Issues of intergranular embrittlement of VVER-type nuclear reactors pressure vessel materials

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Abstract. In light of worldwide tendency to extension of service life of operating nuclear power plants – VVER-type in the first place – recently a special attention is concentrated on phenomena taking place in reactor pressure vessel materials that are able to lead to increased level of mechanical characteristics degradation (resistibility to brittle fracture) during long term of operation. Formerly the hardening mechanism of degradation (increase in the yield strength under influence of irradiation) mainly had been taken into consideration to assess pressure vessel service life limitations, but when extending the service life up to 60 years and more the non-hardening mechanism (intergranular embrittlement of the steels) must be taken into account as well. In this connection NRC “Kurchatov Institute” has initiated a number of works on investigations of this mechanism contribution to the total embrittlement of reactor pressure vessel steels. The main results of these investigations are described in this article. Results of grain boundary phosphorus concentration measurements in specimens made of first generation of VVER-type pressure vessels materials as well as VVER-1000 surveillance specimens are presented. An assessment of non-hardening mechanism contribution to the total ductile-to-brittle transition temperature shift is given.

1. Introduction

The VVER-type reactors pressure vessels (RPV) are produced from cylindrical shells joint by welding. The materials of RPV are low-carbon low-alloyed steels. The chemical content and manufacturing technology of these steels provide high strength properties and brittle fracture resistance ensuring safe operation of a nuclear power plant during its service life.

The influence of neutron irradiation and high temperature leads to an increase in yield strength and a decrease in brittle fracture resistance [1]. The ductile-to-brittle transition describable by critical transition temperature $T_K$ is characteristic feature of bcc RPV steels. $T_K$ is determined by impact tests of V-notched Charpy specimens. The tests allows taking into account two mechanisms of the mechanical properties degradation: the strengthening of ferrite matrix caused by formation of nanosized precipitations under irradiation enriched by Ni and Mn in the case of VVER-1000 RPV and generally by Cu in the case of VVER-440 RPV [2, 3] that leads to increase in yield strength and $T_K$ and nonstrengthening mechanism caused by
segregation of impurities (P in the first place) and alloying elements on prior austenite grain boundaries that leads to intergranular embrittlement [3].

Taking into account existing projects to extend service life of VVER-1000 up to 60 years and more NRC “Kurchatov Institute” has initiated a number of works on investigations of non-hardening mechanism contribution to the total embrittlement of reactor pressure vessel steels. The main results of these investigations are described in this article. Results of grain boundary phosphorus concentration measurements in specimens made of first generation of VVER-type pressure vessels materials as well as VVER-1000 surveillance specimens and assessment of non-hardening mechanism contribution to the total ductile-to-brittle transition temperature shift is given are presented.

2. First generation of VVER-type reactors

The intergranular embrittlement of the 1st generation of VVER-type RPV materials in the USSR was not considered as a key factor, limiting their service life, because the critical element of these RPV is the weld joint metal (WM). This phenomenon is not characteristic of these WM because of microstructure peculiarity [4]. But the fact itself of grain boundary (GB) segregation of phosphorus and alloying elements in the base metal (BM) of VVER-440 RPV was mentioned in literature [5] where the non-equilibrium irradiation-induced character of the segregations was noted.

For the first time a significant effect of intergranular embrittlement was revealed when investigating BM trepans cut out of a decommissioned reactor-prototype pressure vessel wall [6]. The irradiation temperature was 275°C, fast neutron (E > 0.5 MeV) flux at inner surface of RPV wall was about 1·10\(^{16}\) m\(^{-2}\) s\(^{-1}\).

The chemical content of this BM is quite similar to this of VVER-1000 but impurities content is characteristic of VVER-440 BM and Cr content is increased: C – 0.24 wt. %, Si – 0.28 %, Mn – 0.49 %, S – 0.04 %, Cr – 3.3 %, Mo – 0.40 %, Ni – 1.07 %, P – 0.018 %, Cu – 0.01 %, Fe – bulk. It must be noted that such a combination of rather high content of P, Ni and Cr can promote GB segregation of P [3, 7].

