Defect and Diffusion Forum Vols. 273-276 (2008) pp 81-86
online at http://www.scientific.net
© (2008) Trans Tech Publications, Switzerland
Online available since 2008/Feb/11

The Clustering of Cu atoms in Neutron Irradiated Reactor Pressure Vessel Steels Studied by Positron Annihilation

Jakub Cizek[1,a], Ivan Prochazka[1b] and Jan Kocik[2c]

[1]Faculty of Mathematics and Physics, Charles University, V Holesovickach 2, CZ-180 00 Praha 8, Czech Republic

[2]Nuclear Research Institute Rez, plc., CZ-250 68 Husinec-Rez 130, Czech Republic

[a]jakub.cizek@mff.cuni.cz, [b]ivan.prochazka@mff.cuni.cz, [c]koc@ujv.cz

Keywords: Positron Annihilation, Conicidence Doppler Broadening, Reactor Pressure Vessel Steels, Copper Clusters, Neutron Irradiation

Abstract. Defect studies of neutron-irradiated Cr-Mo-V (VVER-440) type reactor pressure vessel steels were performed in the present work. The steels were irradiated in the nuclear power plant reactor under the conditions of a regular operation. Characterization of the irradiation induced defects was performed by two complementary techniques of positron annihilation spectroscopy: (i) positron lifetime spectroscopy was used for identification of defects and determination of defect densities, (ii) coincidence Doppler broadening was employed for investigation of Cu atom aggregates. Long range diffusion of Cu atoms is assisted by the irradiation induced vacancies. The solute Cu atoms form small clusters in the irradiated steels. Subsequent isochronal annealing of the irradiated steel leads to vacancy assisted clustering of Cu atoms and formation of small precipitates. The Cu clusters exhibit maximum diameter at 400^{o}C. Above this temperature the clusters dissolve again in the matrix.

Introduction

The neutron irradiation induced degradation (embrittlement) of reactor pressure vessel (RPV) steels begins from creation and migration of the irradiation induced vacancies and interstitials. These defects consequently influence diffusion and precipitation of admixture atoms. Obviously, a thorough microstuctural characterization 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. Using the atom probe experiment [1] it was found that the matrix Cu content in neutron irradiated steels was reduced and this reduction was accompanied by formation of Cu enriched precipitates, which could play the key role in the embrittlement. Long range diffusion of solute Cu atoms is enhanced by irradiation induced vacancies. For these reasons it is very important to characterize irradiation induced vacancy-like defects in RPV steels.

Positron lifetime (PL) spectroscopy is a well developed non-destructive technique with very high sensitivity to open-volume defects (e.g. vacancies, vacancy clusters, dislocations etc.) [2]. It enables to identify types of defects and to determine their concentration. The coincidence Doppler broadening (CDB) is another technique based on measurement of positron annihilation radiation. Although the CDB technique was introduced almost 30 years ago [3], it became widely used in materials science mainly on the last decade. The CDB technique brings information about chemical nature of atoms surrounding positron annihilation site. Thus, it allows for the analysis of chemical environment of open volume defects as well as chemical nature of solute atom clusters or precipitates. It should be mentioned that CDB technique was already successfully employed in microstructure characterizations of various types of RPV steels [4].

In the present work we investigated irradiation assisted clustering of Cu atoms in VVER-400 type RPV steel specimens. The PL spectroscopy was employed for characterization of irradiation-induced defects and the CDB technique was used for investigation small Cu clusters and their development with temperature.

Experimental Details

Specimens. The VVER-440 type low alloyed Cr-Mo-V RPV steel was studied in the present work. The chemical composition of the steel is given in Table 1. The Cu content in the steel is only around 60 at. ppm. The thermal treatment of the materials and specimen preparation were described in details in papers [5,6]. A well annealed high-purity α -iron and copper (99.9999%) were used as reference specimens for CDB measurements.

