cta physica slovaca vol. 45 No. 1, 37 – 43 February 1995

MÖSSBAUER AND ELECTRON-POSITRON ANNIHILATION STUDY OF A REACTOR PRESSURE VESSEL STEEL[1]

J. Haščík, J.Lipka, L. Kupča†, V. Slugeň[2], M. Miglierini, R. Gröne, I. Tóth, K. Vitázek

Department of Nuclear Physics and Technology, Slovak Technical University 812 19 Bratislava, Slovakia

†*Nuclear Power Plant Research Institute, Trnava, Slovakia*

Received 2 December 1994, accepted 19 December 1994

Mössbauer spectroscopy and electron-positron annihilation measurements have been applied to a reactor pressure vessel steel in order to investigate the influence of neutron irradiation and post-irradiation heat treatment. Room temperature Mössbauer spectra revealed slight structural changes originating from irradiation process whereas a post-irradiation heat treatment under vacuum permits the initial structure to recover as derived from the hyperfine parameters. The present Mössbauer results are supported by electron-positron annihilation measurements using lifetime and angular correlation techniques.

Resistance against neutron enbrittlement is the most relevant parameter to be considered when selecting materials for a reactor pressure vessel (RPV). The V-230 type RPV features rather specific design with relatively small diameter. Neutron fluxes in reactor walls must be taken into account in this respect. Neutron embrittlement causes changes of microstructure in the material and, consequently, mechanical properties of the RPV steel deteriorate. Neutrons with the energy $E_n > 0.5$ MeV initiate collision chains by scattering with atoms of the crystal lattice. At the same time, vacancies and interstitials created recombine and, depending on temperature, grow to clusters and dislocations.

Unit 1 and 2 RPVs of the nuclear power plant Jaslovské Bohunice have been manufactured in former Soviet Union from the 15CH2MFA steel with anti-corrosion austenitic cladding. They belong to the first generation of the VVER-440/230 reactors with high content of residual elements in the vessel steel as listed in Table 1 [1]. The vessel have six circumferential and one longitudinal weld in the bottom part. The highest neutron fluxes appear in the belt segments located nearest to the active core (Fig.1). As a

[1]Presented at the Colloquium on Mössbauer Spectroscopy in Material Science, Kočovce, Slovakia, October 3-6, 1994

[2]E-mail address: slugen@elf.stuba.sk

0323-0465/95

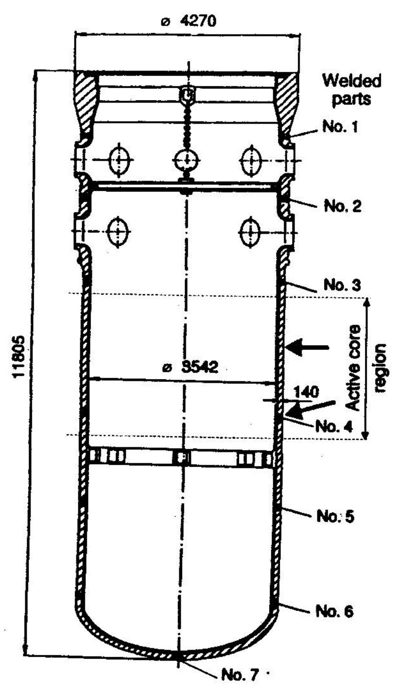

Fig. 1. The reactor pressure vessel VVER 440/230 (broad arrows indicate places where from the material for sample preparation has been collected).

consequence, pronounced structural changes are expected in the welded part which is situated between the fourth and fifth RPV-segments.

Mechanical properties of the construction materials and influence of neutron radiation damage on them are routinely investigated by macroscopic methods. Hardness, strain of fraction, etc. are measured using the so-called witness samples. We think, however, that microscopic methods yielding information on the origin of structural changes on atomic and/or nuclear level should be also employed.

In the present study, structural changes in a RPV steel which results from irradiation processes are investigated by non-destructive nuclear methods - namely by Mössbauer effect and electron positron annihilation spectroscopies. The main goal was to verify the feasibility of both techniques in assessing the effects of radiation damage caused to a RPV during routine operation.

The most significant advantage of Mössbauer spectroscopy, with regard to the investigation of steels, is its high sensitivity to changes in atomic configuration of resonant atoms comprising local crystal symmetry and lattice defects. To our knowledge, Mössbauer spectroscopy was rarely used in the investigations of nuclear power plant materials [2-6].