Results of mechanical tests (impact and tensile tests) of this BM are presented in table 1 [6]. Few through-thickness (12 cm) trepans were cut out of a decommissioned reactor-prototype pressure vessel wall. The trepans were cut into layers, standard Charpy specimens (10x10x55 mm) and tensile specimens were manufactured of every layer. The results demonstrate a critical increase in \(T_K\) that implies an extremely high level of embrittlement. The character of fracture surfaces of specimens fractured at temperatures lower than \(T_K\) was almost fully brittle and predominantly intergranular (almost fully intergranular at the highest fluence). This denotes mainly intergranular embrittlement mechanism. Results of P content in GB measurements obtained by Auger electron spectroscopy (AES) are presented in figure 1. Measurement procedures are described in [6]. An increase in P content in GB with the fast neutron fluence is seen in the figure and, as will be shown below, these values at fluences above 4·10\(^{23}\) m\(^{-2}\) are much higher than the values typical of VVER RPV BM.

Unfortunately the reference unirradiated BM of this RPV was absent but the data presented affirms that the non-hardening mechanism is able to make an important contribution to RPV embrittlement under neutron irradiation. A significant share of intergranular fracture in RPV upper cover specimens fracture surface must be noted as well. This material was subjected to the operation temperature influence only during the whole operation time. It can be an indirect evidence of intergranular embrittlement under the operational temperature, though the absence of the reference material does not allow to assert this.
Table 1. Results of mechanical tests of RPV BM (steel 25Cr3NiMo).

| State of BM                           | $T_K$ (°C) | $\Delta T_K$ (°C) | $R_{p,0.2}$ (MPa) |
|---------------------------------------|------------|-------------------|-------------------|
| Inner layer of trepan, $F=6.2 \times 10^{23}$ m$^{-2}$ | more than $260$ | more than $305$ |                      |
| 1/4 of trepan thickness, $F=4.2 \times 10^{23}$ m$^{-2}$ | $+168$ | $165$ | $949$ |
| 3/4 of trepan thickness, $F=2.2 \times 10^{23}$ m$^{-2}$ | $+107$ | $152$ |                      |
| Outer layer of trepan, $F=1.4 \times 10^{23}$ m$^{-2}$ | $+120$ | $165$ |                      |
| Annealed material (650°C/2 h) | $-45^*$ | |                      |
| RPV upper cover | $-22$ | $23$ | $612$ |

accepted as $T_0$.

![Graph](image)

Figure 1. P content in GB of RPV BM (steel 25Cr3NiMo).

One more example of intergranular embrittlement of VVER-type reactors era results of investigation of two trepans of another decommissioned reactor [8]. The material was irradiated up to fast neutron fluence ($E>0.5$ MeV) of $1.05 \times 10^{24}$ m$^{-2}$ (inner layer of the RPV wall) at 290°C. Fast neutron flux at inner surface of RPV wall was equal to $3.4 \times 10^{15}$ m$^{-2}$s$^{-1}$.

Table 2. The results of Charpy impact tests.

| Location                     | $T_{10}$ (°C) | $F$ (10$^{22}$ m$^{-2}$) | $T_K$ (°C) | $\Delta T_K$ (°C) |
|------------------------------|---------------|--------------------------|------------|-------------------|
| Trepan 1, inner layer        |               | $105$                    | $+34$      | $78$              |
| Trepan 2, outer layer        | $-44$         | $11.8$                   | $+29$      | $73$              |
| Trepan 1, re-irradiated inner layer | $150$         | $+46$                    | $90$       |                   |

The chemical content of the steel is: C – 0.14 wt. %, S – 0.26 %, Mn – 0.46 %, S – 0.024 %, Cr – 2.6 %, Mo – 0.59 %, Ni – 0.34 %, V – 0.26 %, P – 0.016 %, Cu – 0.096 %. The same steel was used to manufacture VVER-440 RPV shells but the irradiation temperature is higher than that in VVER-440 (270°C).

The results of Charpy impact tests are presented in table 2.

Though detailed SEM study of Charpy specimens fracture surfaces has not been carried out, brief survey showed the significant part of intergranular areas on the surfaces of speci-
mens tested at DBTT (up to 80-90%). The specimens were cut out of different locations of the trepans and investigated using AES. Additionally a part of Trepan 1 inner layer was annealed at 475°C/100h and another part was re-irradiated with a fluence of $0.5 \times 10^{24} \text{m}^{-2}$ at a flux $3 \times 10^{16} \text{m}^{-2}\text{s}^{-1}$ and temperature of 270°C. The re-irradiated material was also investigated by AES. The results of the investigations are presented in figure 2.

Though the re-irradiation conditions differ from that at initial irradiation, the lower temperature and the higher neutron flux during the re-irradiation could mitigate the GB segregation process rather than promote it. The reference un-irradiated material was absent too, this is why P content in the initial state in figure 2 was calculated according the equilibrium GB segregation model [9].

