

INVESTIGATION OF NEUTRON INDUCED AGING OF NPP KOZLODUY WWER RPV STEELS

St. Vodenicharov, Tz.Kamenova

Institute of Metal Science- BAS, 67 Shipchenstypohod Str., 1574 Sofia, Bulgaria

e-mail tz.kamfifiims.bas.bg

I. INTRODUCTION

The energy, produced by Bulgarian NPP Kozloduy, represents 45% from energy available in Bulgaria. Five nuclear units type WWER440 and WWER1000 are in operation in NPP Kozloduy at the moment (table 1)

Table 1

NPP Kozloduy	Type	Year of commission
Unit 1	WWER 440/230	1974
Unit 2	WWER 440/230	1975
Unit 3	WWER 440/230	1980
Unit 4	WWER 440/230	1982
Unit 5	WWER 1000	1987
Unit 6	WWER 1000	1991

The reactor pressure vessel (RPV) is the main component of nuclear reactor and it is in great extent responsible for safety operation of nuclear plant. A process of RPV metal aging is running due to exploitation conditions [1,2,3]. Neutron induced embrittlement is the main mechanism of this aging process. Determination of changes of metal properties is of great importance for RPV integrity assessment and for safe NPP exploitation. Therefore the control and monitoring of properties degradation and radiation life time assessment are the privilege tasks of surveillance program.

II. DETERMINATION OF EMBRITTLEMENT RATE OF RPV METAL.

Ductile to brittle fracture transition temperature (critical temperature of embrittlement) is the parameter which is commonly used for RPV radiation life time assessment. T_{kf} could be presented by next equation:

$$T_{kf} = T_{ko} + \Delta T_{kf} + \Delta T_{kn} + \Delta T_{kt} \quad (1)$$

where T_{ko} - ductile to brittle fracture transition temperature of unirradiated metal state, ΔT_{kf} -neutron induced shift, ΔT_{kn} - cyclic loading induced shift, ΔT_{kt} - thermal induced shift; $\Delta T_{kn}=0$, $\Delta T_{kt} < 10^\circ\text{C}$.

The shift (ΔT_{kf}) of ductile to brittle fracture transition temperature (ΔT_{kf}) is the parameter which is used for quantification of neutron embrittlement of RPV rate:

$$\Delta T_{kf} = T_{kf} - T_{ko} \quad (2)$$

The embrittlement rate of RPV metal depends on steel metallurgy (chemical composition, microstructure) and on irradiation condition (temperature, time, neutron flux, neutron energy spectrum).

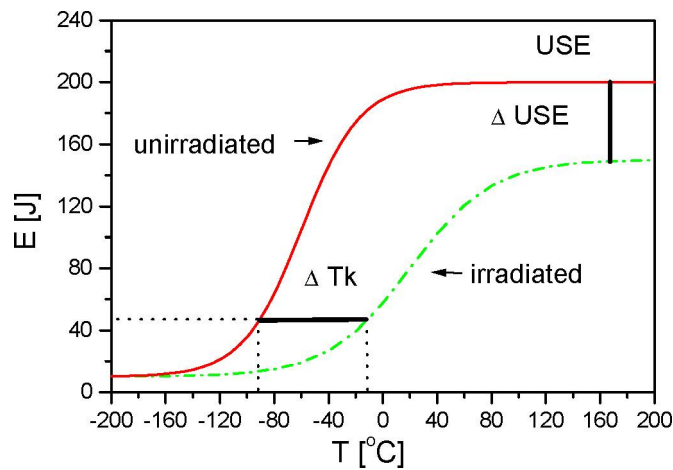


Fig.1 Charpy curve of unirradiated and irradiated metal

Two approaches for ΔT_{kf} determination are accepted in Standards:

Experimental method

- Determination of absorbed fracture energy by Three point impact bending test (Charpy test) of standard or subsize specimens manufactured from original RPV steel
- Plotting of temperature dependency of absorbed fracture energy (Charpy curve)
- Determination of T_{kf} and the shift of T_{kf} by Charpy curves of unirradiated and irradiated metal.