The specimens were irradiated for 3 years in surveillance positions welded to the outer surface of the core barrel of the VVER 440 reactor on the nuclear power plant. The irradiation temperature ≈ 275°C was considered to be ≈ 10°C above that of the inlet water. The neutron flux and fluence are given in Table 2. The irradiated specimen was subsequently subjected to isochronal annealing in steps of 100^{o}C / 1h. Each annealing step was performed in Ar protective atmosphere and was finished by quenching into water of room temperature. In addition, other non-irradiated VVER-440 steel specimens were aged at temperature 295°C for 5 and 10 years without any irradiation in order to study separately the influence of the elevated temperature on the microstructure of RPV steel.

Material	C	Si	Mn	S	P	Cr	Ni	Mo	V	Cu
VVER-440 Cr-Mo-V steel base metal	0.16	0.17	0.46	0.016	0.014	2.90	0.07	0.66	0.31	0.07

Note: As: 0.008, Co: 0.009, N: 0.0084, O: 0.0039

Table 1. Chemical composition (in weight %) of RPV steels steels.

Techniques. In general the samples of irradiated steels cannot be measured by a conventional PL spectrometer because they contain ^{60}Co radioisotope which emits simultaneously two photons with energies of 1174 and 1332 keV. It causes a significant distortion of measured PL spectrum by a spurious prompt peak. Therefore, PL spectroscopy of the irradiated steels was performed by a three-detector spectrometer developed specially for irradiated RPV steels [7]. Using the three-detector setup one can select the desired triple gamma ray coincidences belonging to the annihilation events (1274 keV start photon from the ^{22}Na positron emitter plus two 511 keV annihilation photons) and separate them from the undesired two gamma ray coincidences form the ^{60}Co decay events. The spectrometer provides timing resolution of 210 ps (FWHM ^{22}Na) and suppression of the ^{60}Co events by a factor of 200 with respect to the standard two-detector spectrometer. At least 5×10^6 annihilation events were collected in each PL spectrum. A ^{22}NaCl with activity of ≈ 3 MBq deposited on a 2 μm thick mylar foil was used as a positron source. The non-irradiated steels were investigated by a standard fast-fast PL spectrometer with timing resolution of 160 ps (FWHM ^{22}Na) which is described in Ref. [8]. At least 10^7 annihilation events were accumulated in each PL spectrum using ≈1 MBq ^{22}NaCl positron source on 2 μm thick mylar foil.

The CDB spectrometer consists of two HPGe detectors and commercial NIM modules operated by a PC. The overall energy resolution of the spectrometer was 1.0 keV (FWHM) at 511 keV energy. The coincidence count rate amounted of ~ 650 s^{-1} for a 1 MBq ^{22}NaCl positron source (sealed between 2 μm mylar foils). At least 10^8 events were collected in each two-dimensional spectrum, which was subsequently reduced into the one-dimensional Doppler profile and instrumental resolution cuts. The relative changes of Doppler profiles were followed as ratio curves of the Doppler profile normalized counts to those of proper reference profile (well annealed α-Fe or non-irradiated RPV steel). The CDB profiles were made symmetrical with respect to the origin and only the parts corresponding to positive Doppler shifts are shown in the paper.

Experimental positron annihilation studies were compared with theoretical calculations of positron lifetimes and high momentum profiles (HMP) from which the CDB ratio curves for a direct comparison with experiment were constructed. The calculations were performed by so called atomic superposition (ATSUP) method [9]. The correlation part of the positron potential was determined using the parameterization obtained by Boroński and Nieminen [10] within the framework of the local density approximation for positrons. The HMPs were computed according to the scheme described in Ref. [11] using the generalized gradient approximation [12].

Neutron Fluence (E>0.5 MeV)	Irradiation time	Neutron Flux (E>0.5 MeV)	τ_1	I_1	τ_2	I_2	τ_3	I_3	ρ_D
(10^{24} m^{-2})	(year)	(10^{16} $m^{-2}s^{-1}$)	(ps)	(%)	(ps)	(%)	(ps)	(%)	(10^{14} m^{-2})
-	-	-	64(5)	14.1(7)	151.6(8)	85.9(6)	-	-	2.3(4)
3.32	3	4.18	17(3)	11.3(8)	150	77.9(7)	260(10)	10.8(3)	2.0(4)
aged 5 years at 290°C			52(4)	14.7(4)	150.5(6)	85.3(4)	-	-	2.3(5)
aged 10 years at 290°C			50(5)	14.1(5)	150.1(8)	85.9(4)	-	-	2.5(5)

Table 2. A summary of PL spectroscopy results, one standard deviation is given in parenthesis.

