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# Defects Investigation in Neutron Irradiated Reactor Steels by Positron Annihialtion

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## Abstract

Positron annihilation spectroscopy (PAS) based on positron lifetime measurements using the Pulsed Low Energy Positron System (PLEPS) was applied for the investigation of defects of irradiated and thermally treated reactor pressure vessel (RPV) steels. PLEPS results showed that the changes in microstructure of the RPV-steel properties caused by neutron irradiation and post-irradiation heat treatment can be well detected. From the lifetime measurements in the near-surface region (20-550 nm) the defect density in Russian types of RPV-steels was calculated using the diffusion trapping model. The post-irradiation heat treatment studies performed on non-irradiated specimens are also presented.

**Keywords:** reactor pressure vessel, steel, neutron embrittlement, positron annihilation, defects

## 1. Introduction

The fundamental task of nuclear reactor safety research is assessing the integrity of the reactor pressure vessel (RPV) and its reliable lifetime prediction [1]. Since about 1985 positron annihilation spectroscopy (PAS) has been repeatedly used in the study of RPV steels. The positron lifetime (PL) technique is a well-established method for studying open-volume type atomic defects and defect impurity interactions in metals and alloys [2]. For the interpretation of results from PL measurements, the standard trapping model (STM) can be used [3]. In inhomogeneous problems, the diffusion of positrons from the various implantation sites to the trapping centres has to be considered as well [4]. However, the mathematical difficulties associated with the corresponding diffusion-trapping model (DTM) [5] so far have prevented exact solutions in all but the simplest problems [6]. Thus it was impossible to analyse qualitatively the very detailed experimental results obtained with the pulsed positron beam. The application of improved DTM combined with the pulsed positron beam technique is described in detail in ref. [7].

## 2. Experimental

In the framework of the "Extended Surveillance Specimen Program", started in 1995 at the nuclear power plant (NPP) Bohunice (Slovakia), several specimens, which were prepared originally for Mössbauer spectroscopy measurements, but because of the proper size (10x10x0,05 mm) and the polished surface also suitable for PLEPS measurement, were selected and measured before their placement into the irradiation chambers, near the core of the operated nuclear reactor, and after 1, 2 and 3 years resistance there (neutron fluence in the range from 7.8 $10^{23}$ $m^{-2}$ up to 2.5 $10^{24}$ $m^{-2}$). The chemical composition and the irradiation conditions of the studied RPV-steel specimens are shown in Table 1 and Table 2.

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

| Code | Type of steel | Contents of alloying elements in RPV specimens (wt.%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Si | Mn | Mo | Ni | Cr | Cu | P | S | V | Co | Total |
| ZM - Base metal WWER-440 | 15Kh2MFA | 0.14 | 0.31 | 0.37 | 0.58 | 0.20 | 2.64 | 0.091 | 0.014 | 0.017 | 0.27 | 0.019 | 4.651 |
| ZK - Weld metal WWER-440 | Sv10KhMFT | 0.048 | 0.37 | 1.11 | 0.39 | 0.12 | 1.00 | 0.103 | 0.043 | 0.013 | 0.13 | 0.020 | 3.347 |
| BM - Base metal WWER-1000 | 15Kh2NMFA | 0.18 | 0.24 | 0.52 | 0.62 | 1.26 | 2.22 | 0.08 | 0.01 | 0.013 | 0.08 | 0.008 | 5.231 |

Table 2 Irradiation conditions of specimens at the 3rd unit of nuclear power plant Bohunice (Slovakia)

| | Material | Code of sample | Time of irrad. [eff. days] | Neutron Fluency [$m^{-2}$] | Total activity [kBq] | Thickness of sample [μm] |
|---|---|---|---|---|---|---|
| 1 | Base material – non-irradiated | 4 ZAE | 0 | 0 | 0 | 60 |
| 2 | Base material – 1 year irradiated | 9 ZAE | 280.8 | 7.81E23 | 62 | 50 |
| 3 | Base material – 2 year irradiated | 15 ZAG | 578.5 | 1.64E24 | 109 | 40 |
| 4 | Base material – 3 year irradiated | 15 ZAG | 894.3 | 2.54E24 | 89 | 30 |
| | | | | | | |
| 5 | Weld – non-irradiated | 5 ZBE | 0 | 0 | 0 | 55 |
| 6 | Weld – 1 year irradiated | 240 ZBI | 280.8 | 7.81E23 | 30 | 45 |
| 7 | Weld – 2 years irradiated | 237 ZBE | 578.5 | 1.64E24 | 48 | 25 |
| 8 | Weld – 3 years irradiated | 83 ZBG | 894.3 | 2.54E24 | 110 | 47 |