Charpy test of “in vessel” irradiated surveillance specimens is the base conception for T_{kf} assessment of Kozloduy Unit 5 and 6 RPV metal.

This method is not applicable for WVER440/230 where no surveillance specimens are provided for irradiation. In this case small templates could be cut from RPV inner wall (when no RPV cladding is present) and Tkf is determined by Charpy test of subsize specimens, manufactured by template material. The last method is applied for determination of real RPV metal state of Unit 1 and 2 NPP Kozloduy.

Numerical method

By Russian standard [4] ATkf could be calculated by the equation

$$ATkf = Af \cdot (F/Fo)^{0.3333} \quad (3)$$

Af- chemical factor, F (n/cm²) - neutron fluence, Fo= 10¹⁸ n/cm².

Af depends on Phosphorus, Copper and Nickel concentrations in metal.

An empirical relation is used in Russian standard for WVER 440 weld metal Af calculation:

$$Af=800 (P\% + 0.07Cu\%) \quad (4)$$

where P% and Cu% are Phosphorus and Copper concentration in weld metal respectively . Formula (1) and (4) represent the unique method for Tkf prediction of RPV with cladding (for example Unit 3 and 4 Kozloduy).

Ni presence is not taken into account in relation (4) so it is not applicable for WVER 1000 RPV metal. The experimental Af values, obtained by surveillance specimens testing are recommended for Tkf evaluation in this case.

III. UNIT 1 RADIATION LIFE TIME ASSESSMENT

III.1. PHOSPHORUS AND COPPER CONCENTRATION DETERMINATION

During manufacturing of Unit 1 RPV the P and Cu concentration have not been determined for Weld 4. A value based on factory statistics or on empirical formula have been used in documentation.

For resolving this problem, connected to Tkf calculation, the following activities aiming determination of impurity elements Phosphorous and Copper in Weld 4 metal are realized:

- wet chemical analysis of chips taken during annealing - 1989
- direct spectral analysis on RPV wall - 1995
- wet chemical and spectral analyses of microtemplate material - 1996
- spectral analysis on templates - 1996
- Phosphorous depth distribution - 1996
- Phosphorous distribution on grain boundaries - 1996

III.2. PHOSPHORUS CONCENTRATION DETERMINATION AND “IN DEPTH” DISTRIBUTION

The aim of investigations, performed in IMS [5,6], was to obtain more accurate data for the real P concentration in depth of weld 4 Unit 1 and to determine the character of P distribution on the grain boundaries. For this propose two additional microtemplates were cut from the RPV inner wall during fulfillment of Unit 1 RPV metal characterization program (1996). Copper concentration (0.10%) in weld metal was determined by atom emission analysis [7].

Wet chemical analysis

Chips from microtemplate at five depth levels (up to 7,1 mm) were taken. The determination of P content was performed according EN 10184 AC: 1991. Two independent analyses were made for each layer. The results of both analyses for P distribution in depth are demonstrated separately in Fig.2. The average value of P concentration is 0.046% (the lowest values 0.0390 and 0.0394 are omitted). A very slow decrease of P content is observed with depth increase.

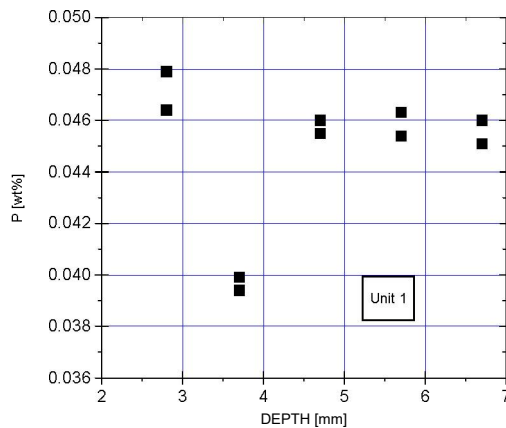


Fig. 2 Phosphorus “in wall depth” distribution, wet chemical analysis

The measured P concentrations were in good accordance with results obtained by emission spectroscopy on the same microtemplate and with the results from “on RPV wall” analysis, reported by IMS in 1995.