Results and Discussion

Non-irradiated steels. The PL results for the studied specimens are shown in Table 2. The results for the non-irradiated steels have been extensively discussed in Ref. [5]. Thus, here we give only a short summary of the main conclusions. The steel exhibits tempered bainitic-ferritic microstructure. Two components with lifetime τ_1 and τ_2 were found in PL spectra of the non-irradiated steels. The majority of positrons is trapped at dislocations and contributes to the longer component with lifetime $\tau_2 \approx 150$ ps, while the shorter component is a contribution of free positrons. The mean dislocation density derived from the PL results is shown in the last column of Table 2.

The CDB ratio curves (related to the well-annealed Fe) for the non-irradiated steels are plotted in Fig. 1A together with the curve for pure reference Cu. The Fig. 1B shows the calculated CDB ratio curve (related to Fe) for Cu compared with the experimental curve. One can see that there is a good qualitative agreement of the calculated curve with experiment. Both curves exhibit characteristic shape with a pronounced maximum at 22×10^{-3} m_0c occurring due to positron annihilations with 3p Cu electrons. It should be noted that the contribution of valence electrons is not considered in the HMP computations. Thus, comparison of the calculated CDB curves with experiment is meaningful only for moments larger than $\approx 8 \times 10^{-3}$ m_0c, where the valence electron contribution becomes negligible (see the hatched area in Fig. 1B), and one can achieve only a qualitative agreement with experiment.

Irradiated steels. The PL results for the irradiated steel are shown in Table 2. A new component with a longer lifetime $\tau_3 \approx 260$ ps appeared in PL spectrum after irradiation. It is a contribution of positrons trapped at small vacancy clusters created by neutron irradiation. The size of these clusters can be deduced from comparison with theoretical calculations of positron lifetime for clusters consisting of various numbers of vacancies [9]. From comparison of our experimental results with the theoretical modeling we can conclude that the irradiation-induced vacancy clusters consist *on average* of 5 vacancies. Most probably there is certain size distribution of the vacancy clusters in the irradiated steel. The obtained lifetime corresponds to the mean value of this distribution. It is known that vacancies in Fe become mobile below room temperature and have a remarkable tendency to form small clusters [13]. Migration of these clusters takes place in the temperature range (230-330)°C, which covers also the irradiation temperature. In steels, vacancies can also form a pairs with interstitial C atoms. However, it was found that such vacancy-C pairs dissociates at 220°C, i.e. already below the irradiation temperature [13]. During irradiation of the steels at 275°C equilibrium is established between continuous creation of vacancies and their agglomeration into small clusters on one side, and vacancy recombination by annihilation with interstitials and diffusion into sinks as well as disintegration of the vacancy clusters. These equilibrium conditions are interrupted when the specimen is taken out of the reactor core. It results in certain residual concentration of vacancy clusters which are stable at room temperature and were detected in the irradiated specimen. This picture is supported by the fact the concentration of the irradiation-induced vacancy clusters is practically independent on the neutron fluence [6]. One can see in Table 2 that there is virtually no change of dislocation density in the irradiated steel.

The CDB ratio curve for irradiated steel is plotted in Fig. 1A. One can see a remarkable increase in the range corresponding to annihilations with Cu electrons compared to the non-irradiated specimen. In order to see only the effect of irradiation we plot in Fig. 2A the ratio curve for the irradiated steels related to the non-irradiated steel. The ratio curve w for the irradiated steel can be well fitted (see the solid lines in Fig,. 2A) by a curve $w = w_{Cu}\, x + 1\text{-}x$, where w_{Cu} is the ratio curve for pure Cu and x is the fraction of positrons annihilating with Cu electrons. From the fit we obtained that 15 % of positrons annihilate with Cu electrons in the irradiated steel. This fraction is two orders of magnitude higher than concentration of Cu atoms in the steel. Thus, the CDB results can not be explained by positron annihilations with randomly distributed dissolved Cu atoms. The obtained results testify that there is a strong preferential annihilation of positrons with Cu atoms. Indeed, the difference of positron affinity for Fe and Cu is ΔA = 0.97 eV [14]. Hence, aggregates of Cu atoms represent attractive sites for positrons and can confine positron wave function. The minimum radius of a Cu cluster capable of positron trapping is given by the relation [2] $r_{\min}$ $[\text{Å}] = 3.1\sqrt{\Delta A[\text{eV}]}$ = 3.05 Å, which corresponds to ≈ 14 Cu atom spherical cluster. Thus, even a small cluster consisting of tens of Cu atoms is capable of positron trapping.