For the first time an improved pulsed low-energy positron system (PLEPS) [8] was used for the investigation of neutron-irradiated RPV-steels. This system enables the study of the micro structural changes in the region from 20 to 550 nm (depth profiling) with small and very thin (<50 μm) specimens, therefore reducing the disturbing $^{60}Co$ radiation contribution to the lifetime spectra to a minimum [9]. Such a disturbance is the limiting factor for the investigation of highly-irradiated RPV specimens with conventional positron lifetime systems. In comparison to a triple coincidence setup of positron-lifetime spectroscopy, reported in [12,13], PLEPS reduces the time for the measurements by about a factor 500, resulting in qualitatively comparable spectra and enables in addition the estimation of the defect concentrations. The time resolution of PLEPS was about 240 ps FWHM. All spectra of irradiated RPV specimens contained about $3x10^7$ events at a peak to background ratio in the range 30:1 to 100:1 [9].

Results for the mean lifetimes after various irradiation treatments are shown in Fig.1 and Fig.2. Each lifetime spectrum can be well described by two lifetime components, which after about 100 nm remain fairly constant over the full range of distances (see Fig.3 and Fig.4). The lifetime $\tau_1$ of about 170 ps is the dominant steel component with intensity of about 97% in the bulk. The second component $\tau_2$ with intensity of the order of 3% or less and value of about 400-500 ps can be assigned to the contribution of large vacancy clusters. The intensity of this component is much higher (up to 10-12 %) in the case of specimens which were not thermally treated (reference specimens ZMNF and ZKMF). Such large agglomerations of vacancies are observed also in the case of irradiated specimens.

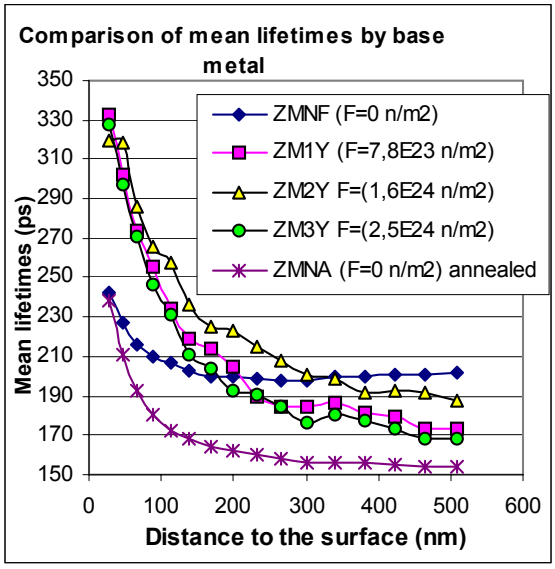


Fig. 1 Comparison of mean lifetimes of different neutron-irradiated 15Kh2MFA (base metal) steel specimens. Annealing was performed in vacuum at 385 °C for 1 hour, which, according to Hollomon-Jaffe´s equation, is comparable to a long-term stay at 290 °C for 1 year. F is the neutron fluence.