Scanning electron microscopy

Specimens of 1 mm² cross section, manufactured from microtemplate, were impact fractured in the analyzing chamber of Auger analyzer at minus 120°C. The identification of morphological fracture features was made by Scanning electron microscopy. It was established that the character of fracture was transgranular (Fig.3).

Numerous facets 1 to 30 mm size were produced by cleavage and quasi-cleavage. The scattering of sizes was especially high when the main crack propagated through the fan-like

central zone of weld. Elements of ductile fracture were rarely observed. No expressed intercrystal fracture was found on the surface. Some areas could be interpreted as intercrystal but the high magnification observations always revealed typical transcrystal features (Fig.3). Single intercrystal facets of few micron size could be present only in the zones of ultrafine morphology or along the secondary cracks edges, but they could not be surely resolved.

Auger Electron Analysis

The distribution of P on grain boundaries was investigated by Auger electron spectroscopy [8]. Auger electron spectroscopy showed that the large areas of transgranular fracture morphology contained mainly Iron. Some P enrichment was registered in zones containing ultrafine facets as well as in single facets along the secondary cracks edge. The ratio of Phosphorous to Iron Auger peak-to-peak heights (P/Fe) in these regions was in the range 0.20 - 0.26..

In depth distribution of P was studied using Argon ion sputtering, performed in the analyzing chamber of Auger analyzer. The depth profile was obtained by accumulation of Auger spectra after different etching times. The normalized relative intensity of P peaks plotted as a function of etching time is demonstrated in Fig.4.

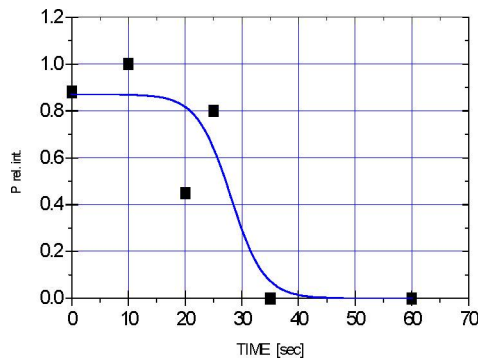


Fig.4 Phosphorus grain boundaries distribution

The results clearly show that the P-enriched layer has a limited thickness of approximately 10-20 nm. The obtained shape of depth profile is more representative for the case of P-containing precipitations than of P monolayer (segregation on grain boundary). This conclusion is supported by the presence of disperse particles on a part of the high angle grain boundaries (transmission electron microscopy observation) [9,11]. The size of precipitations and their relatively rare registration correspond well with the thickness of P enriched layer and with the frequency of their registration on the fractured surface.

No dramatic deterioration of mechanical properties, especially of toughness could result from this character of P distribution.

III.3. UNIT 1 RPV RADIATION LIFE TIME PREDICTION

Obtained values for P and Cu concentration were used for Unit 1 weld 4 metal Af calculation and for T_{kf} trend curve plotting. This allows a prognosis for Unit 1 rest live time to be made (fig-5)-

