ADVANCED CHARACTERISATION OF THE NEUTRON IRRADIATED VVER WELD MATERIALS

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1. Introduction

The phenomenon of radiation embrittlement is a complex process, generally related to formation of radiation induced defects. The effect of irradiation on the microstructure of nuclear structural materials has been extensively studied and reported in last 30 years [1]. Important contribution to understanding of the phenomenon has been achieved with the application of various non-destructive testing methods (NDT) [2,3].

Although a number of papers have been published on non-destructive testing of irradiated VVER materials, the correlation with the results of mechanical tests was not always satisfactory. The main reasons might be small variations in chemical compositions (various model alloys were derived from VVER materials) and/or in the irradiation parameters (flux, fluence, temperature). This has resulted in many contradictory findings reported in the literature in last two decades. It is therefore extremely important to consider not only the individual parameters, but also their complex interactions.

In principle, all processes involved in the radiation embrittlement (precipitation, segregation, void swelling etc.) affect the electronic properties of materials and change their electrical and thermal conductivity. This phenomenon is utilized in the electrical resistivity and thermo-electric power (TEP) measurements, which were successfully applied in the radiation embrittlement studies in the past. The EC-JRC institutional project AMES has led to several scientific papers on the role of Cu, P, Ni and Mn on the radiation stability. Although the effect of alloying / impurity elements on both material stability and thermoelectric parameters was well characterized, the effect of embrittlement on the TEP measurement was not fully understood yet.

The effect of neutron flux on the formation of irradiation-induced clusters at fixed fluence in reactor pressure vessel (RPV) steels was studied using the small-angle neutron scattering [8]. There was observed a visible effect of neutron flux on cluster size, whereas the total volume fraction of irradiation-induced clusters was insensitive to the level of flux. The result is compatible with a rate theory model according to which the range of applied fluxes covers the transition from a flux-independent regime at lower fluxes to a regime of decelerating cluster growth.

In contrast to current general opinion, it seems, that degradation of the material microstructure do not have to be necessarily accompanied by significant changes (increase) of the Seebeck coefficient. The value of Seebeck coefficient tends to increase on the one hand, due to precipitation of Cu, but to decrease on the other hand, due to contribution of dislocation loops. This can results into negligible shift of thermo-electric parameters in certain stages of irradiation.

In the present paper, the measurement of Seebeck coefficient are discussed together with hardness measurements of the VVER1000 weld material irradiated to ~10^{24} m^{-2}. The results were discussed in the light of the published literature in order to determine the key factors which affect the thermoelectric properties of the VVER materials and further the future nuclear structural materials.

2. Experimental

For measurement the Sv12Ch2N2MAA type of weld material was used. Typical composition of selected components is shown in Table 1. The studied material was irradiated with neutron to 5 different neutron fluencies (26; 40; 59; 89 and 110 x 10^{22} m^{-2}) at 288 ± 10 ºC (En > 0.5 MeV). The irradiation experiment was carried out in research reactor LVR15 in Nuclear Research Institute Řež (CZ) in the frame of project: "Accelerated irradiation of RPV materials of VVER-1000". The maximal bulk activity after irradiation reaches 2,852 10^4 Bqm^{-3}. Consequently all the handling with the irradiated samples was done in semi-hot cells and hot cells of NRI Řez.

Tab. 1. *Selected elements in chemical composition of studied VVER-1000 weld metal Sv12CH2N2MAA.*

	C	Mn	Cr	Ni	Mo	Cu
Min.	0.04	0.65	1.4	1.2	0.45	-
Max.	0.1	1.1	2.1	1.9	0.75	0.1

Samples in as received state were measure in the laboratory conditions. To perform measurements of irradiated materials, the specimens were taken from the hot cell and put behind a lead shielding wall of semi-hot cells, where they were fixed in the measuring equipment. The thermoelectric properties were measured using a STEAM device (Seebeck and Thomson Effect on Aged Materials) developed at JRC-Petten [4].

This STEAM measuring system consists on two copper blocks, on top of which is placed the sample. One of the blocks is heated. The temperature difference between the two sample's tips causes thermal flux across the sample and, therefore, the Seebeck and Thomson effects. Thermoelectric voltage (Δ E) and temperature difference (ΔT) are measured. The ΔS (so called relative Seebeck coefficient) corresponds to the slope of the Δ E versus ΔT curve and it is related to the chemical composition and microstructural arrangement of the material. The measurements of the relative Seebeck coefficient have been carried out on as-received and irradiated samples. The specimens were placed on two copper blocks and fixed with the constant pressure lever. The "hot" copper block was kept to have the temperature $T_2=T_1+50°C$, where T_1 is the temperature of "cold" block, equal to room temperature. The results have been obtained through the average of three measurements. Sufficient time between measurements was allowed for the device to keep the "cold" block on the constant temperature. Special attention was paid to the cleanness of the surface of both, copper blocks and the samples. All samples were mechanically polished in order to remove oxide layer resulting from the irradiation environment.

3. Results and discussions

The Seebeck coefficient of the iron-based solid solutions depends strongly on the alloying elements as their concentration especially as the content is higher than 0.1wt%. Most of the elements lower the Seebeck coefficient of iron which may result to close to zero or even negative relative value, when material is measured against copper (hereinafter the thermoelectric power coefficient is always given as a relative Seebeck coefficient or ΔS measured against copper, unless stated otherwise).

The value of ΔS obtained from our experiments for as-received material (0.61 μV/ºC) is in accordance with expectations since, in particular, nickel with weight content of 1.2 – 1.9% plays important role in lowering the coefficient of iron . This element is widely used in the thermoelectric applications due to its high (negative) Seebeck coefficient (S_{Ni} = -15 μV/ºC). Dependence of the relative Seebeck coefficient on the neutron fluence is shown in the Fig.1.

