DOPPLER BROADENING SPECTROSCOPY STUDY OF MODEL STEELS IN AS-RECEIVED STATE

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1. Introduction

Reactor Pressure Vessel (RPV) embrittlement represents one of the limiting factors in the lifetime of vessels of today's nuclear power plant (NPP). The present work is aimed at the investigation of the role of selected alloying elements and impurities in the RPV mechanical behaviour and its sensitivity to radiation damage [1, 2, 3]. In order to understand the role and influence of Ni, Si, Cr and Mo as alloying elements and certain impurities as Cu and P on the properties of steels, a large spectrum of ferritic steels with parametric variation of alloying elements, as well as impurities content, were developed at JRC Petten (the Netherlands). As a result 12 "model steels" were manufactured with a basic composition typical to WWER-1000 and particular cases of PWR reactor pressure vessel materials. The WWER-1000 steels contain a higher amount of some specific elements such as Cr, Mo, Ni and V when compared to typical PWR- materials. However, the Cu content considered as one of the main hardening agents in western steels, is of similar range. All other constituents are very similar in both RPV-steels.

The neutron irradiation of the steels used in the construction of nuclear reactor pressure vessel can lead to embrittlement of these materials, i.e. to the increase of the ductile-to-brittle transmission temperature and to decrease of the fracture energy, which can limit the lifetime of the NPP. It is necessary to emphasize that besides the chemical composition and initial structure of the material, the irradiation temperature, neutron fluence, neutron flux and neutron spectra play important roles in neutron embrittlement.

The present work reviews the results of as-cast model steels testing in view of identifying the possible influence of alloying elements on material properties. The next step will be the neutron irradiation of such model steels in the High Flux Reactor - LYRA irradiation facility (Petten, the Netherlands) up to a neutron fluence of about 2.5×10^{19} n.cm^{-2} and the further comparison of material properties before and after irradiation.

2. Experimental details

The nominal base compositions of the 12 model steels are derived from typical Russian and Western RPV materials: WWER-1000 (15Cr2NiMoV steel grade) and PWR (ASTM A533-B steel grade). This material matrix choice has been optimised to reveal the possible distinction of different compositions in their sensitivity to the deleterious element components during irradiation. The studied materials include mainly various Cr and Ni combinations and quite narrow range of Mo and Si content (see Table 1). More details on material preparation can be found in [4] and on previous basic material testing in [5]. For measurement purposes of Positron Annihilation Spectroscopy, the samples were prepared from as-received material by cutting the steels sheets into suitable pieces (10x10x0.2 mm), two from each material type. In order to remove surface impurities, the samples surfaces were polished after the cutting almost into a mirror quality. During the measurement of Doppler broadening of positron annihilation spectra (DBS) the momentum of the electron-positron pair is transferred to the photon pair. The motion of the annihilating pair causes a Doppler shift of the annihilation energy ΔE i.e. the broadening of the 511 keV annihilation line. Since the energy deviations ΔEγ from 511 keV are dominated by the moment of the electrons due to the relative velocities of the positron and electron before the annihilation, a line shape of the DBS carries the information about the material, where the annihilation has occurred [6].

Tab. 1. *Chemical composition of the produced model steels (in mass %) with Fe bal..*

Steels	Elements (wt. %)									
	C	**Si**	Mn	**Cr**	**Ni**	**Mo**	V	Cu	S	P
A	0.11	**0.28**	0.43	**2.22**	**<0.02**	**0.71**	0.10	0.09	0.008	0.010
B	0.11	**0.26**	0.38	**2.19**	**0.99**	**0.70**	0.10	0.10	0.008	0.010
C	0.12	**0.24**	0.38	**2.13**	**2.00**	**0.69**	0.10	0.10	0.008	0.010
D	0.11	**0.23**	0.83	**2.13**	**2.00**	**0.68**	0.10	0.09	0.008	0.009
E	0.12	**0.33**	0.77	**2.16**	**1.02**	**0.70**	0.10	0.10	0.008	0.009
F	0.12	**0.33**	1.37	**2.15**	**1.02**	**0.70**	0.10	0.10	0.008	0.010
G	0.11	**0.32**	1.36	**2.06**	**1.99**	**0.69**	0.10	0.10	0.008	0.009
H	0.12	**0.51**	1.31	**2.07**	**2.00**	**0.69**	0.10	0.10	0.008	0.010
K	0.17	**0.35**	0.78	**0.10**	**0.58**	**0.64**	-	0.07	0.005	0.009
L	0.18	**0.35**	0.77	**0.08**	**0.96**	**0.63**	-	0.05	0.005	0.010
M	0.16	**0.37**	0.74	**0.09**	**1.90**	**0.61**	-	0.05	0.005	0.010
N	0.16	**0.33**	1.27	**0.07**	**1.97**	**0.63**	-	0.06	0.005	0.010