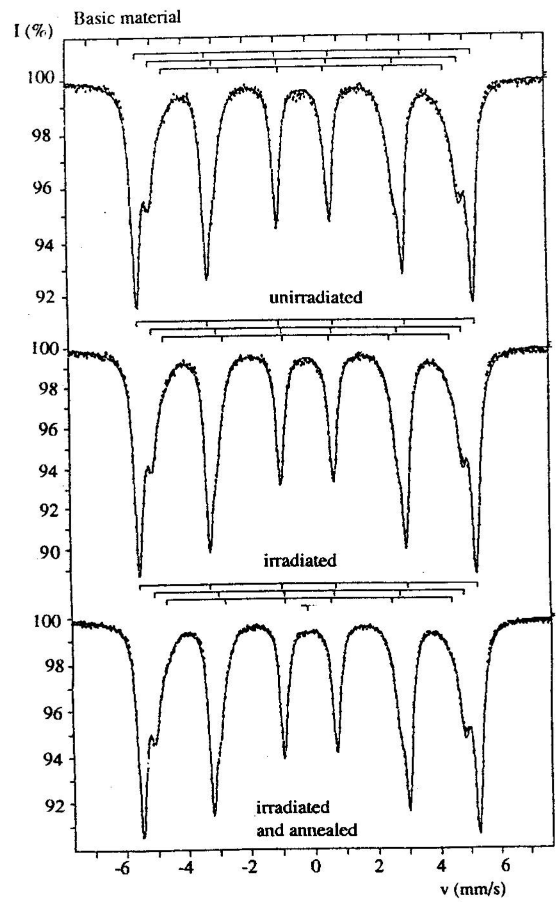

Fig. 2. Room temperature Mössbauer spectra of the basic material subjected to different treatments.

Diagnostic potential of electron positron annihilation techniques in the study of metals arises from the fact that positrons are trapped in localised states of defect regions. Positrons can form bound states in dislocations, interstitial clusters, single vacancies or in vacancy clusters of various sizes. Presence of defect sites in the sample studied is manifested via longer positron lifetimes [7]. Similarly, annihilations with high-moment core electrons are reduced relative to low-moment valence electrons. The resulting shapes of gamma-gamma coincidences with respect to the moments of electrons are more narrow for positron annihilations in lattice defects.

Deterioration of mechanical properties of RPV steels during irradiation in a nuclear power plant is known as neutron embrittlement [5]. The only possibility to reduce irra-

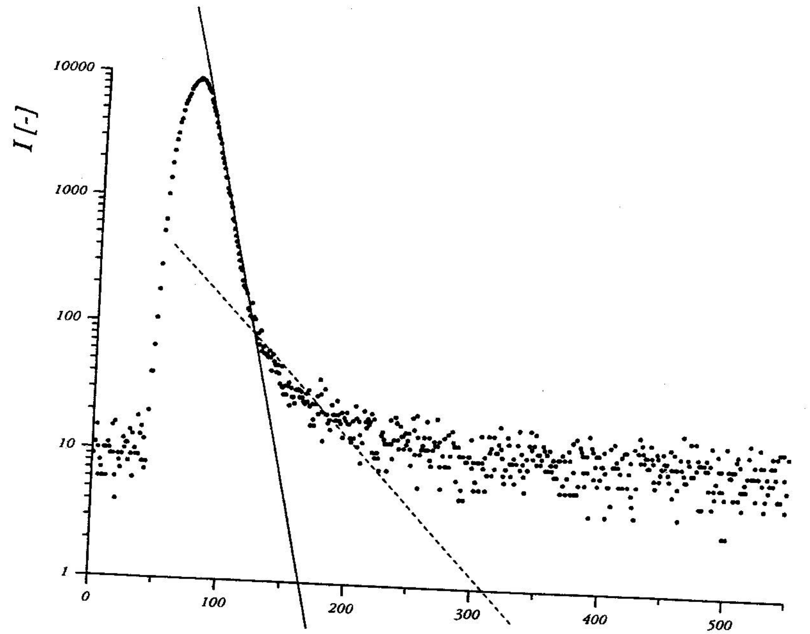

Fig. 3. Positron lifetime spectrum of the basic material after annealing.

diation embrittlement and, thus, to increase the safety margin against brittle fracture of the RPV is thermal annealing. Aiming to reveal the impact of neutron irradiation and post-irradiation heat treatment on structural changes which are manifested in spectral parameters we have performed Mössbauer effect and electron-positron annihilation measurements.

