ELSEVIER

Journal of Nuclear Materials 302 (2002) 89–95

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Positron annihilation studies of neutron irradiated and thermally treated reactor pressure vessel steels

V. Slugen [a,*], G. Kögel [b], P. Sperr [b], W. Triftshäuser [b]

[a] *Department of Nuclear Physics and Technology, Slovak University of Technology, FEI STU Bratislava, 81219 Bratislava, Slovak Republic*

[b] *Institut für Nukleare Festkörperphysik, Universität der Bundeswehr München, 85577 Neubiberg, Germany*

Received 9 October 2001; accepted 22 February 2002

Abstract

Positron annihilation lifetime measurements using the pulsed low energy positron system (PLEPS) were applied for the first time for the investigation of defects of irradiated and thermally treated reactor pressure vessel (RPV) steels. PLEPS results showed that the changes in the microstructure of the RPV-steel properties caused by neutron irradiation and post-irradiation thermal treatment can be detected. The samples originated from the Russian 15Kh2MFA and Sv10KhMFT steels, commercially used at WWER-440 reactors, were irradiated near the core at NPP Bohunice (Slovakia) to neutron fluences in the range from 7.8×10^{23} to 2.5×10^{24} m^{-2}. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Irradiation with a high neutron dose and thermal treatment induce various changes in mechanical properties of the nuclear reactor construction materials [1,2]. Therefore, the investigation of radiation damage is an interesting issue for solid-state science and applied research. The fundamental task of nuclear reactor safety research is assessing the integrity of the reactor pressure vessel (RPV) and its reliable lifetime prediction. The effect of intensive fluxes of neutrons results in considerable changes of material structures and properties. In particular, the development of the fine scale of radiation-induced defects, which impede the dislocation motion under the applied stress, known as the irradiation embrittlement, leads to degradation of mechanical properties, which can result in the partial loss of plasticity and in the increase of brittle fracture [3–8]. 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 the dislocation substructure and precipitates. These irradiation-induced diffusion processes result in the formation of defect clusters, dislocation loops and irradiation-induced precipitates [9].

Since the year 1985, positron annihilation spectroscopy (PAS) has been repeatedly used in the study of RPV steels [6–24]. 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. The lifetime of positrons trapped at radiation-induced vacancies, vacancy–impurity pairs, dislocations, microvoids, etc. is longer than the one of free positrons in the perfect region of the same material. As a result of the presence of open-volume defects, the average positron lifetime observed in structural materials is found to increase with radiation damage [13,18].

According to previous work it seems to be generally accepted that, in the RPV steels (containing more than 0.1 wt% copper), the copper and phosphorus rich precipitates play a dominant role in thermal and radiation embrittlement [3,5,25–27]. In case of Russian-type RPV

---

[*] Corresponding author. Tel.: +421-7 6029 1247; fax: +421-7 6542 7207.

E-mail address: slugen@elf.stuba.sk (V. Slugen).

PII: S0022-3115(02)00815-2

steels, the formation of carbides has been proposed as an additional micro-structural mechanism derived from comprehensive PAS [10] and transmission electron microscopy (TEM) studies [28,29], respectively. Therefore, the main purpose of the present investigation was to look for differences between non-irradiated, annealed, irradiated and post-irradiation thermally treated WWER-440 base and weld RPV materials by means of the unique positron annihilation technique (pulsed low energy positron system, PLEPS).

For the interpretation of results from PL measurements, the standard trapping model (STM) can be used [30], if the sample is homogeneous. This premise, however, does not hold for RPV-steels completely. In inhomogeneous samples, the diffusion of positrons from the various implantation sites to the trapping centres has to be considered as well [31,32]. However, the mathematical difficulties associated with the corresponding diffusion-trapping model (DTM) [33], have prevented up to now exact solutions in all but the simplest cases [34,35]. Thus it was impossible to analyse quantitatively 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. [36].

