_2$, $I_3$. Generally, the increase of positron lifetime $\tau_2$ means increase of the size of the vacancy
type defects and increase of I$_2$ means an increase of the concentration of these types of defects. Due to well-known origin and relative small contribution (about 2%) of the third component we neglect it in our considerations.

Fig. 5 shows the positron lifetimes $\tau_1$ and $\tau_2$. First component $\tau_1$ could be assigned to the bulk of the material but varying positron lifetimes in this case could indicate presence of shallow traps which are created by the superposition of the reduced bulk component [21, 26] and another component which can be expressed by a bit higher values of positron lifetimes containing partial dislocations [42]. Intensities of the first component $\tau_1$ are, with some deviation, reaching levels of about 70% (Fig. 6).

Positron lifetimes in defects $\tau_2$ could be according to the results, where the $\tau_2$ reached the level of about 190 - 200 ps, assigned to the combination of screw and edge dislocations and vacancy type defects, particularly and most probably to the di-vacancies. In the case of P141 WM, there was measured a bit higher value of $\tau_2$, reaching 237 ps. In this case, 3-4 of agglomerated vacancies can occur as dominant. The intensities corresponding to the defects (Fig. 6) have reached values of about 20% (in the case of P141 WM) to about 30% and within the deviations there were no major differences observed. Increased levels of I$_2$ can be found in specimens P141 BM, P151 BM and P370 WM (up to 50%).

![Graph showing positron lifetimes $\tau_1$ and $\tau_2$ for selected CARINA/CARISMA steels.](image)

$\text{Fig. 5 - Positron lifetimes } \tau_1 \text{ and } \tau_2 \text{ for selected CARINA/CARISMA steels.}$
The small defects present in the specimens come from the fabrication process. They can be identified as a mixture of dislocation and mono-, di- and 3-vacancies according to their measured positron lifetimes [25].

The total concentration of these defects can be reduced in annealing process. The vacancies are released at temperature over 300 °C and diffuse to dislocations, grain boundaries or become bound to non-iron constituents. The measured lifetimes of the annealed but non-irradiated specimens indicate that the small vacancy clusters are not longer present but dislocations remain in the specimen.

According to the lifetime values from our measurements performed on CARINA/CARISMA RPV-steels and theory published in [26,30], the total trapping rate $\kappa$ in ns$^{-1}$ as well as the total defect concentration $c_d$ (the same values but in ppm) are on the level of about 2 ppm. According to our previous experiences reported in [31], these values will slightly increase to about 20 ppm for both base and weld materials as a function of the irradiation dose during the expected 40-years operating time.

We would like to mention that the small-angle neutron scattering study was performed at neutron-irradiated material of specimen P370 WM [32]. The experiment was focused on the influence of neutron flux and on the formation of irradiation-induced clusters at fixed fluence. There was observed a pronounced effect of neutron flux on cluster size, whereas the total volume fraction of irradiation-induced clusters is insensitive to the level of flux. Despite of the observed flux effect on cluster size, both yield stress increase and transition temperature shift turned out to be independent on the flux. This was in agreement with the volume fraction of irradiation-induced clusters being insensitive to the level of flux.

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**Fig. 6 - Intensities $I_1$ and $I_2$ corresponding to the positron lifetimes.**
2.4 PALS results from irradiated Russian RPV-steels

The non-irradiated specimens of Russian RPV-steels in form of two pairs of slabs 10x10x0.3 mm were studied in the framework of the Slovak surveillance specimens program and now measured again after 15 years of storage. Results were almost identical. PAS measurement using conventional lifetime technique was performed in PAS Laboratory at STU Bratislava. Results are summarized in Table 6.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>τ₁ [ps]</th>
<th>Δτ₁ [ps]</th>
<th>I₁ [%]</th>
<th>ΔI₁ [%]</th>
<th>τ₂ [ps]</th>
<th>Δτ₂ [ps]</th>
<th>I₂ [%]</th>
<th>ΔI₂ [%]</th>
<th>τ₃ [ps]</th>
<th>Δτ₃ [ps]</th>
<th>I₃ [%]</th>
<th>ΔI₃ [%]</th>
<th>MLT</th>
<th>Fit Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZAE-ZM</td>
<td>107</td>
<td>1</td>
<td>29.90</td>
<td>2.10</td>
<td>174</td>
<td>3</td>
<td>67.70</td>
<td>2.10</td>
<td>848</td>
<td>66</td>
<td>2.42</td>
<td>0.26</td>
<td>170.0</td>
<td>1.09</td>
</tr>
<tr>
<td>ZBG-ZK</td>
<td>105</td>
<td>2</td>
<td>41.40</td>
<td>1.20</td>
<td>186</td>
<td>4</td>
<td>56.60</td>
<td>1.20</td>
<td>1000</td>
<td>97</td>
<td>1.92</td>
<td>0.21</td>
<td>168.2</td>
<td>0.95</td>
</tr>
</tbody>
</table>

