

## 2D-Coincidence Doppler Broadening Measurements on Neutron-Irradiated VVER-Type Reactor Pressure Vessel Steels

Jakub Čížek<sup>1</sup>, Frantisek Bečvář<sup>1</sup>, Ivan Procházka<sup>1,a</sup> and Jan Kocik<sup>2,b</sup>

<sup>1</sup>Dept. of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-18000 Prague 8, Czech Republic

<sup>2</sup>Nuclear Research Institute Rez, plc., CZ-25068 Husinec-Rez 130, Czech Republic

<sup>a</sup>ivanp@mbox.troja.mff.cuni.cz, <sup>b</sup>koc@nri.cz

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**Abstract.** The results of the two-detector coincidence measurements of the Doppler broadening of annihilation radiation on a variety of the reactor pressure vessel steels of VVER type are reported. The following subjects were studied: (i) The non-irradiated materials. (ii) The changes induced by neutron irradiation as a function of fluence and flux. (iii) The effect of the regeneration annealing of irradiated materials. The irradiation-induced migration of Cu atoms towards positron annihilation sites in dislocations was observed which turned out to be removed by annealing at 475 °C.

### Introduction

The neutron irradiation induced degradation (embrittlement) of reactor pressure vessel (RPV) steels begins from the creation and migration of the irradiation induced vacancies, self-interstitials and solute atoms. These defects consequently influence the migration and precipitation of admixture atoms. Obviously a thorough microstructural characterisation of the embrittlement and its thermal recovery is necessary for understanding the service degradation of reactor materials – a factor important for the service life and safety of nuclear reactors. The two-detector coincidence measurement of the Doppler broadening of annihilation radiation (2D-DB) is well suited for the investigation of the above processes since it is sensitive to the chemical surroundings of positron annihilation sites.

As a continuation of our recent positron lifetime study of neutron irradiated RPV steels [1], we have therefore performed 2D-DB measurements on a variety of the VVER-type RPV steels in the present work<sup>1</sup>. It involved (i) the characterisation of non-irradiated materials, (ii) the investigation of changes induced by neutron irradiation as a function of fluence and flux and (iii) the characterisation of the irradiated specimens subjected to regeneration annealing.

### Experimental

**Specimens.** The RPV materials studied in the present work and the irradiation conditions are specified in Table 1. The low alloyed Cr-Mo-V steel contain typically (in wt. %) 0.15 C, 2.5 Cr, 0.7 Mo and max. 0.3 V, the Cr-Ni-Mo-V steel also max. 1.5 Ni. Copper content is very low (< 0.07), except the material E, which was additionally alloyed 0.3 Cu. The base and weld metals (referred hereafter as BM and WM, respectively) were investigated and their detailed chemical composition was given in Ref. [1]. The thermal treatment of materials and specimen preparation were described in more details in paper [2]. The “well annealed” high-purity  $\alpha$ -iron and copper (AF and AC, respectively) were used for reference measurements.

**Measurements.** A 2D-DB coincidence spectrometer employed in the present work consisted of two HPGe detectors and commercial NIM modules operated by a PC. The energy resolution of the spectrometer was  $\Delta E = 1.65$  keV (fwhm) at 511 keV energy and the coincidence count rate amounted of  $\sim 650$  s<sup>-1</sup> for a 1 MBq <sup>22</sup>NaCl positron source (sealed between 2  $\mu$ m mylar foils). At least 10<sup>8</sup> events were collected in each two-dimensional spectrum, which was subsequently reduced into the

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one-dimensional Doppler profile and instrumental resolution cuts. The relative changes of Doppler profiles were followed as ratios of normalised counts to those of proper reference profile.