2. Neutron irradiation and thermal treatment of specimens

According to our previous work and experiences [12,22–24] a suitable set of RPV steel specimens was selected and prepared for the investigation.

In the framework of the 'Extended Surveillance Specimen Program' [24], started in 1995 at the nuclear power plant (NPP) Bohunice (Slovakia), several specimens, prepared originally for Mössbauer spectroscopy measurements [37], but because of the proper size ($10 \times 10 \times 0.05$ mm^3) and their polished surfaces also suitable for PLEPS measurement, were selected and measured before and after their irradiation, near the core of the nuclear reactor. The samples remained for 1, 2 and 3 yr at a neutron fluence in the range from 7.8×10^{23} to 2.5×10^{24} m^{-2}. Taking into account the enhancement of the irradiation due to the closer position to the reactor core ('accelerating' factor of about 10), the radiation treatment of the specimens after 3 yr is equivalent to about 30 yr of the real pressure vessel (projected lifetime of WWER-440 reactors). The chemical composition and the irradiation conditions of the studied RPV-steel specimens are shown in Tables 1 and 2.

The temperature during the irradiation was measured, using melting monitors placed inside of special containers, and reached values in the region of 285–298 °C. Neutron monitors measured the level of the neutron fluence [38].

3. Application of the pulsed low energy positron system

For the first time the PLEPS [39,40] 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 [41]. Such a disturbance is the limiting factor for the investigation of highly irradiated RPV specimens with conventional PL systems.

Several approaches to tackle the problem of the ^{60}Co prompt-peak interference with the physical part of the PL spectra have been considered so far [10,20,42,43]. Besides the PLEPS technique, one of the other acceptable solutions seems to be a triple-coincidence method using a ^{22}Na-source [20]. In this case three γ-rays – one with energy of 1274 keV and two with 511 keV – accompany each event of positron annihilation, while only two γ-rays result from the ^{60}Co decay. However, compared to conventional two-detector systems, the requirement of the triple coincidence reduces drastically the rate of accumulation of PL spectra [18,20] and in

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

Code	Type of steel	Contents of alloying elements in RPV specimens											
		C	Si	Mn	Mo	Ni	Cr	Cu	P	S	V	Co	Total
ZM-base metal	15Kh2-MFA	0.14	0.31	0.37	0.58	0.20	2.64	0.091	0.014	0.017	0.27	0.019	4.651 (wt%)
		0.65	0.62	0.38	0.34	0.19	2.84	0.088	0.025	0.030	0.29	0.018	5.471 (at.%)
ZK-weld metal	Sv10K-hMFT	0.048	0.37	1.11	0.39	0.12	1.00	0.103	0.043	0.013	0.13	0.020	3.347 (wt%)
		0.22	0.74	1.13	0.23	0.11	1.07	0.09	0.078	0.023	0.14	0.019	3.851 (at.%)

The possible nitrogen concentration is not given in the steel certificate. Nevertheless, we assume its presence approximately at the level of carbon.

Table 2
Description of the investigated specimens irradiated at the 3rd unit of NPP Bohunice (Slovakia) during 1995–1998

Sample	Material	Time of irradiation (eff. days)	Neutron fluence ($E_n > 0.5$ MeV) (m^{-2})	Total activity (kBq)	Thickness of sample (μm)
ZMNF	Base metal non-irradiated	0	0	0	60
ZM1Y	Base metal 1 yr irradiated	280	7.81E23	62	50
ZM2Y	Base metal 2 yr irradiated	578	1.64E24	109	40
ZM3Y	Base metal 3 yr irradiated	894	2.54E24	89	30
ZMNA	Sample ZMNF annealed 1 h in vacuum at 385 °C	0	0	0	60
ZKNF	Weld non-irradiated	0	0	0	55
ZK1Y	Weld 1 yr irradiated	280	7.81E23	30	45
ZK2Y	Weld 2 yr irradiated	578	1.64E24	48	25
ZK3Y	Weld 3 yr irradiated	894	2.54E24	110	47
ZKNA	Sample ZKNF annealed 1 h in vacuum at 385 °C	0	0	0	60

comparison, PLEPS reduces the measuring time by a factor 500 and enables in addition the estimation of the defect concentration.