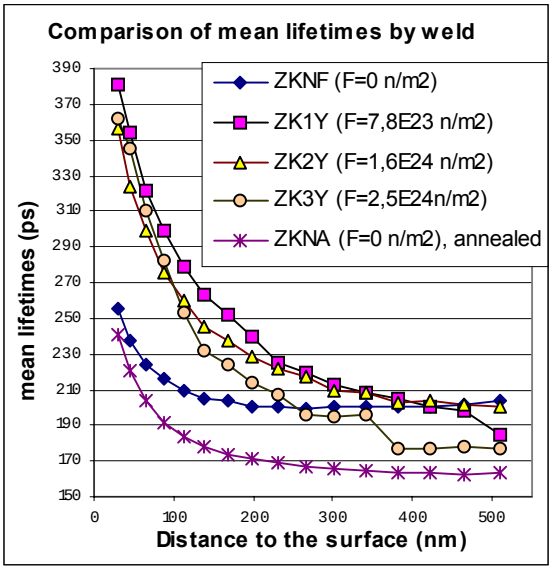


Fig. 2 Comparison of mean lifetimes of different neutron-irradiated Sv10KhMFT (weld) steel specimens. Annealing was performed in vacuum at 385 °C for 1 hour, which, according to Hollomon-Jaffe´s equation, is comparable with a long-term stay at 290 °C for 1 year. F is the neutron fluence.

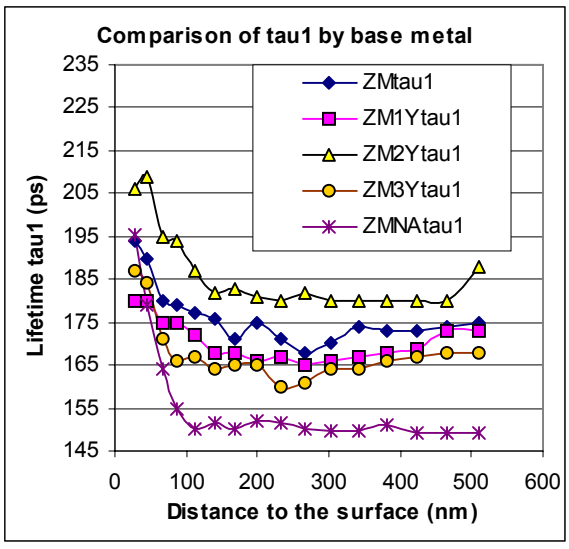


Fig.3 Comparison of RPV steel specimens (base metal) after different residence times in the operated nuclear reactor. Specimen ZMNF is the reference not irradiated and not thermally treated sample. Specimen ZMNA is the same sample after annealing in vacuum at 385 °C for 1 hour. This treatment is equivalent to the 290 °C treatment for 1 year.

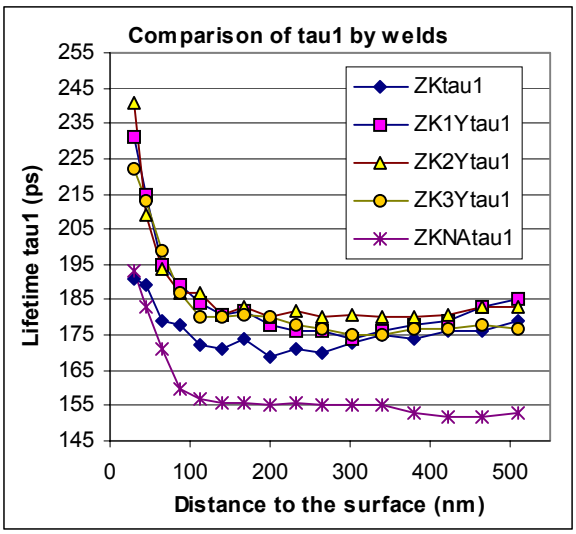


Fig.4 Comparison of RPV steel specimens (weld) after different residence times in the operated nuclear reactor. Specimen ZKNF is the reference not irradiated and not thermally treated sample. Specimen ZKNA is the same sample after annealing in vacuum at 385 °C for 1 hour. This treatment is equivalent to the 290 °C treatment for 1 year.

The most interesting result of the measurements of irradiated specimens presented in Fig.3 and Fig.4 for the defect structure in the bulk, is a decrease of the positron lifetime $\tau_1$ (after maximal culmination after 2-years irradiation in the reactor for both the base and weld metals) indicating a decrease of the average free volume associated with small defects formation and recovering of the large defects.