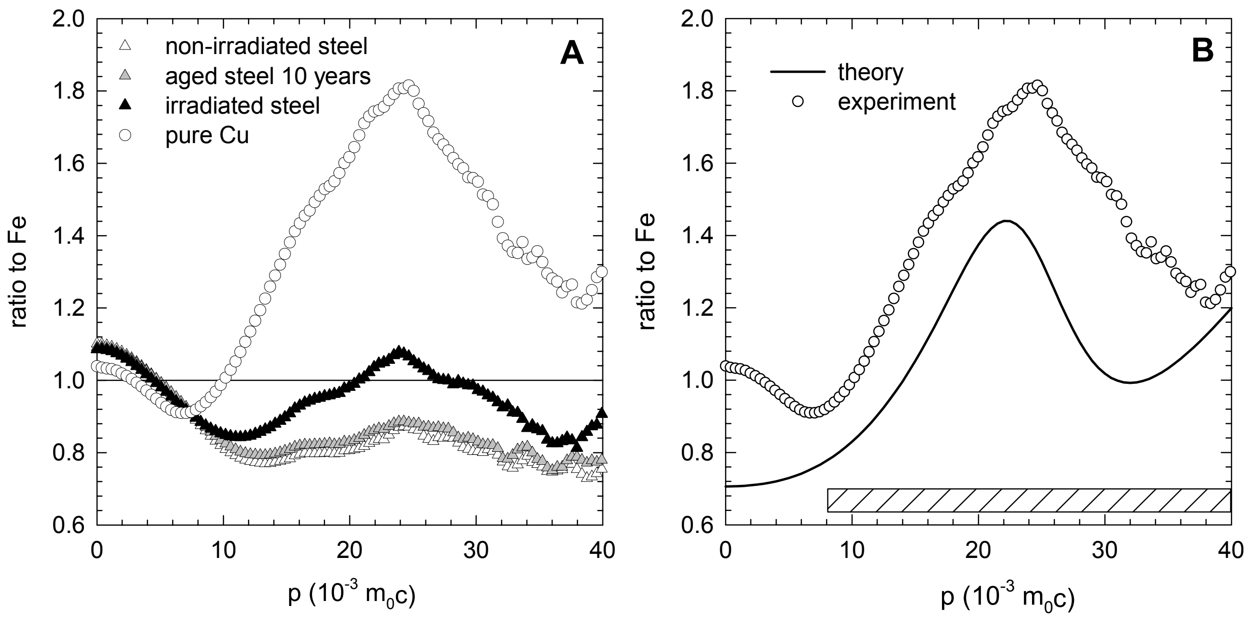

Fig. 1. (A) CDB ratio curves (related to Fe) for the studied steel, (B) calculated CDB ratio curve (related to Fe) for pure Cu compared with the experimental curve.