The time resolution of PLEPS was about 240 ps FWHM. All lifetime spectra of irradiated RPV specimens contained about 3×10^7 events at a peak to background ratio in the range between 30:1 and 100:1 [41].

4. Results

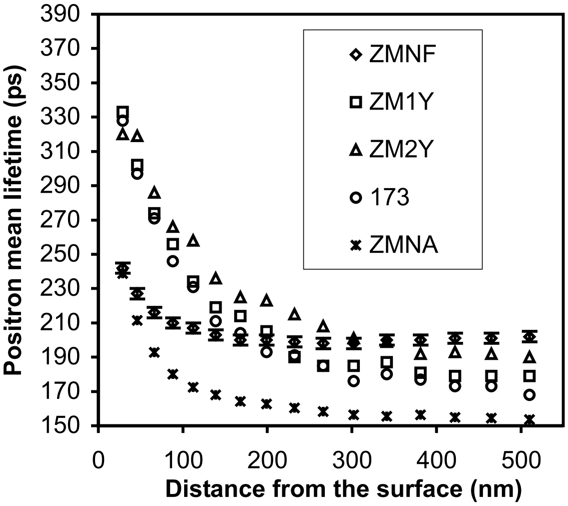

Fig. 1. Comparison of mean lifetimes τ_m of different neutron-irradiated 15Kh2MFA (base metal) steel specimens.

Table 3
Calculated PLS for different types of defects in pure iron and different carbides in low alloy Cr–Mo–V steel

Material	Positron lifetime (ps)	Reference
Fe-bulk	110	[44]
Fe-dislocations	165	[45]
Fe-monovacancy	175	[44]
Fe-divacancy	197	[45]
Fe-3 vacancy cluster	232	[45]
Fe-4 vacancy cluster	262	[45]
Fe-6 vacancy cluster	304	[45]
VC	99	[46]
$V_{0.86}Cr_{0.09}Mo_{0.04}Fe_{0.01}C$	105	[46]
Mo_2C	112	[46]
$Mo_{1.4}Cr_{0.6}C$	116	[46]
Cr_7C_3	107	[46]
$Cr_{23}C_6$	112	[46]
$Mn_{26}C_6$	99	[46]
Fe_3C	101	[46]

The calculated PLs for different types of defects in pure iron and different carbides in low alloy Cr–Mo–V steel are shown in Table 3. Experimental results for the mean PL τ_m after various irradiation treatments are shown in Figs. 1 and 2. τ_m is plotted versus the mean positron implantation depth. The characteristic decrease of τ_m with increasing positron implantation depth is typical for measurements with a low energy pulsed positron beam. It is due to the back diffusion of positrons to the surface and subsequent trapping at a surface state or in the oxide layer. The bulk value τ_1 is achieved asymptotically for larger positron implantation depths and the average value τ_1 for each specimen was obtained from six values in the depth region of more than 300 nm. The condition of the sample surfaces was not at all perfect. Because of the long irradiation period as well as the time between measurements, the surface was oxidized. The bulk mean lifetime values are shown in Fig. 3.