The long-term exposure to the irradiation temperature at about 290°C allows recovery of some defects acting in an opposite way to normal radiation damage. A decrease of the mean positron lifetime after annealing of the non-irradiated 15Kh2MFA specimens in vacuum at 385 °C for 1 hour from 200 ps to about 160 ps in case of base material and from 200 ps to 170 ps in case of weld material was observed. According to the comparison of the dominant steel components $\tau_1$, the annealing of small sized defects is not so effective in the case of weld material (from 170 ps to 155 ps) as in the case of base material (from 170 ps to 150 ps). A similar effect, less significant, was observed also in the case of the sample irradiated 1 year.

The effect due to long-term annealing at temperature of about 290 °C during the reactor working conditions is in the opposite direction to the creation of the radiation induced defects due to long-term neutron irradiation. After changes during the first years the effects are balanced out or the influence of annealing seems to be more significant.

## 3. Concentration of defects

Of particular interest is the concentration of defects as a function of irradiation dose and thermal treatment. Generally, this effect can be obtained from positron studies only if the bulk lifetime can be resolved from the shortest lifetime, attributed to annihilation from defects. In the present case of saturation trapping this was impossible. Therefore, from the individual lifetime spectra we can only conclude a total trapping rate $\kappa$ larger than about $10^{10}s^{-1}$.

However, from the variation of the mean lifetime $\tau_{av}$ as a function of positron implantation energy, we can estimate $\kappa$ even in the case of saturation trapping. The problem was fully analysed in [7]. The mean lifetime $\tau_{av}$ for a homogeneous specimen of mean lifetime $\tau_\infty$ with a very thin surface layer of positron lifetime $\tau_s$ (transition to the surface layer limited by back-diffusion) depends on the positron implantation energy E according to:

$$\tau_{av}(E) = \tau_\infty + (\tau_s - \tau_\infty) G(\alpha z_0(E)).$$

Here we have used the abbreviation:

$$G(y) = 1 - y \int_0^\infty e^{-uy^2} e^{-u^2} du \quad ,$$

the generally accepted approximation for the implantation profile $n_{impl}(z)$ of positrons:

$$n_{impl}(z) = -\frac{d}{dz} \exp\left(-\left(\frac{z}{z_0(E)}\right)^2\right)$$

and for the elements of the iron group

$$z_0(E) \approx 5\ nm\ .[E\ /\ keV]^{1,6}$$

The total trapping rate into defects is related to the parameter $\alpha$ as derived from the observed variation of $\tau_{av}(E)$ by

$$\kappa = D\alpha^2 - \frac{1}{\tau_b}$$

Here D denotes the diffusion of positrons in the matrix and $\tau_b$ is the bulk lifetime.

Unfortunately, our specimens exhibit a certain surface oxidation. Thus, the surface layer can not be considered as negligibly thin. On the other hand, it cannot exceed a thickness of about 20 nm, because $\tau_{av}(E)$ decreases rapidly as a function of E already at E=3 keV. For these reasons we have derived $\alpha$ (and hence $\kappa$) from the observed variation of $\tau_{av}(E)$ for an energy range, where the influence of surface contamination was expected to be small and where, on the other hand, the variation of $\tau_{av}(E)$ was large enough to obtain clear information about $\alpha$. The best choice was to select an energy value ($E_{0.25}$) where $\tau_{av}$ was dropped to 25% of the full variation between surface and bulk, i.e.

$$\tau_{av}(E_{0.25}) = \tau_{\infty} + 0.25\,(\tau_s - \tau_{\infty})$$

The values for $\tau_s$ and $\tau_\infty$ are derived by extrapolation of $\tau_{av}(E)$ to E=0 and E=$\infty$, respectively. After evaluation of $E_{0,25}$ we obtain (using D=1cm$^2$/s)

$$\kappa = 1.6x10^{13}\,(E_{0.25}/keV)^{-3.2} - \frac{1}{\tau_b}$$

$$c_d = \frac{\kappa}{\kappa_{spec}}$$

In Fig.5 and Fig.6 results for the evaluation of $\kappa$ as obtained by the procedure described, are presented together with plausible values for the corresponding total defect concentration

For $\kappa_{spec}$ the plausible value $10^{15}$ ($s^{-1}$) [3] has been assumed. Because of slight surface oxidation, this evaluation of $\kappa$ results in a systematic underestimate. A lower limit of $10ns^{-1}$ for $\kappa$ may by derived within the framework of the STM since we have observed saturation trapping at defects.