There are small differences between both types of steels from the PAS lifetime measurement point of view. The τ₁ values can be assigned to bulk or more probably to shallow traps [42] and τ₂ values to positron lifetime in small defects like mono- or di-vacancies or dislocations. We will neglect τ₃ value (in-flight annihilation) also due to very low intensity [34].

According to the results from our comprehensive positron annihilation lifetime measurements performed between 2000-2010 on different irradiated Russian RPV-steels, the total trapping rate κ in ns⁻¹ as well as the total defect concentration c₃ (the same values but in ppm) increases slightly for both base and weld materials as a function of the irradiation dose (see Fig.7).

Fig.7 - The total trapping rate κ versus Hollomon-Jaffe’s parameter at RPV specimens from WWR-440 base (ZM) and weld (ZK) alloys after 1, 2 and 3 years residence in reactor irradiation chambers (neutron fluency in the range from 7.8 10²³ m⁻² to 2.5 10²⁴ m⁻²). The lower limits for κ, as derived from saturation trapping according to the Standard trapping model [26] is 10 ns⁻¹.
The WWER-440 weld material (ZK, Sv10KhMFT) seems to be less sensitive to the changes caused by neutron-irradiation or by post-irradiation heat treatment than the base material (15Kh2MFA) [31]. Nevertheless, the differences in the positron trapping rate \( \kappa \) are not too large. It seems reasonable to relate the observed trapping rates with the ones which have been derived for trapping into precipitated carbides from electron microscopic images [35]. Accordingly, in the type of steel 15Kh2MFA the trapping rate into chromium carbides (\( \text{Cr}_7\text{C}_3, \text{Cr}_{23}\text{C}_6 \)) is predicted as \( \kappa_{\text{Cr}}=1.8\times10^8 \text{s}^{-1} \) and into vanadium carbides as \( \kappa_{\text{VC}}=2.2\times10^{10} \text{s}^{-1} \). Thus precipitated vanadium carbides could be responsible for the observed trapping rates. But on the other hand, as shown by calculations [36], positrons experience a repulsive potential from carbides embedded in an iron matrix. Thus only the defects at the iron-carbide interface could provide an acceptable trapping site for positrons.

### 2.5 PALS results from irradiated German RPV-steels

The CARISMA materials were irradiated in a German test reactor, the VAK (Versuchsatomkraftwerk Kahl), in the 1980s in the frame of a dedicated irradiation program in order to make provisions for future changes of RPV safety requirements and possible Long Term Operation (LTO) measures. The irradiation temperature was mainly in a range between 280 and 290 °C.

The well-known hardening effect due to irradiation in dependence on neutron fluence is obviously shown and more pronounced for the specimen materials with higher Cu (P370 WM) and Ni (P16 WM) content. This was the reason why we have focused in our positron annihilation studies on these two materials. The chemical composition of selected specimens is shown in Table 4.

All 3 specimens P370 WM (two irradiated D-77 and D-161, as well as one non irradiated CD159) are from the same bulk but cut at different positions. The same is valid also for both P16 WM specimens (S103 and GS67). Unfortunately, there was not specimen from non irradiated P16 WM material.

Mean positron lifetime (MLT) includes positron annihilation in air and therefore some variables can be introduces into the data evaluation. Therefore, average lifetime was calculated from measured data, including only annihilation in components \( \tau_1 \) and \( \tau_2 \).

It was proved that performed irradiation treatment caused increase of positron lifetimes in studied specimens. In the case of both P370SG specimens, the increase of \( \tau_{\text{avg}} \) parameter was from 142 ps to 147ps and 157 ps, respectively (Fig.8).

Results achieved for the average lifetime were at level of about 172 ps for the both P16SG specimens (Fig. 8).

The positron lifetime in defects, characterized via parameters \( \tau_2 \) and \( I_2 \), are shown in Fig.8 and Fig.9. In the case of P16WM steels, the lifetime \( \tau_2 \) is at the level of about 195 ps. It shows the presence of the small vacancy clusters with the size of about 1-2 vacancies. In the case of the steel P370WM, the lifetimes in defects are higher and with values of about 210 ps. It could indicate vacancy clusters of 2-3 vacancies [27-29]. For better orientation, please, see Table 7.