Each lifetime spectrum can be well analysed by two lifetime components, which below a depth about 300 nm remain fairly constant over the full depth range (see Figs. 4 and 5). The shorter lifetime τ_1 of about 170 ps is

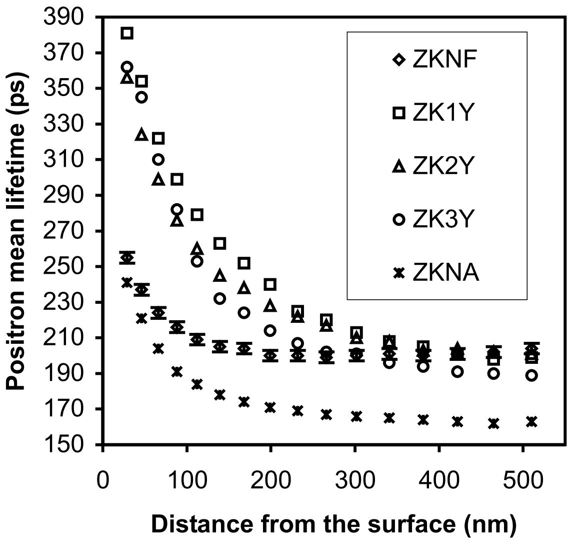

Fig. 2. Comparison of mean lifetimes τ_m of different neutron-irradiated Sv10KhMFT (weld) steel specimens.

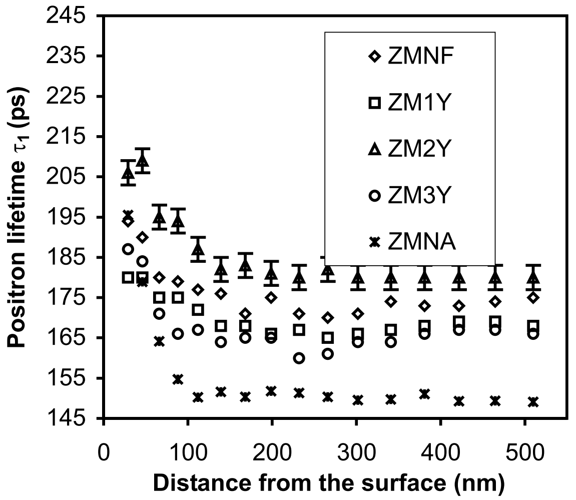

Fig. 4. Comparison of lifetimes τ_1 of RPV steel specimens (base metal) after different neutron irradiation.

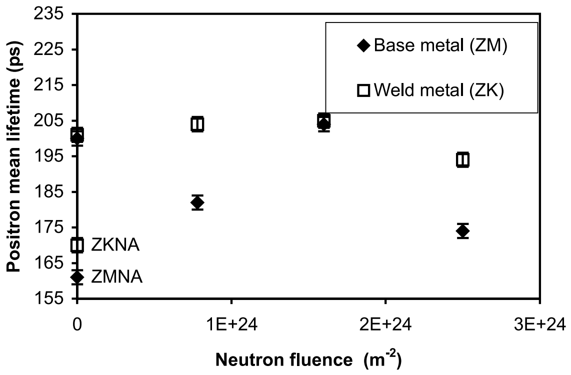

Fig. 3. Comparison of the mean lifetime τ_m of neutron irradiated RPV-steel specimens. These values were obtained as the average of six measurements in depth regions between 300 and 500 nm.

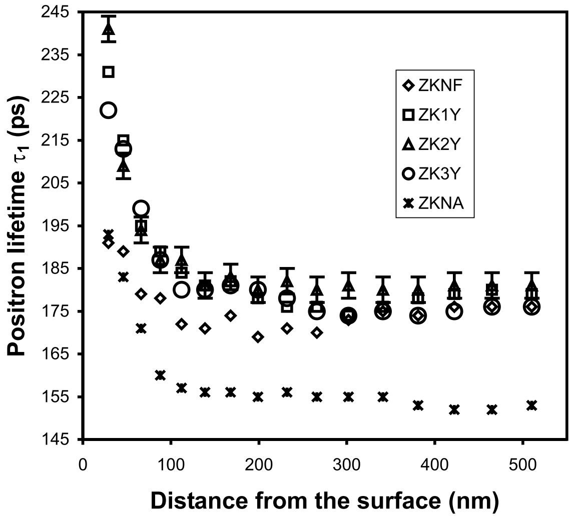

Fig. 5. Comparison of lifetimes τ_1 of RPV steel specimens (weld) after different neutron irradiation.