The motion of positron-electron pairs prior to annihilation causes Doppler broadening of the photo-peak in the measured energy spectrum of the annihilation photons, characterized by the line shape parameter S. The S value is higher for positrons trapped at/annihilated in open-volume defects (corresponds to positron annihilation with valence electrons) and it is sensitive to the size and concentration of vacancy-like defects. In this case, the electron-positron annihilation results in a very narrow broadening of the 511keV peak. The W parameter (“wing” or core annihilation parameter) is taken given mostly by "high-energy" electrons from inner orbitals, thus results in a more pronounced broadening of the annihilation peak. Since the positron annihilation takes place with core electrons, the W parameter probes the chemical surrounding of the annihilation site. The parameters S and W are calculated as the normalized area of the curve in a fixed energy interval (Fig. 1). The correlation between both parameters varies for different defect types [7, 8, 9, 10].

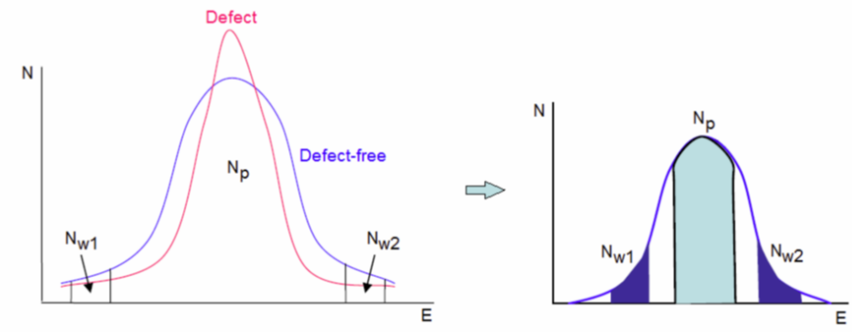

Fig.1: *Doppler broadening spectra with detailed S and W parameter determination [8, 9].*

In Fig. 1 can be seen a short procedure of the S and W estimation. N_p is a number of counts near the peak are and N_{w1}, N_{w2} represent the number of counts in wings areas. For the S parameter determination the following shall apply [11]:

$$S = \frac{N_p}{N_{total}} \tag{1}$$

$$S_{defect} > S_{defect\ free} \tag{2}$$

Parameter W is always determined from the wings of the measured data:

$$W = \frac{N_{w1} + N_{w2}}{N_{total}} \tag{3}$$

In this paper the determination of S and W parameters has been done by CDBtools3 software developed at INPE [11].

To obtain the spectra two identical coaxial HPGe detectors were used. They were shielded with led in order to decrease the noise. For Doppler broadening measurements a ^{22}Na positron source ~ 0.35 MBq, prepared by deposition of ^{22}NaCl was sandwiched between two kapton foils. Subsequently the ^{22}Na positron source was sandwiched between two equal samples. The spectra were taken until more than 10^7 counts had been accumulated in the peak. The spectral resolution was set as 0.132 keV. For S and W parameters determination the momentum intervals $(0 – 2.5) \times 10^{-3}$ m_0.c and $(12 – 20) \times 10^{-3}$ m_0c were used, respectively [6].