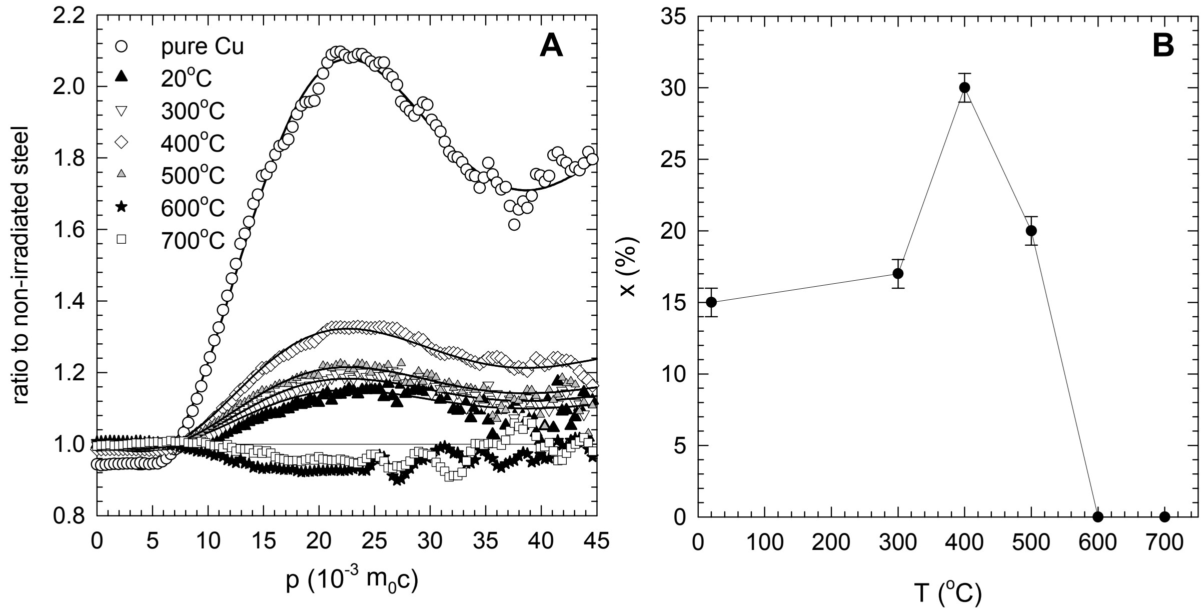

Fig. 2. (A) CDB ratio curves (related to non-irradiated steel) for the irradiated specimen subjected to isochronal annealing, (B) the fraction *x* of positrons annihilating with Cu electrons obtained from fit of the CDB ratio curves.

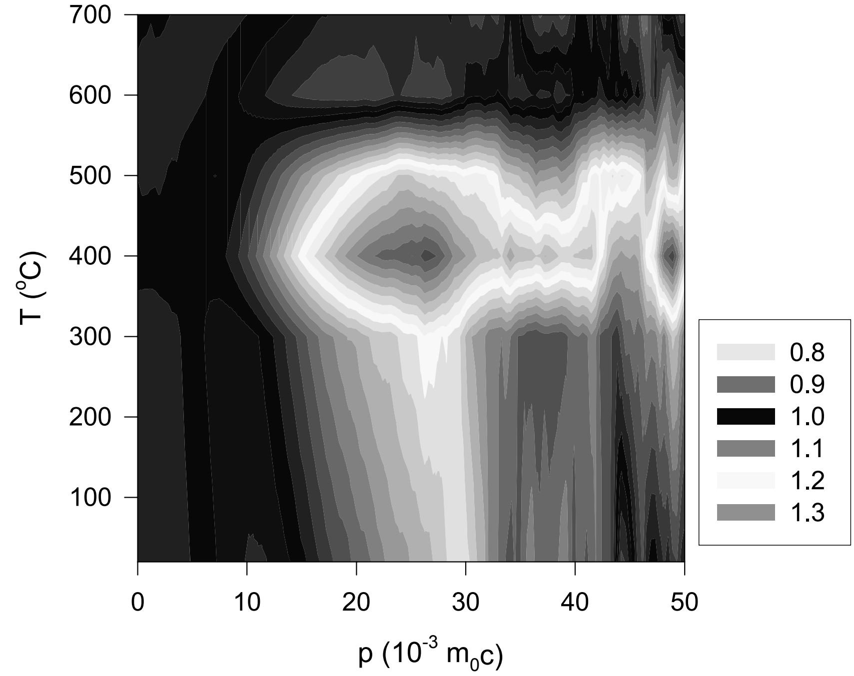

Fig. 3. A map of electron momentum for irradiated steel annealed at various temperatures.