the dominant steel component (most likely iron monovacancies) with an intensity of about 97% in the bulk. The longer lifetime τ_2 with an intensity of about 3% or less and a value of about 400–500 ps can be assigned to the contribution of large vacancy clusters. The intensity of this component is surprisingly much higher (up to 10–12%) for those specimens, which were not thermally treated (reference specimens ZMNF and ZKMF), indicating that large vacancy clusters are already present in the material before irradiation.

The interesting results for the irradiated specimens, in respect of the defect structure in the bulk, presented in Figs. 4 and 5, are the almost constant value of τ_1 for the weld alloy as well as the oscillating behaviour of τ_1 for the base alloy, where the resulting lifetime indicate that after one year and three years irradiation obviously only dislocations are present, whereas after two years of neutron irradiation a mixture of iron mono- and divacancies is produced. The average values τ_1 in the bulk, calculated from six measurements in depths between 300 and 500 nm, are shown in Fig. 6.

However, in both base and weld alloys, the concentration of large vacancy clusters is reduced from about 12% before irradiation to 3% after irradiation. It is very likely that in addition small radiation-induced precipitates (probably carbides) with sizes of about 1–2 nm [47] developed, which are not so effective for trapping positrons.

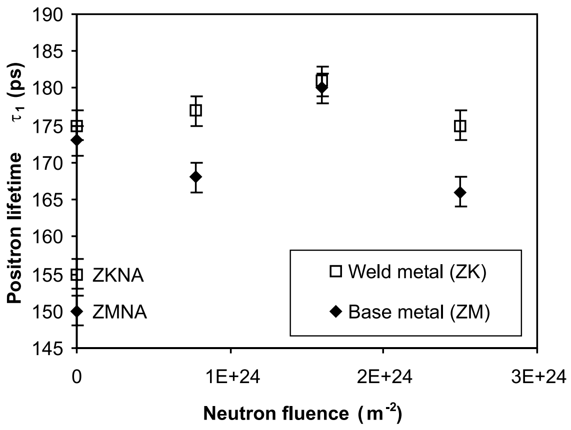

Fig. 6. Changes in lifetime τ_1 as a function of the neutron fluence. These values τ_1 were calculated as an average of six measurements in depth regions between 300 and 500 nm.

As a measure of the total thermal treatment, the Hollomon–Jaffe's parameter (H_p) was used [10,29]. The contribution of various isothermal, and isochronal treatments are summarised according to

$$H_p = \sum_i T_i(20 + \log t_i)10^{-3}, \tag{1}$$

where T_i is the annealing temperature in Kelvin and t_i is the heating time in seconds for the *i*th temperature treatment, respectively.

Decrease of the mean PL τ_m after annealing of the non-irradiated specimens (ZMNF and ZKNF) in vacuum at 385 °C for 1 h (calculated as an equivalent thermal treatment using Eq. (1)) decreased from (200 ± 3) to (161 ± 3) ps in the case of base metal (ZM) and from (201 ± 3) to (170 ± 3) ps in case of the weld metal (ZK) (see Fig. 3).

The annealing effect due to the temperature of about 290 °C and due to the neutron irradiation is in competition with the creation of the new radiation-induced defects by the neutron irradiation. This finding is supported also by the results from 1D-ACAR and Mössbauer spectroscopy (MS) measurements performed on identical specimens [37,41].

According to the MS results, the deteriorating mechanism of RPV-steel specimens because of the fast neutron bombardment is exhibited in the decrease of the pure α-iron component (hyperfine field H_{hf} of pure α-iron component was fixed in all analysis at $H_{hf,2} = 33.0$ T). This significant decrease (up to 10%) was observed in all specimens.