3. Results and Discussion

In order to enhance the differences among different spectra, the ratio curves were constructed i.e. the spectra in examination were divided by the spectrum of pure Fe which was chosen as a reference. The whole series of CDB spectra is characteristic by well-defined peaks, the change in the shape of the Doppler broadened spectrum due to annihilation with core electrons is small and it is difficult to appreciate the differences among individual spectra. As it is seen from Tab. 2 the values of S parameter vary from 0.3469 (sample K) to 0.3586 (sample C).

Tab. 2. *Obtained DBS parameters.*

DBS parameters	Steels											
	A	B	C	D	E	F	G	H	K	L	M	N
S [10^{-4}]	3516	3562	3586	3559	3554	3539	3537	3546	3469	3485	3517	3536
W [10^{-4}]	303	299	298	305	302	309	311	306	325	321	305	307

Due to the fact that individual elements can play important role in the behavior of studied materials, we compared our experimentally obtained ratio curves to the curves simulated for individual elements [12] (see Fig. 2).

Fig 3. compares the ratio curves of two steels (A and C) which are having high Cr content and mostly differ in content of Ni. Steel A contains <0.02 mass % of Ni while steel named as C is containing of about 2.00 mass %. From Fig. 3 is evident that the absence of Ni caused an increase of the curve for A alloys in the area 15 to 27 x $10^{-3}m_0c$ and decrease for C alloy in the same region. We expect that the decrease is caused by Cr and the increase by Ni content in the sample. If the steels A, B and C are compared together (see Fig. 4) the gradual increase of Ni content is lowering the ratio curves in the "Cr area" (7 to 30 x $10^{-3}m_0c$).

If we compare ratio curves of K, L, M and N steels (stable content of Si, Mo, low Cr but gradually increased Ni and increase of Mn for steel N) it seems that if more parameters is included into comparison (Mn content for example), Ni is not playing so important role anymore. If only K and L steels are compared, with almost identical content of all elements besides of Ni content, their behavior in the Ni region is not in accordance with simulation. The possible synergetic effect of Ni with other alloying elements on microstructure formation will by a subject for further study.

The ratio curves showed on Fig. 6 compare steels B,C,L and M i.e. materials with high Cr and Mo content (materials B and C) with those with their low(er) content (materials L and M). Steels B and C contain more than 2 mass % of Cr while L and M only up to 0.09 mass %. The difference in amount of Mo ranges from 0.70 mass % for steel A to 0.61 mass % for steel M. The ratio curves corresponding to B and C alloys lie over those corresponding to L and M alloys. This can be caused due to Cr as well as Mo content. According to the simulation (see Fig. 2) most of the influence of Cr and Mo lies in the range from 4 to 19 x $10^{-3}m_0c$.

The Si influence on the shape of ratio curves is seen from the G and H steels behavior. From Tab. 2 is evident that H is containing 0.51 mass % of Si while G alloy only 0.32 mass %. From ratio curves (see Fig. 7) is seen that in the area from 8 to 27 x $10^{-3}m_0c$ the ratio curve of H (higher Si content) is lying under ratio curve corresponding to G steel (lower Si content). Fig. 7shows that both ratio curves in designated area are reaching in the y axis values over 1. This could be caused by influence of other containing elements as well as by its affinity to positrons [13]. In this context it is important to note that from the elements of interest only Si having higher positron affinity than Fe, which means that small changes in Si concentration can be more visible in ratio curves.