**Table 1.** Specifications of RPV steels studied.

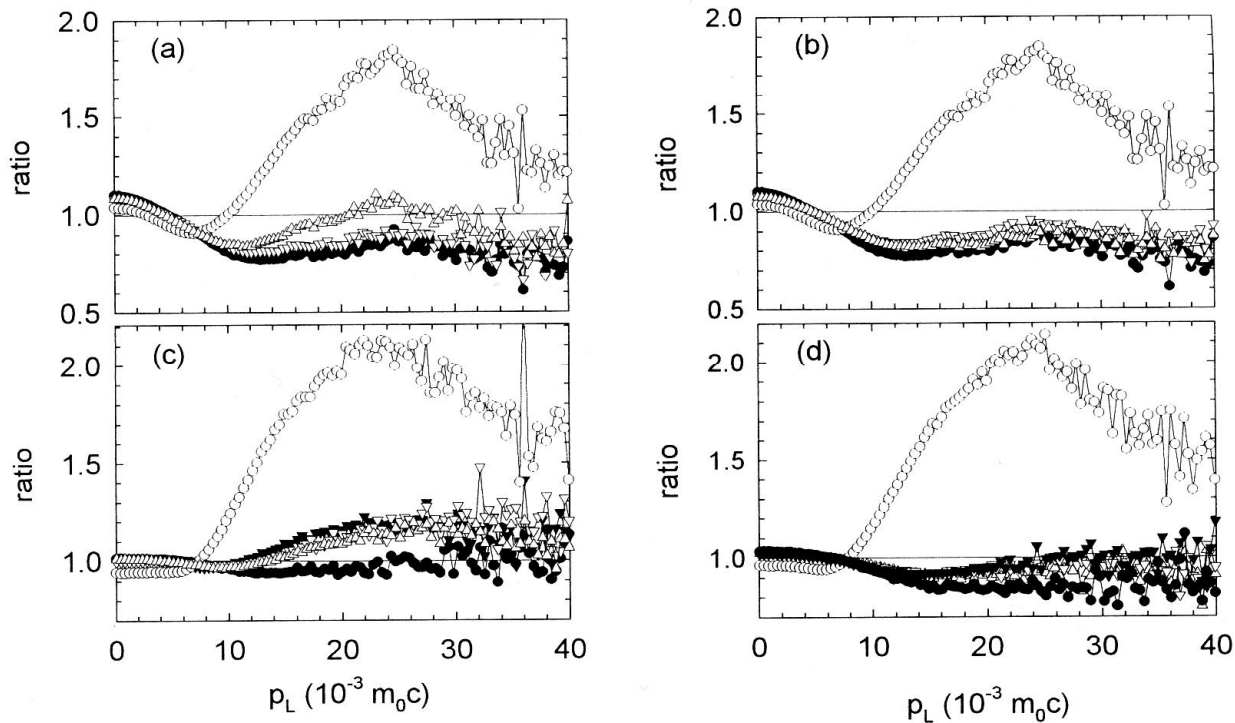
Identifier	Material	Irrad. Time <sup>a</sup> [year]	Flux <sup>b</sup> [ $\times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$ ]	Fluence <sup>b</sup> [ $\times 10^{24} \text{ m}^{-2}$ ]
A11	15Kh2MFA, Cr-Mo-V, BM VVER-440	—	—	—
A12		5	1.16	1.79
A8 <sup>c</sup>		5	1.09	1.41
A6		5	4.56	5.89
A1		1	3.66	1.12
B9	Sv10KhMFT, Cr-Mo-V, WM VVER-440	—	—	—
B7		5	2.19	2.97
B8 <sup>c</sup>		5	3.52	4.78
B6		5	3.87	5.26
B2		1	4.17	1.22
C0	A533-B Cl.1-JRQ, BM	—	—	—
D0	15Kh2NMFA, Cr-Ni-Mo-V, BM, VVER 1000	—	—	—
E0	15Kh2NMFA, Cr-Ni-Mo-V +Cu, BM <sup>d</sup>	—	—	—

<sup>a</sup> Irradiated at surveillance position of VVER-440 power reactor at 275°C. <sup>b</sup> Neutrons with energy above 0.5 MeV. <sup>c</sup> Post-irradiation annealing 475°C/165 h. <sup>d</sup> Experimental alloy (0.3 wt% of Cu).