4.1. Additional post-irradiation thermal treatment

The steel specimens irradiated for one year were also isochronally annealed for 30 min in the temperature range of 400–550 °C in steps of 25 °C. This region was selected according to previous lifetime measurements on the same type of unirradiated material [22]. It was reasonable to start from 400 °C because the previous isothermal treatment (one year at about 290 °C) is comparable with annealing at 400 °C for 30 min. Results are shown in Fig. 7. The results from measurements performed on high-irradiated RPV-steels, which are presented in Fig. 7, show a general decrease in the steel component τ_1 as a function of increasing H_p. However, there is a marked depression of τ_1 in the range $15.0 < H_p < 17.5$ (minimum at about $H_p = 16.5$, which can be assigned to the region of about 475–500 °C of isochronal annealing). According to similar studies, performed on non-irradiated and thermally treated Russian RPV-steels, commercially used in WWER-440 and WWER-1000 reactors [22,23], it is assumed that this depression in τ_1, measured actually for the highly irradiated RPV-steels, can be correlated to the maximum of hardness (HV10 test).

For the interpretation of this correlation, a calculation of defect concentrations in neutron-irradiated RPV-steels based on the time dependent diffusion trapping equations for positrons implanted into inhomogeneous solids was performed [48]. According to these calculations the total defect concentration c_d responsible for trapping positrons for both base and weld materials, as a function of the irradiation dose, is less than in the starting material.

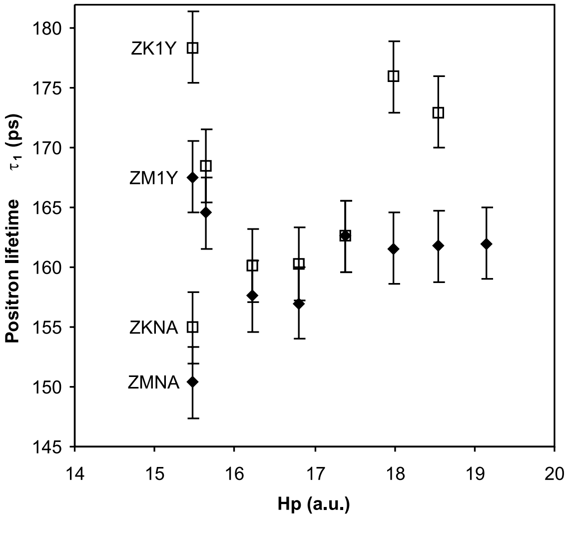

Fig. 7. Lifetimes τ_1 (average values from six measurements in depth regions between 300 and 500 nm) versus Hollomon–Jaffe's parameter for one year irradiated RPV-steels ZM1Y and ZK1Y. Lifetimes τ_1 of equivalent thermally treated but non-irradiated specimens ZMNA and ZKNA are added for comparison.

This is a surprising result. The small vacancy clusters present in the samples from the production process can be identified as divacancies and trivacancies according to their measured PL. The total concentration of these clusters is reduced in the irradiation process and most likely new defect types, e.g. precipitated carbides [20] or other complexes develop which are obviously not so effective for trapping positrons. The vacancies of these clusters are released and can 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 rather a high density of dislocations remain in the sample.

5. Conclusion

The PLEPS was used for the first time successfully in the study of intense neutron irradiated RPV-steels. Using this system, depth profiling from the surface to a specimen depth of about 500 nm was performed. Furthermore, with this system it is possible to study the microstructural changes in very small and thin specimens, thereby reducing the disturbing contribution of ^{60}Co radiation in the lifetime spectra to a minimum.