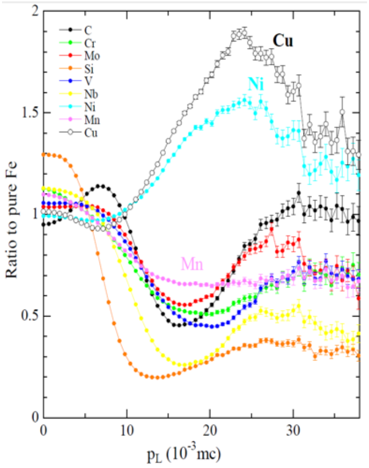

Fig.2: *Simulated DBS ratio curves [12].*

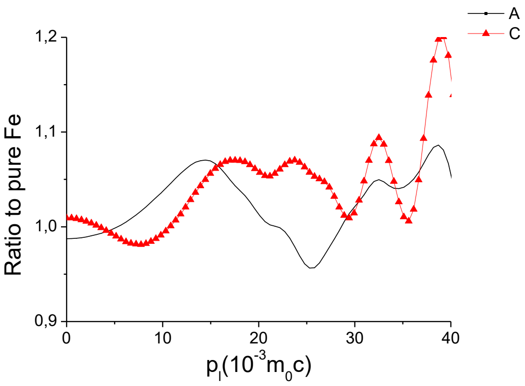

Fig.3: *Comparison of experimentally obtained ratio curves for A and C steels.*

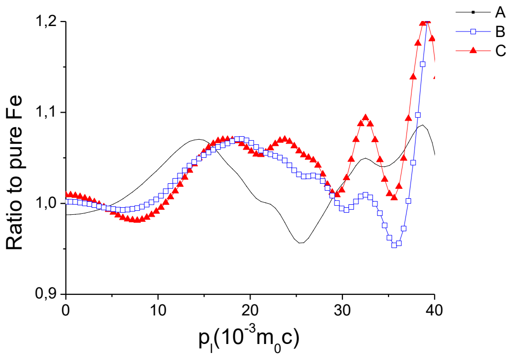

Fig.4: *Comparison of experimentally obtained ratio curves for A, B and C steels.*

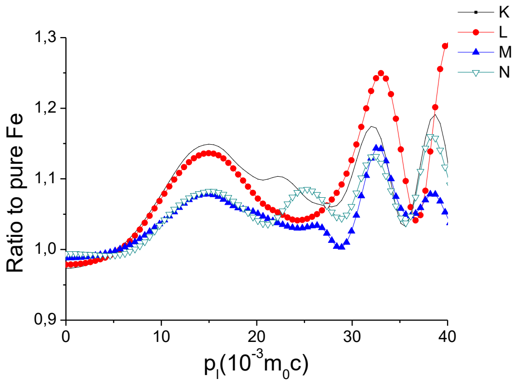

Fig.5: *Comparison of experimentally obtained ratio curves for K, L, M and N steels.*

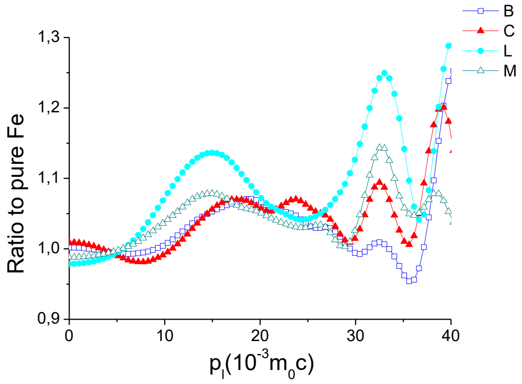

Fig.6: *Comparison of experimentally obtained ratio curves for B, C, L and M steels.*

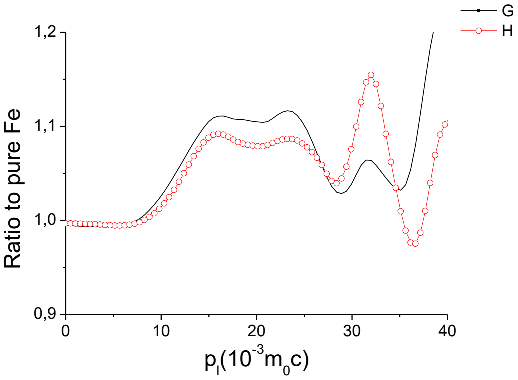

Fig.7: *Comparison of experimentally obtained ratio curves for G and H steels.*

4. Conclusions

The present work reviews the results obtained on as-cast model steels by Doppler broadening spectroscopy. The next step will be the neutron irradiation of such model steels in the High Flux Reactor -LYRA irradiation facility (Petten, the Netherlands) up to a neutron fluence of about 2.5×10^{19} n.cm^{-2} in view of identifying possible influence of alloying elements on material properties and the further comparison of material properties change due to irradiation.

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