![Figure 2. P content in GB of RPV BM (steel 15Cr2MoVA).](image)

Even taking into account uncertainties mentioned above, an irradiation dose dependence of P content in the GB of this BM can be supposed. The changes in $T_K$ were significant but lay under the normative limitations and P content in the GB was considerably lower than in the previous case. Nevertheless the prevailing intergranular fracture of irradiated specimens denotes an contribution of GB embrittlement.

Thus the above data shows that increased irradiation temperatures and Ni content can promote intergranular embrittlement of VVER-type RPV. The both factors are typical of VVER-1000 reactors.

3. **VVER-1000 reactors**

Though typical P content in VVER-1000 RPV materials is about two times lower than that in the 1st generation steels, the necessity of taking into account of the non-hardening mechanism contribution to the total embrittlement is conditioned by existing projects to extend service life of VVER-1000 up to 60 years and more. The results obtained in NRC “Kurchatov Institute” by AES [10, 11] in the frame of surveillance specimens investigations definitely reveal a significant increase in P content in GB of both base and weld metals (together with brittle intergranular fracture share [3]) at fluences typical to unextended service life. Some of the results are presented in figure 3. The AES procedures were improved by means of use of
modern AES spectrometer, by increase of measurement number and proper selection of areas in fracture surfaces [10].

Moreover the following tendencies were revealed:

- The increase in P content in GP during fast neutron irradiation is evident but significantly lower in comparison with the 1\textsuperscript{st} generation materials due to lower P content;
- The effect of intergranular embrittlement is higher in the case of WM where Ni content is higher (up to 2 wt. % when compared with about 1% in BM);
- Segregation of P to GB takes place at the operational temperature 320°C in unirradiated BM of nozzle shells, although to a lesser degree;
- Irradiation in a research reactor at high fast neutron fluxes (up to 2 orders of magnitude higher than in the case of surveillance specimens) does not lead to a significant increase of P content in GB of these materials;
- An annealing at 565°C/100 h provides recovery of irradiated WM to the initial state including GB.

It is impossible to predict VVER-1000 RPV materials behavior under irradiation during extended service life basing on the surveillance specimens tests because of the absence of specimens irradiated up to 60 years. The only way to do this is the use of accelerated irradiations in research reactors. But, as was mentioned above, the irradiation at high flexes can lead to underestimation of GB embrittlement. On the basis of mechanical tests data base analysis and a model of thermally-stimulated P accumulation in GB a procedure of using the results of accelerated irradiation to expand the application range of the dependence based on surveillance specimens testing [12]. This dependence presents $T_K$ shift as a sum of two items. The first is the $T_K$ shift after accelerated irradiation and it takes into account hardening mechanism only (due to irradiation defects and irradiation-induced precipitation). The second item takes into account intergranular embrittlement using the model of P segregation.

To estimate possible changes in $T_K$ due to increase in P content in GB a data base of AES results vs Charpy tests results was used. To avoid an influence of ferrite matrix hardening, only unirradiated VVER-1000 BM were selected with the similar yield stress values. The materials included unirradiated surveillance specimens, thermal sets of surveillance specimens and BM subjected to special heat treatments – see figure 4.
Using the least-squares method a dependence was derived: $T_K = -168 + 74 \cdot C_P^{0.2} \ (\sigma=10^\circ C)$. The dependence is also presented in figure 4 with upper and lower envelope. It predicts up to $2^\circ C$ increase in $T_K$ with 1% increase of P coverage of GB. Therefore the total $T_K$ shift during extended service life can reach tens of $^\circ C$ and must be controlled carefully.

4. Conclusions
The non-hardening mechanism conditioned by segregation of impurities (mainly P) in GB of VVER-type RPV materials under operating factors (fast neutron fluence, high temperature) can lead to a significant degradation of mechanical characteristics of the steels. The first generation RPV base metals demonstrate a propensity to intergranular embrittlement particularly at high Ni content that is typical of VVER-100 RPV.

Both VVER-1000 base and especially weld metals are liable to intergranular embrittlement but in the lesser degree than the 1st generation materials. The necessity of VVER-1000 service life extending up to 60 years forces to pay special attention to this phenomenon and take it into account when forecasting mechanical properties of RPV materials during extended service life using accelerated irradiation in research reactors. The total $T_K$ shift during extended service life can reach tens of $^\circ C$ and must be controlled carefully. The annealing procedure can be used to recover the operation characteristics of the steels.

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