In spite of some deficiencies, e.g. surface oxides, which occurred during manipulation in hot cells and/or at the long-term storage times (up to 5 yr), new results have been obtained. During this investigation which will still continue with specimens irradiated for 5 and 10 yr in NPP Bohunice (Slovakia), the specimen preparing technology as well as the PAS methodology for irradiated RPV steels with high ^{60}Co content were tested. These experiences were effectively used in the frame of ‘Modern Surveillance Specimen Program’ started at NPP Mochovce (Slovakia) in 1998 [38]. Such programs are suitable also for the evaluation of the microstructural changes in RPV-steels and can in this way contribute to the nuclear safety of NPP. In the future, PAS techniques can be applied for the development of new types of steels with well-defined parameters (materials for fusion reactors, etc.) or by the evaluation of the effectiveness of post-irradiation thermal treatments. Application of a scanning positron microscope in the RPV-steel investigation would be surely one of the ways in the future [49].

Acknowledgements

V.S. would like to thank the IAEA (Research contracts SLR 10994, 11120) for financial support. For the specimen preparation we acknowledge the help of the NPP Research Institute VUJE Trnava (Slovakia).

References

[1] W.J. Phythian, C.A. English, J. Nucl. Mater. 205 (1993) 162.

[2] L.M. Davies, Int. J. Pres. Ves. Pip. 76 (1999) 163.

[3] Y.A. Nikolaev, A.V. Nikolaeva, A.M. Kryukov, Y.I. Shtrombakh, P.A. Platonov, in: Proceedings of the TACIS Workshop on the RPV Life Predictions, PCP3-ENUCRA-D4, 2000.

[4] M.M. Ghoniem, F.H. Hammad, Int. J. Pres. Ves. Pip. 74 (1997) 189.

[5] J. Kohopaa, R. Ahlstrand, Int. J. Pres. Ves. Pip. 76 (2000) 575.

[6] L. Debarberis, U. von Estorff, S. Crutzen, M. Beers, H. Stamm, M.I. de Vries, G.L. Tjoa, Nucl. Eng. Desg. 195 (2000) 217.

[7] U.S. NRC Regulatory Guide 1.99, Rev.1, 1977.

[8] K. Suzuki, IAEA report IWG-LMNPP-98/3, 1998.

[9] J. Kocik, E. Keilova, I. Prochazka, J. Cizek, ASTM STP (1999) 1366.

[10] G. Brauer, L. Liszkay, B. Molnar, R. Krause, Nucl. Eng. Desg. 127 (1991) 47.

[11] R. Pareja, N. De Diego, R.M. De La Cruz, J. Del Rio, Nucl. Technol. 104 (1993) 52.

[12] C. Lopes Gil, A.P. De Lima, N. Ayres De Campos, J.V. Fernandez, G. Kögel, P. Sperr, W. Triftshäuser, D. Pachur, J. Nucl. Mater. 161 (1989) 1.

[13] M. Valo, R. Krause, K. Saarinen, P. Hautojärvi, R. Hawthorne, ASTM STP 1125, Stoller, Philadelphia, PA, 1992.

[14] J. Koutsky, J. Kocik, Radiaton damage of structural materials, Academia Prague, 1994.

[15] J.H. Hartley, R.H. Howell, P. Asoka-Kumar, P.A. Sterne, D. Akers, A. Denison, Appl. Surf. Sci. 149 (1999) 204.

[16] F. Becvar, J. Cizek, L. Lestak, I. Novotny, I. Prochazka, F. Sebesta, Nucl. Instrum. Meth. A 443 (2000) 557.

[17] M.K. Miller, K.F. Russel, J. Kocik, E. Keilova, J. Nucl. Mater. 282 (2000) 83.

[18] J. Cizek, F. Becvar, I. Prochazka, Nucl. Instrum. Meth. A 450 (2000) 325.

[19] J. Cizek, I. Prochazka, J. Kocik, E. Keilova, Phys. Stat. Sol. A 178 (2000) 651.

[20] L. Van Hoorebeke, A. Fabry, E. van Walle, J. Van de Velde, D. Segers, L. Dorikens-Vanpraet, Nucl. Instrum. Meth. A 371 (1996) 566.