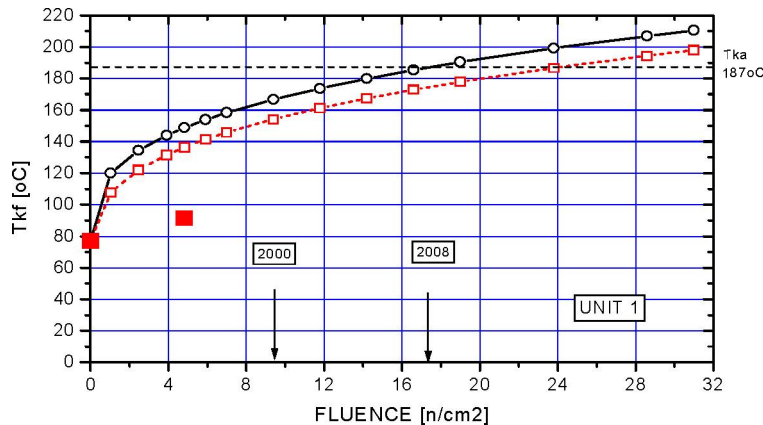


Fig.5 T_{kf} trend curve according Standard and experimental data

It is clearly seen that the radiation life time of Unit 1 will be exhausted till 2008. A second RPV metal annealing before 2008 could prolong the radiation life time of Unit 1.

III.4. CONCLUSIONS

1. The average Phosphorous content in weld 4 metal up to 8 mm depth of RPV inner wall is definitely proven to be 0.046%.
2. No typical intercrystal fracture develops in Auger specimen impact fractured at minus 120°C.
3. Phosphorous enriched zones are rarely registered on fracture areas containing small size facets. The shape of P depth distribution curve in these zones is more representative for the case of phase precipitation than for case of P segregation on grain boundaries.
4. No dramatic deterioration of mechanical properties, especially of weld metal toughness can be expected due to the registered average Phosphorous concentration in the metal and the character of Phosphorous distribution on grain boundaries.
5. The radiation life time of Unit 1 is exhausting not early than 2008.
6. Second annealing of RPV metal before 2008 will extend radiation life time of Unit 1.

IV. UNIT 5 RPV RADIATION LIFE TIME ASSESSMENT

IV.1. MATERIAL AND IRRADIATION CONDITIONS

Standard Charpy V-notched specimens, manufactured from Unit 5 RPV Weld 3 metal, were irradiated in WWER1000 surveillance positions at three different values of neutron fluence F1, F2 and F3 (Table 1). The neutron fluence on specimens was determined by measurement of Mn 54 activity of each specimens. The irradiation temperature was expected to be in the range 305 ± 5 °C.

IV.2. MICROSTRUCTURAL INVESTIGATIONS

The microstructure of weld 3 metal in unirradiated and irradiated state was investigated by means of Light, Scanning electron and Transmission electron microscopes [12]. The structure in as received state is built by layers of tempered bainite, corresponding to successive welding passes. Each layer contains two characteristic zones: central fan-like zone and periphery zone. The central zone contains coarse columnar grains diverging towards weld depth (Fig.6a,b), the periphery is built by equiaxial fine grains (Fig.6c). Carbide particles are arranged along grain boundaries, their size reaches 200 nm on high angle boundaries and 30 - 50 nm on low angle boundaries (Fig.6d). Needle-like phase (probably Mo - carbides) up to 80 nm long and rounded particles up to 10 nm are precipitated in the grains volume (Fig.6e).

No significant changes of microstructure are observed after irradiation at fluence up to $5 \times 10^{18} \text{ n/cm}^2$ except for single defects of dislocation loops contrast (size up to 10 nm) in separate regions (Fig.6f) and some increase of rounded precipitates number.

The low damage dose could explain the absence of typical dislocation loops and non-significant changes of precipitations number. The observed microstructural changes after irradiation are in good correspondence to the registered low hardening of the weld metal.

IV.3. MECHANICAL TESTING

Standard Charpy-V specimens ($10 \times 10 \times 55 \text{ mm}^3$) were tested using 300J pendulum impact testing machine. The dependence of absorbed fracture energy on testing temperature was obtained for each irradiation state. Hyperbolic tangent function was used for curve fitting. The ductile to brittle transition temperatures T_{kf} were determined at energy levels postulated according Russian standard [10].

IV.4. RESULTS

The energy criteria for Tk evaluation by Charpy curves are: 39J ($R_{0.2} < 549\text{Mpa}$) for non-irradiated and 47J ($R_{0.2} > 549\text{MPa}$) for irradiated weld metal. The experimental values of critical transition temperature are given in Table 2 together with the mean values of fluence in transition zone of Charpy curve.