We have studied samples of a VVER-440 reactor steel taken from: (1) the original, i.e. unirradiated material, (2) the material which was irradiated for 15 years, and (3) the material from (2) subsequently thermally annealed. Using a milling machine, sawdust-like pieces have been taken from the original material and directly from the reactor vessel to prepare the samples (1) and (2), respectively. The latter was heat treated at 450° C for 168 hours in a vacuum to obtain the samples (3). Two batches of the samples comprising the basic material of the vessel and material from the welded parts have been prepared. The welded material was not available in its original, i.e. unirradiated form.

Room temperature Mössbauer effect measurements were carried out in transmission geometry on a standard constant accelerator device working with a ^{57}Co source in Rh matrix. Electron-positron annihilation spectra have been taken by home-made equipments with ^{22}Na sources. The source for lifetime technique (activity ca. 10μCi) was closed in a 3-μm nickel foil. In angular correlation measurements, a 1.25 mCi Amersham source deposited on a Pt substrate was used.

Mössbauer spectra in Fig.2 which correspond to the basic material samples show

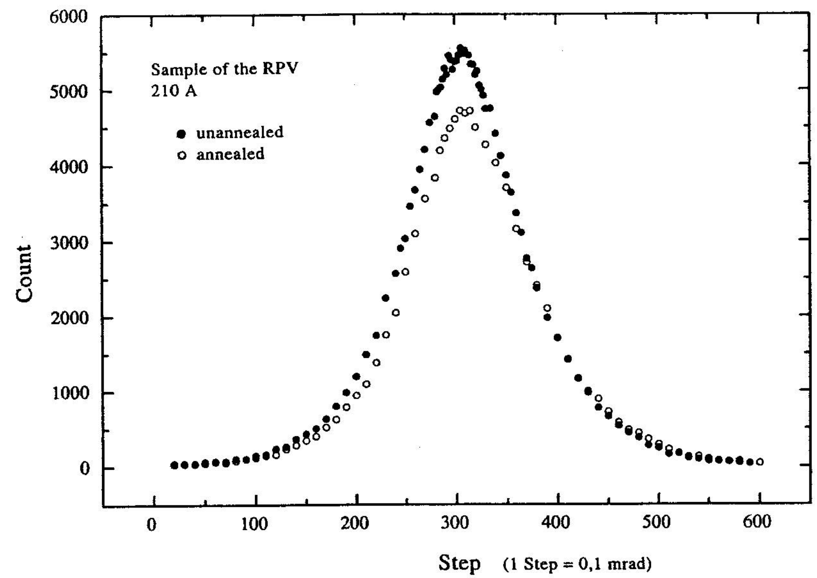

Fig. 4. Angular correlation dependences of the basic material before (full circles) and after (open circles) annealing.

typical behaviour of dilute iron magnetic alloys which can be described by three sextets. Their relative areas are close to the theoretical values calculated from a random distribution model of impurities in a bcc structure (5% of 12 elements in total). All corresponding hyperfine parameters were free during the fitting procedure. The spectrum parameters of the original, irradiated and post-irradiation annealed samples are listed in Table 2. Slight increase of the hyperfine magnetic field values, B, in the third component as well as an increase in the line-width, Γ, and the relative area, A_{rel}, of the first sextet after the irradiation can be interpreted as a consequence of increased structural disorder due to neutron bombardment. After annealing, B and A_{rel} - values resumed almost original values. Decrease in Γ for the second and third components in the annealed samples with regard to their original unirradiated values is due to annealing out of the defects which leads to improved structural ordering. The same trends were observed when the irradiated sample has been taken from the welded part of the RPV.

Results obtained from the positron lifetime measurements are summarised in Table 3. Typical positron lifetime spectrum of the basic material after annealing can be seen in Fig.3. Decrease in lifetimes for both the basic and the welded material implies a release of structural defects after annealing. Angular correlation spectra of the irradiated basic material before and after annealing are shown in Fig.4. Because the experimental conditions including sample dimensions, their placement as well as time of the mea-

Table 1. Chemical composition of a RPV steel. Number in the brackets represents an error in the last figure.