[21] K. Ghazi-Wakili, U. Zimmermann, J. Brunner, P. Tipping, W.B. Waeber, F. Heinrich, Phys. Stat. Sol. A 102 (1987) 153.

[22] V. Slugen, D. Segers, P.M.A. De Bakker, E. DeGrave, V. Magula, T. Van Hoecke, B. Van Waeyenberge, J. Nucl. Mater. 274 (1999) 273.

[23] V. Slugen, V. Magula, Nucl. Eng. Des. 186 (1998) 323.

[24] V. Slugen, IAEA report, SLR10994, 2000.

[25] M. Davies, A. Kryukov, C. English, Y. Nikolaev, W.L. Server, ASTM STP1366, 2000.

[26] Y. Nagai, Z. Tang, M. Hasegawa, T. Kanai, M. Saneyasu, Phys. Rev. B 63 (2001) 131110.

[27] I. Mukouda, Y. Shimomura, Mater. Sci. Eng. A 309–310 (2001) 190.

[28] V. Magula, J. Janovec, Ironmak Steelmak 21 (1994) 64.

[29] J. Kocik, E. Keilova, J. Cizek, I. Prochazka, in: METAL 2000, Proc. of 9th Int. Conf. on Metallurgy, May 2000 Ostrava, Czech Republic, Tanger Ltd., 2000, CD-ROM.

[30] W. Brandt, in: A.T. Stewart, L.O. Roelling (Eds.), Positron Annihilation, Academic Press, New York, 1967, p. 155.

[31] W. Frank, A. Seeger, Appl. Phys. 3 (1974) 61.

[32] A. Seeger, Appl. Phys. 4 (1974) 183.

[33] R.N. Nieminen, J. Laakkonen, P. Hautojärvi, A. Vehanen, Phys. Rev. B 19 (1979) 1397.

[34] W.E. Frieze, K.G. Lynn, D.O. Welch, Phys. Rev. B 31 (1985) 15.

[35] D.T. Britton, J. Phys.: Condens. Matter 3 (1991) 681.

[36] G. Kögel, Appl. Phys. A 63 (1996) 227.

[37] V. Slugen, J. Lipka, I. Toth, J. Hascik, NTD and E Int. (2002), in press.

[38] L. Kupca, P. Beno, Nucl. Eng. Desg. 196 (2000) 81.

[39] P. Sperr, G. Kögel, P. Willutzki, W. Triftshäuser, Appl. Surf. Sci. 116 (1997) 78.

[40] W. Bauer-Kugelmann, P. Sperr, G. Kögel, W. Triftshäuser, Mater. Sci. Forum 363–365 (2001) 529.

[41] V. Slugen, J. Hascik, R. Gröne, P. Bartik, A. Zeman, G. Kögel, P. Sperr, W. Triftshäuser, Mater. Sci. Forum 363–365 (2001) 47.

[42] G.H. Dai, P. Moser, J.C. Van Duysen, Mater. Sci. Forum 105–110 (1992) 941.

[43] I. Prochazka, I. Novotny, F. Becvar, Mater. Sci. Forum 255–257 (1997) 772.

[44] P. Hautojärvi, L. Pöllönen, A. Vehanen, J. Yli-Kauppila, J. Nucl. Mater. 114 (1983) 250.

[45] A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kauppila, P. Moser, Phys. Rev. B 25 (1982) 762.

[46] G. Brauer, M. Sob, J. Kocik, Report ZfK-647, 1990.

[47] J. Böhmert, M. Grosse, in: Proc. of Jahrestagung Kerntechnik 1998, Inforum, Bonn, 1998, p. 741.

[48] V. Slugen, G. Kögel, P. Sperr, W. Triftshäuser, Appl. Surf. Sci. 7893 (2002) 1.

[49] A. David, G. Kögel, P. Sperr, W. Triftshäuser, Phys. Rev. Lett. 87 (2001) 067402.