Table 2

Weld metal	Fluence ($E > 0.5\text{MeV}$) [n/cm ²]	Tk [°C]
As received	-	-47
Irradiation - F1	4.07E18	-26
Irradiation - F2	5.90E18	-28
Irradiation - F3	13.24E18	-14

Experimental and predicted by Russian Guide [4] ATkf and Af values calculated according relation (4) on the basis of experimental ATk and fluence data are presented in Table 3.

Table 3.

Weld metal	ATkf measured	ATkf predicted by Guide	Af
Irradiation - F1	21	32	12.5
Irradiation- F2	19	36	10.5
Irradiation- F3	33	47	14.0
Af mean value			12.3

Table 4.

Af mean value	Ni, %	P, %	Cu, %	Af
Balakovo 1	1.88	0.009	0.028	29
Kalinin 1	1.76	0.010	0.040	35
Novovoronezh 5	1.21	0.014	0.040	8
S. Ukraine 1	1.72	0.008	0.050	16
S.Ukraine 2	1.72	0.005	0.060	6
NPP Kozloduy	1.70	0.009	0.030	12

It is seen from Table 3 that the experimental Tk shifts are lower than the expected by Guide [4] for all fluence rates. The scatter of Af values can be explained by the variation of fluence and the microstructural unhomogeneity of weld metal. The mean Af value is compared to data from other Surveillance programs [9,10,11].. The obtained Af value is close to the value of S.Ukraine 2, higher than Novovoronezh 5 and S. Ukraine 1 data and considerably lower than Balakovo 1 and Kalinin 1 - Table 4 The content of Ni , Cu and P in the irradiated weld metals of the above mentioned NPPs is presented in the table as well.

The Tkf shift dependence on fast neutron fluence for Unit 5 is demonstrated on Fig.7.

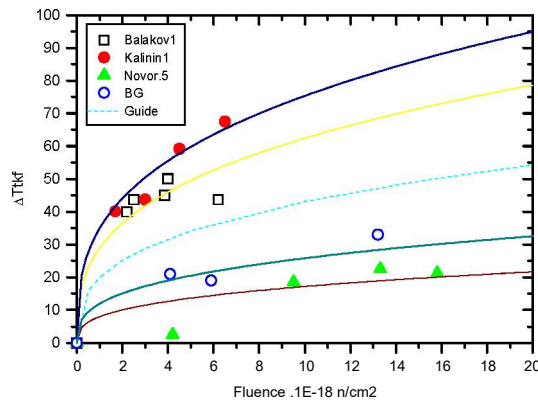


Fig.7 Tkf shift dependence on neutron fluence

The comparison of ATkf experimental curve with the trend curve calculated according Guide [10] and with the surveillance trend curves for the other three NPP Units [16,17] shows that the embrittlement rate in NPP Kozloduy our case is lower than expected by Guide, Balakovo 1 and Kalinin 1 data and close to Novovoronezh 5 data.

The observed differences in embrittlement rates could not be explained by the variations of Ni content in weld metal only. The variations of P and Cu concentration should be taken into account also, disregarding their low values. The fluence gradient on specimens, the microstructural unhomogeneity and the small number of specimens in the tested series contribute to the Af scattering also.

IV.5. UNIT 5 RPV RADIATION LIFE TIME PREDICTION

Tkf trend curve, calculated on the base of Af and Tko values obtained by surveillance specimens testing is presented on Fig.8.