For the first component \( \tau_1 \) are the positron lifetimes from about 100 – 115 ps and this could be caused by the superposition of the reduced bulk component [21, 26] and
another component which is expressed by a bit higher values of positron lifetimes containing some partial dislocations (shallow traps) [42].
Fig. 9 – Intensities of positron lifetimes $I_1$ and $I_2$.

Table 7 - Calculated positron lifetimes for different types of defects in pure iron and different carbides in low alloyed RPV steel.

<table>
<thead>
<tr>
<th>Material</th>
<th>Positron lifetime (ps)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-bulk</td>
<td>110</td>
<td>[27]</td>
</tr>
<tr>
<td>Fe-dislocations</td>
<td>165</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe-monovacancy</td>
<td>175</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe-divacancy</td>
<td>197</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe-3 vacancy cluster</td>
<td>232</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe-4 vacancy cluster</td>
<td>262</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe-6 vacancy cluster</td>
<td>304</td>
<td>[28]</td>
</tr>
<tr>
<td>VC</td>
<td>99</td>
<td>[29]</td>
</tr>
<tr>
<td>$V_{0.86}Cr_{0.09}Mo_{0.04}Fe_{0.01}C$</td>
<td>105</td>
<td>[29]</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>112</td>
<td>[29]</td>
</tr>
<tr>
<td>Mo$<em>{1.4}Cr</em>{0.6}C$</td>
<td>116</td>
<td>[29]</td>
</tr>
<tr>
<td>Cr$_7$C$_3$</td>
<td>107</td>
<td>[29]</td>
</tr>
<tr>
<td>Cr$_{23}C_6$</td>
<td>112</td>
<td>[29]</td>
</tr>
<tr>
<td>Mn$_{26}C_6$</td>
<td>99</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe$_3$C</td>
<td>101</td>
<td>[28]</td>
</tr>
</tbody>
</table>

Considering the data from the plot of intensities (Fig. 9) assigned to the first lifetime component ($I_1$) and defect ($I_2$) structures can be seen that the intensities of defects in the case of high Ni (1.69 wt.%), low Cr 0.07 wt.% and low Cu (0.08 wt.%) P16 WM steels are at level of about 75%. This means that the smaller defects (dislocation lines and mono- or divacancies) in relatively high amount are more homogeneously distributed in the microstructure of P16 WM. In the case of steels with relatively low Ni (1.11 wt.%) but high Cr (0.74 wt.%) and Cu (0.22 wt.%), the intensities of defects are much lower but the lifetimes in defects are higher. So the defects are bigger (2-3 vacancies) and not so homogeneously distributed. This can be due to Cu precipitation after irradiation.

For the comparison of irradiated and as-received (non-irradiated) specimens we have got only P370 WM material. Unfortunately, there were only irradiated specimens from P16 WM and the non-irradiated material absent completely. So, the direct comparison can be performed only on P370 WM – irradiated D77, D161 and the not irradiated CD159, which were from chemical composition point of view identical and cut from one bulk. Unfortunately, due to probably long term storage at different positions as well as perhaps not ideal material homogeneities, some small microstructural differences were registered. Nevertheless, the differences of both irradiated specimens from the same materials are in frame of the error bars.

According to the lifetimes values from our measurements performed on CARINA/CARISMA RPV-steels we calculated the total trapping rate $\kappa$ in $\text{ns}^{-1}$ as well as the total defect concentration $c_d$ (the same values but in ppm). A quantitative analysis of the
trapping rates and the vacancy concentration can be calculated using the two-state trapping model. The positron trapping rate for vacancy $\kappa_v$ can be calculated as

$$\kappa_v = \mu_v C_v = (\tau_{av} - \tau_b)/\tau_b (\tau_v - \tau_{av})$$  \hspace{1cm} (3)

where $\kappa_v$ is the trapping coefficient for defects (vacancy), $C_v$ is the vacancy concentration, $\tau_b$ and $\tau_v$ are the positron annihilation lifetime in bulk and in vacancy, respectively. The concentration of vacancies is calculated from Eq. (3) by giving the value of the specific trapping coefficient for a single vacancy in pure Fe, $\mu_v = 1.1 \times 10^{15}$ s$^{-1}$. For more defects $N$, as clusters of vacancies, can be the specific trapping coefficient calculated as $\mu_N = N \mu_v$ [28, 37]. Results are summarised in Table 8.

$$\tau_b = (I_1/\tau_1 + I_2/\tau_2)^{-1}$$  \hspace{1cm} (4)

We registered only a slight increase of the concentration of vacancies due to irradiation - from 1.35 to 3.09 and 2.38, respectively in the case of P370 WM. This fact is visible. Nevertheless, much higher concentration of vacancies we observed in the case of P16WM (in comparison to P370WM). Unfortunately, this concentration after irradiation can be not compared with not irradiated material, because the not irradiated P16WM was not available for measurement.