## 4. Discussion and conclusions

According to the results from our measurements performed on different irradiated RPV-steels, the total trapping rate $\kappa$ in $ns^{-1}$ as well as the total defect concentration $c_d$ (the same values but in ppm) increases slightly for both base and weld materials as a function of the irradiation dose (see Fig.6).

The weld material (Sv10KhMFT) seems to be less sensitive to the changes caused by neutron-irradiation or by post-irradiation heat treatment than the base material (15Kh2MFA) (see Fig.5). 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 [12]. Accordingly, in the type of steel 15Kh2MFA the trapping rate into chromium carbides ($Cr_7C_3$, $Cr_{23}C_6$) is predicted as $\kappa_{Cr}$=1,8x10$^8$ $s^{-1}$ and into vanadium carbides as $\kappa_{VC}$=2,2x10$^{10}$ $s^{-1}$ [12]. Thus precipitated vanadium carbide could indeed account for the observed trapping rates. But on the other hand, as shown by calculations [13], 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.

The total trapping rate $\kappa$ and the defect concentration $c_d$ are stable or increase slightly for 15Kh2MFA steel as a function of Hollomon-Jaffe´s parameter [2,14]. Between 15.5 to 16.5 (corresponding to the temperature region 400 to 450°C) the defect concentration increases. On the other hand (Fig.5), in the same range, there is a marked decrease in the lifetime of defects. A simple explanation could be the dissolution of precipitates and defect clusters which would reduce the average size of the defects, and, by the same process, would increase the concentration of the defects.

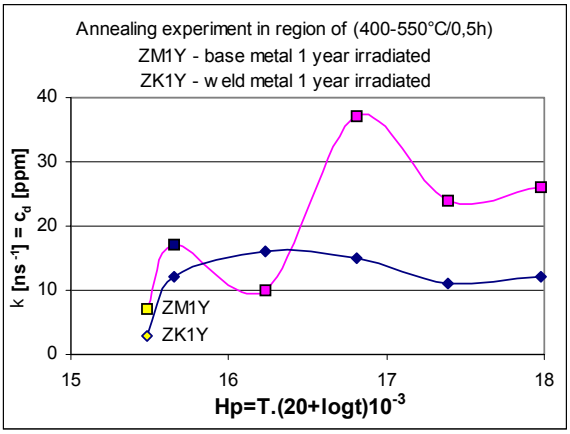


Fig.5 The total trapping rate κ versus Hollomon-Jaffe´s parameter at isochronal annealed (step 25°C) specimens of base (ZM) and weld (ZK) alloys after 1 year of irradiation in the reactor (fluency of about 7.8 $10^{23}$ $m^{-2}$). The lower limits for κ, as derived from saturation trapping according to the STM, is 10 $ns^{-1}$.

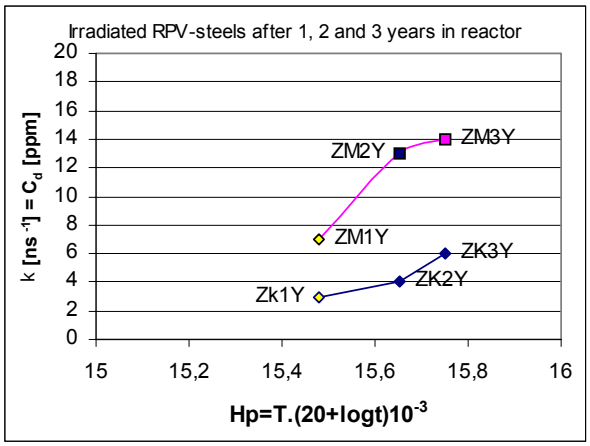


Fig.6 The total trapping rate κ versus Hollomon-Jaffe´s parameter at RPV specimens from base (ZM) and weld (ZK) alloys after 1, 2 and 3 years residence in reactor irradiation chambers (neutron fluency in the range from 7.8 $10^{23}$ $m^{-2}$ to 2.5 $10^{24}$ $m^{-2}$). The lower limits for κ, as derived from saturation trapping according to the STM, is 10 $ns^{-1}$.

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