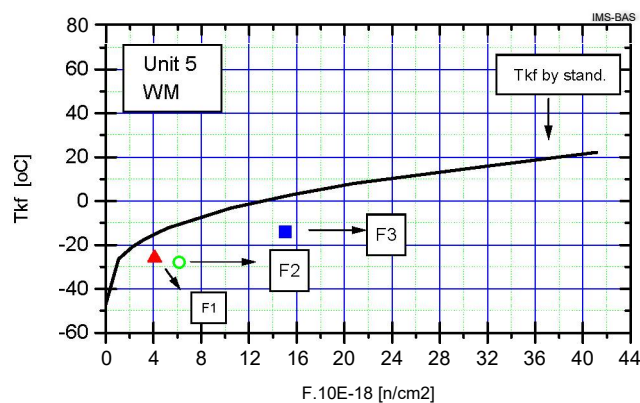


Fig.8 T_{kf} standard trend curve and experimental T_{kf} value

The prognostic curve shows that RPV integrity will be assured during the whole Unit 5 designed time.

IV.6. CONCLUSIONS

1. No significant changes of the microstructure was registered after irradiation up to $F=5E18n/cm^2$ except for a small number of defects of dislocation loops type and some increase of rounded precipitates number in grain volume.
2. The embrittlement rate of investigated weld metal at a fluence value up to one quarter of end life time RPV fluence is lower than expected.
3. The obtained A_f values are considerably lower in comparison to other WWER1000 reactors regardless of the similar Ni content.
4. Additional irradiation experiments with new surveillance assemblies design which guarantees homogenous neutron field distribution are necessary in order to obtain more reliable characteristics of embrittlement process.
5. Unit 5 RPV integrity is assured for the whole designed time.

REFERENCES

1. Iu.Balandin, I.Gorinin, Iu.Zvezdin and V.Marcov, Konstruktionnie materialy AEC, Energoatomizdat, Moskva, 1984
2. Reactor Pressure Vessel Embrittlement, IAEA-TECDOC-659, Vienna, 1992

3. R.Odette and J.Lucas, Irradiation Embrittlement of Reactor Pressure Vessel Steels: Mechanisms, Models and Data Correlation, in Steel L. (ed), ASTM STP 909, Philadelphia, 1986, pp.206 -241.
4. Regulatory Document PNAE-G-7-002-86, Strength analysis standard for equipment and piping at nuclear power plants),1986, Moskow, Energoatomizdat.
5. Technical Report Siemens-IMS, 1996
6. St.Vodenicharov, Tz.Kamenova, V.Gaidarova, E.Momchilova, Phosphorus content and distribution in NPP Kozloduy RPV 1 weld 4 metal, Nuclear Engineering and Design, 191, (1999), 335-339
7. E.Vapirev, M.Teneva, P.Tsokov, L.Dimitrov and G.Dimova, In-depth Elemental Analysis of Weld 4 of RPV of Unit 1 of KzNPP, in IAEA Report “Kozloduy Unit 1 Reactor Pressure Vessel Integrity, WWER-Sc-200, 1997
8. St.Vodenicharov, G.Zlateva, and Tz.Kamenova, Microstructure of the Metal of RPV Weld 4, Nuclear Engineering and Design, 191, (1999), 327-333
9. Kryukov A.M., Yu.N.Nikolaev, T.Palnman, P.A.Platonov, Basic results of Russian WWER1000 surveillance program, Nucl. Engin. Des. 173,1997, 333-339.
10. Planman T., H.Keinanen, R. Rintamaa, R.Ahlstrand, A.Kryukov, V.Nikolaev, Yu.Dragunov, Integrity assessment of the VVER 1000 RPVs, including embrittlement aspects, 5th. Int.Conf. on Material issues in design, manufacturing and operation of NPP structure component, St. Petersburg,Russia, June 19-26,1998, pp. 306-317.
11. Mlahov I.V.,The aspects of RPV radiation embattlement of S.Ukraine.NPP,
12. IAEA TC Project RER/9/035,WWER-SC-193,1997
13. Tz.Kamenova, St.Vodenicharov, On neutron induced embrittlement of WWER1000 weld metal, IAEA Specialist meeting on “Irradiation embrittlement and Mitigation”, Madrid, Spain,1999, IAEA DOC.IWG-LMNPP-99/2 , pp.344-354