The irradiated steel was subsequently subjected to isochronal annealing. Fig. 2A shows the CDB ratio curves for various annealing temperatures. The fraction of positrons *x* annihilating with Cu electrons obtained from a fit of the CDB ratio curves is plotted in Fig. 2B as a function of temperature. One can see a significant increase in *x* with temperature in the interval (300-400)°C due to clustering of Cu atoms. The long range diffusion of Cu atoms which is required for growth of the Cu aggregates is assisted by the irradiation-induced vacancy-like defects. The maximum contribution of positron annihilations with Cu electrons $x \approx 30\%$ is seen at 400°C indicating the maximum size of Cu aggregates. At higher temperatures the Cu clusters dissolve again in the matrix which is reflected by a decrease of the fraction of positrons annihilating with Cu atoms. A complete dissolution can be seen at 600°C where the fraction of positrons annihilating with Cu electrons becomes even lower than in the initial non-irradiated steel. A map of electron density is plotted in Fig. 3 as a function of temperature. One can clearly see the clustering of Cu atoms at ≈ 400°C.

Fig. 1A shows also the CDB ratio curve of the steel aged for 10 years at 295°C without neutron irradiation. This curve is practically identical with that for the initial non-irradiated steel showing thus no indication of Cu atoms clustering. It demonstrates that the irradiation-induced vacancy-like defects are necessary for the clustering of Cu atoms and without their assistance the clustering does not occur in this temperature range even in the time scale of years.

Summary

Defect studies of Cr-Mo-V RPV steel neutron irradiated for 3 years in VVER-440 reactor of a nuclear power plant were performed in the present work. Small vacancy clusters consisting on average of 5 vacancies were identified in the irradiated steel. Moreover, it was shown that the irradiation induced defects enhance diffusion of solute Cu atoms resulting in a formation of fine Cu aggregates. An increase of temperature from 300 to 400°C leads to coarsening of the Cu clusters. At higher temperatures the clusters dissolve again in the matrix.

Acknowledgement

This work is a part of the Research Plan MSM 0021620834 that is financed by the Ministry of Education, Youth and Sports of the Czech Republic.

References

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

[2] P. Hautojärvi, C. Corbel, in: *Proceedings of the International School of Physics "Enrico Fermi", Course CXXV*, edited by A. Dupasquier, A.P. Mills, IOS Press, Varena (1995), p. 491.

[3] K.G. Lynn, J.E. Dickman, W.L. Brown, M.F. Robbins, E. Bonderup: Phys. Rev. B Vol. 20 (1979), p. 3566.

[4] J. Cizek, F. Becvar, I. Prochazka, J. Kocik: Mater. Sci. Forum Vol. 445-446 (2004), p. 63.

[5] J. Cizek, I. Prochazka, J. Kocik, E. Keilova: Phys. Stat. Sol. (a) Vol. 178 (2000), p. 651.

[6] J. Kocik, E. Keilova, J. Cizek, I. Prochazka: J. Nucl. Mater. Vol. 303 (2002), p. 52.

[7] J. Cizek, F. Becvar, I. Prochazka: Nucl. Instr. Meth. A Vol. 450 (2000), p. 325.

[8] F. Becvar, J. Cizek, L. Lestak, I. Novotny, I. Prochazka, F. Sebesta: Nucl. Instr. Meth. A Vol. 443 (2000), p. 557.

[9] M.J. Puska, R.M. Nieminen: J. Phys. F - Metal. Phys. Vol. 13 (1983), p. 333.

[10] E. Boroński, R.M. Nieminen: Phys. Rev. B Vol. 34 (1986), p. 3280.

[11] J. Kuriplach, A.L. Morales, C. Dauwe, D. Segers, M. Sob: Phys. Rev. B Vol. 58 (1998), 10475.

[12] B. Barbiellini, M.J. Puska, T. Torsti, R.M. Nieminen: Phys. Rev. B Vol. 51 (1995), p. 7341.

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

[14] R. M. Nieminen, in: *Proceedings of the International School of Physics "Enrico Fermi", Course CXXV*, edited by A. Dupasquier, A.P. Mills, IOS Press, Varena (1995), p. 443.