## Results

**Non-irradiated materials.** In Figs. 1a and 1b, ratios of counts to those of the  $\alpha$ -Fe reference profile as functions of the electron longitudinal momentum  $p_L$  are shown for the non-irradiated RPV materials and for the annealed Cu. A dominating feature seen in the Figure is a strong relative enhancement of momentum components for the annealed Cu in the region around  $25 \times 10^{-3} m_0 c$  compared to the RPV materials and the  $\alpha$ -Fe. In the light of this, an apparent growth of relative counts for Cu-enriched Cr-Ni-Mo-V compared to the other steel specimens, observed in the same momentum region (Fig. 1a), can be easily explained as a consequence of its higher Cu content. Analogously, a slight increase of momentum components in this region suggested by the data of Fig. 1b for the A-533 specimen can obviously be assigned to the same reason. The observed increase in relative counts towards zero momentum should be attributed to dislocations, which were shown to reside in the specimens after initial annealing [2]. Compared to the Cu-enrichment effect, much less differences in the ratios given in Figs. 1a and 1b were obtained between Cr-Mo-V and Cr-Ni-Mo-V (no Cu enrichment) steels as well as between corresponding BM and WM specimens. Thus the data of Fig. 1 demonstrate that the 2D-DB technique is a very useful one for detecting relative Cu enrichment at sites at which positrons annihilate in the material.

**Irradiated RPV steels.** The neutron irradiated Cr-Mo-V specimens were compared to the respective non-irradiated materials as the reference, i.e. A11 for BM and B9 for WM, and the resulting ratios are shown as functions of  $p_L$  in Figs. 1c and 1d, respectively. Again, the data for the annealed pure Cu were included in the Figure, but now they were related to those for the non-irradiated Cr-Mo-V specimens. Together with an increase of the ratios in the low-momentum region, a remarkable growth of the high-momentum components ( $p_L \sim 25 \times 10^{-3} m_0 c$ ) was found for the BM specimens (see Fig. 1c) after irradiation. A similar picture to that of Fig. 1c but less pronounced was exhibited by the WM specimens (Fig. 1d). These changes occur mainly within the first year of irradiation (specimen A1) while for longer periods of irradiation they continue in



**Figure 1.** Ratios of normalised to reference counts vs. momentum  $p_L$ . (a) AC -  $\circ$ , A11 -  $\bullet$ , D0 -  $\nabla$ , E0 -  $\Delta$ . (b) AC -  $\circ$ , A11 -  $\bullet$ , B9 -  $\Delta$ , C0 -  $\nabla$ . (c) AC -  $\circ$ , A1 -  $\Delta$ , A12 -  $\blacktriangledown$ , A6 -  $\nabla$ , A8 -  $\bullet$ . (d) AC -  $\circ$ , B2 -  $\Delta$ , B7 -  $\blacktriangledown$ , B6 -  $\nabla$ , B8 -  $\bullet$ . See explanations in text.

a considerably slower manner. An analogous character of the changes of the positron annihilation parameters (lifetimes,  $S$ -parameters) during irradiation was observed in our recent study [1]. The additional growth of the low-momentum components (Figs. 1c,d) is due to irradiation induced small vacancy clusters (5-6 vacancies) identified in our positron lifetime measurement [1]. On the basis of the preceding paragraph, we attribute the observed growth of the high-momentum components after irradiation to an increased Cu content near sites at which positrons annihilate. This may occur as the decoration of dislocations by migration of Cu atoms facilitated by their coupling to irradiation induced vacancies. Less pronounced irradiation effects in WMs (Fig. 1d) are then correlated to a lower content of dislocations found in WMs by positron lifetimes [2]. The decoration of dislocations by irradiation induced black dots has recently been observed by TEM [1]. A removal of this irradiation induced rearrangement of Cu atoms in both the BM and WM specimens was observed in the annealing experiments presented in Figs. 1c,d, specimens A8 and B8, respectively. This can be ascribed to dissolution of Cu atoms back into the matrix. The disappearance of black dots during annealing was also observed by TEM [1]. Contrary to the dislocations, the irradiation induced vacancy clusters are not likely surrounded by Cu atoms. Positron lifetime measurement [1] revealed out that these clusters were not removed by annealing.

## Conclusions

2D-DB technique proved itself to be an effective tool of the investigations of the neutron irradiation induced embrittlement of RPV steels, in particular the rearrangement of Cu atoms during irradiation. Present observations suggested the irradiation-induced migration of Cu atoms towards dislocations. This Cu atom rearrangement turned out to be removed by annealing.

## References

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