Material	C	Si	Mn	Cr	Ni	Mo
basic	0.140(1)	0.31(2)	0.37(2)	2.64(1)	0.20(1)	0.58(2)
welded	0.048(1)	0.37(2)	1.11(2)	1.00(1)	0.12(1)	0.39(2)
Material	**V**	**S**	**P**	**Co**	**Cu**	**As**
basic	0.27(1)	0.017(2)	0.014(1)	0.019(5)	0.091(1)	-
welded	0.13(1)	0.013(2)	0.043(1)	0.020(2)	0.103(1)	-

Table 2. Refined values of the Mössbauer parameters corresponding to the basic material.

Sample	B (T)	Γ (mm/s)	A_{rel} (%)
unirradiated	33.4	0.25	57
	30.7	0.35	36
	28.0	0.41	7
irradiated	33.4	0.27	61
	30.8	0.34	32
	28.3	0.38	7
irradiated and annealed in vacuum	33.4	0.25	57
	30.7	0.32	36
	28.1	0.37	7
Accuracy	±0.1	±0.02	±1

Table 3. Parameters of the positron lifetime spectra corresponding to the basic and welded material before (ba) and after (aa) annealing.

Material		Lifetime τ_1 (ns)	Lifetime τ_2 (ns)
basic	ba	0.310 ± 0.006	1.52 ± 0.45
	aa	0.262 ± 0.006	1.20 ± 0.45
welded	ba	0.331 ± 0.006	2.06 ± 0.45
	aa	0.187 ± 0.006	1.11 ± 0.45

surements have been preserved in both cases the spectra can be displayed in absolute counts. Decrease of the peak intensity in the annealed sample with respect to the irradiated one can be associated with a decrease in the number of low-moment electrons which can be interpreted in terms of improved structural order after the annealing. In addition, broadening of the annealed spectrum, which can be revealed from normalised curves (not shown), is also in favour of this assumption.

Interpretations of the results obtained from positron lifetime and angular correlation electron-positron annihilation technique are in agreement with the findings from the Mössbauer effect experiments. It has been shown that the combination of both methods yields promising results regarding identification of structural changes which are taking place in the RPV steel due to neutron irradiation and subsequent heat treatment. We have to admit, however, that the deviations in Mössbauer parameters obtained are not

so pronounced as expected. The reason for this lays probably in the way how was the irradiated sample material taken from the reactor vessel. In this respect, the feasibility of Mössbauer spectroscopy could be improved by employing an *in-situ* backscattering technique with a spectrometer directly attached to the RPV. Such experimental arrangement could be realised only when sufficiently small driving system (due to the space available) would be used as reported for example in [8]. Reliability of Mössbauer spectroscopy and electron-positron annihilation results can be also enhanced by preparing the witness samples according to special requirements of both methods. A project utilising samples with proper design which will be placed inside a reactor and inspected after certain operation time is already in progress.

References

[1] L. Kupča, M. Březina, P. Beňo, I. Kníž: *Bulletin RINE* **XI** (1994), 1;

[2] A. A. Efimov, L. N. Moskvin, G. N. Belozerskii, M. I. Kazakov, B. A. Gusev, A. V. Semenov: *Atomnaja energia* **67** (1989), 389;

[3] J. Lipka, J. Blažek, D. Majerský, M. Miglierini, M. Seberíni, J. Cirák, I. Tóth, R. Gröne: *Hyperfine Interactions* **57** (1990), 1969;

[4] J. A. Sawicki, M. E. Brett: *Nucl. Instrum. Meth. Phys. Res.* **B76** (1993), 254;

[5] G. Brauer, W. Matz, Cs. Fetzer: *Hyperfine Interactions* **56** (1990), 1563;

[6] V. I. Khromov, V. V. Kharlamov, A. M. Chekmarev, G. A. Andropova, B. A. Mamet, A. S. Plachinda: *Hyperfine Interactions* **57** (1991), 565;

[7] *Positron annihilation*, Proceedings of the national symposium on positron annihilation held at Delhi, India, April 2-4, 1979.

[8] G. Klingelhofer, J. Froh, P. Held, H. Jäger, E. Kankeleit, R. Teucher: R.: *Hyperfine Interactions* **71** (1992), 1449;