There can not be stated that the small differences in neutron fluencies caused the higher concentrations of defects in studied materials.

### Table 8 - Calculated concentrations of vacancies in irradiated specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>P370 WM-CD159 Not irradiated</th>
<th>P370WM-D77 Irradiated (fluence 2.21E19 cm$^{-2}$ E&gt; 1MeV)</th>
<th>P370WM-D161 Irradiated (fluence 2.23E19 cm$^{-2}$ E&gt; 1MeV)</th>
<th>P16WM-S103 Irradiated (fluence 1.16E19 cm$^{-2}$ E&gt; 1MeV)</th>
<th>P16WM-GS67 Irradiated (fluence 4.81E19 cm$^{-2}$ E&gt; 1MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy concentration [ppm]</td>
<td>1.35</td>
<td>3.09</td>
<td>2.38</td>
<td>12.3</td>
<td>11.2</td>
</tr>
</tbody>
</table>

3. CONCLUSION

The positron annihilation spectroscopy is one of the non-destructive spectroscopic methods which can contribute to the complex evaluation of the RPV-steels microstructure and can in this way contribute to the nuclear safety of NPP.

Several EURATOM framework projects (LONGLIFE, NULIFE, …) are focused on studies towards ensuring of longer NPP operation [38]. In contrast to the first generation, the second generation of WWER-440 RPV materials with low content of impurities has proven very high stability to radiation damage at least up to a neutron dose of 2 dpa at an irradiation temperature of 270 ºC, and their response to radiation is now well understood [39]. In fact several reliable and predictive modeling approaches have been developed, according to which the damage of the material is assumed to be generated by three major contributions and their synergisms:
- copper rich radiation induced nano-precipitates,
- phosphorus segregation at different internal surfaces and
- the basic damage of the material matrix (MD) [40,41].

Based on our PAS results we stated that no large voids or vacancy cluster were formed due to irradiation in Russian as well as in German RPV steels. The performed neutron treatment of RPV steels caused at both studied materials an increased trend of defects concentration with increased neutron doses. Although these doses correspond to the neutron treatment up to 30 years of reactor operation (specimens were placed into irradiation chambers very close to reactor core and the acceleration factor of irradiation was about 11).

According to the comparison of German and Russian commercially used reactor RPV steels, it seems that Russian RPV steels contain more defects in “as received” state (delivered generally from higher MLT). If we focus our attention on so called “small-defect component” – τ₂ value, its intensity is higher in the case of Russian-RPV steels (67% in the case of base metal and 57% in the case of weld) in comparison to German steels, where these intensities are significantly lower (maximal value 49% in the case of weld P370WM). On the other hand, these defects are a little bit larger (about 200 ps) which implies higher concentration of di-vacancies in German steels. In the case of Russian steels we registered higher concentration of dislocations and mono-vacancies.

PAS results from irradiated German and Russian steels confirmed that no large voids or vacancy clusters were formed. This fact can be interpreted in the conclusion that vacancy type defects bear hardly any responsibility for radiation-induced hardening and embrittlement. This mechanism does not limit lifetime of reactor pressure vessel and does not affect significantly the long-term operation of nuclear power plants from safety point of view.

In the future, PAS techniques can be applied effectively also for evaluation of microstructural changes caused by extreme external loads simulating irradiation by proton implantation and for the evaluation of the effectiveness of post-irradiation thermal treatments. Therefore, we would like to use our results collected during last 20 years from measurements of different RPV-steels in “as received”, irradiated and post-irradiation annealed state and compare them to results where the real neutron irradiation will be replaced by proton implantation. This challenge has several open questions having in mind the fact that protons have positive charge and their behavior in metals can be different. Nevertheless, advantages connected with much comfortable handling, transport and measurement with “not radioactive” specimens seems to be very promising and valuable for those who would like to apply additional non-destructive techniques in this study.

Acknowledgement
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4. REFERENCES
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