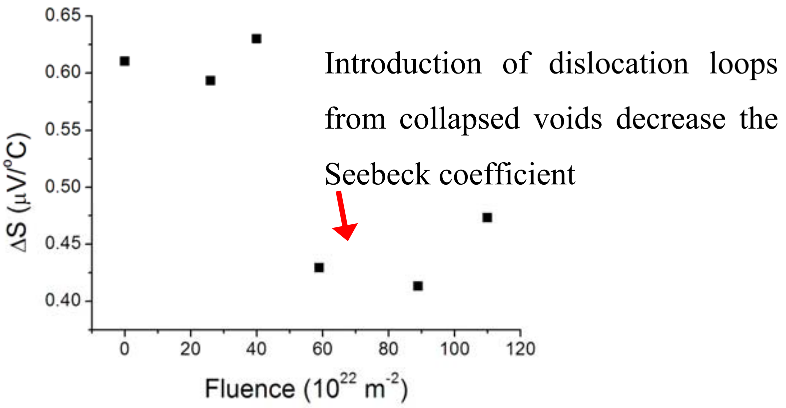

Fig. 1. *Relative Seebeck coefficient of VVER wel material irradiated at different fluence.*

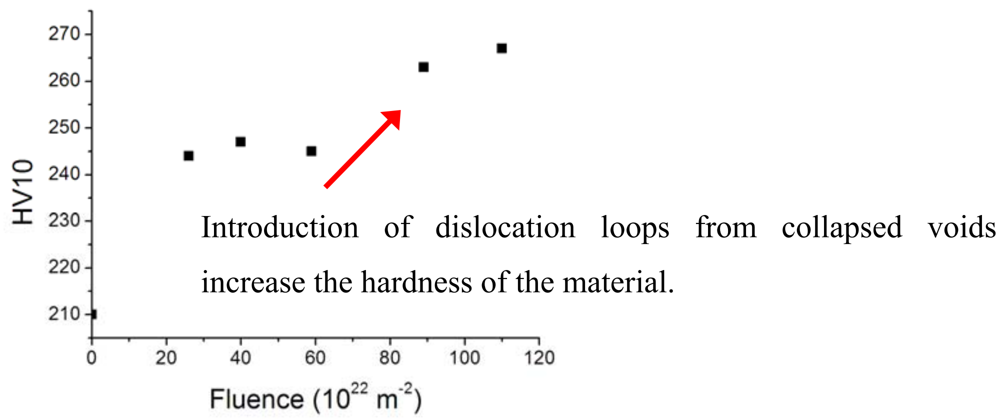

Fig. 2. *HV10 results of the VVER weld material irradiated at different fluence.*

Typically, the behaviour of Seebeck coefficient in irradiated metals is to increase with fluence, which is interpreted as an accumulation of lattice imperfections. This is mostly due to radiation induced defects, which act as scattering centres for electrons and phonons. In addition to this, also the copper precipitation increases the ΔS of irradiated materials, since copper in solid solutions reduces its value. This is, however, only a very general approach to the thermoelectric dependence on the radiation induced microstructural degradation and the phenomenon must be seen in broader context. Typical complication is the precipitation of copper rich clusters (increasing ΔS), which in the same time act as sinks for vacancies (decreasing ΔS) and therefore the mutual effect on the Seebeck parameter might be small. It has been clearly established, that the presence of dislocation in the iron decrease thermoelectric effect as well. We assume that all these competitive processes play role in the microstructure evolution of irradiated VVER weld materials, but with different dominance in different stage of irradiation.

According to positron annihilation studies, the total defect concentration c_d responsible for trapping positrons in weld materials, as a function of the irradiation dose, is less than in the starting material. The small vacancy clusters present in the samples from the production process can be identified as 2-vacancies and 3-vacancies according to their measured positron lifetime. The total concentration of these clusters is reduced in the irradiation process going on the temperature of about 300°C and most likely new defect types, e.g. precipitated carbides 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.

Two distinctive areas can be observed in the TEP results (Fig.1). We assume that in the first stage (fluence < $50x10^{22}$ m^{-2}) mostly point defects and small precipitates define the Seebeck coefficient, which does not change significantly ($0.59 < \Delta S < 0.63$). Also the irradiation and thermal induced annealing of defects presented in the materials before irradiation must be considered in the initial stage (< $30x10^{22}$ m^{-2}). Later stage of irradiation (>$60x10^{22}$ m^{-2}) is characterized by lower values of the Seebeck coefficient ($0.41 < \Delta S < 0.47$). This can be interpreted as effect of mostly dislocations, which have been characterized as to have the dominant contribution to radiation hardening of the VVER materials irradiated at high fluence. This is in agreement with our hardness measurements (Fig.2.), where the step increase of the HV10 value has been observed in the late irradiation stages. Defects concentration c_d in the VVER welds irradiated by fluence over $100x10^{22}$ m^{-2} is of about 2-6 ppm.

The both, TEP and HV10 measurements show not continuous development of material microstructure of under neutron irradiation. Similar multi-stage behavior was reported earlier for the same type of materials. Positron annihilation experiments published by Grafutin et al. [5] shows "unexpected changes" in defects related parameter after irradiation at $60x10^{22}$ cm^{-2}, which can be interpreted as collapsing of these defects into dislocation, which would be in agreement with our experiments. This complexity of processes in irradiated materials must be considered in the future application NDT techniques, particularly in the data evaluation. Combination of various embrittlement related processes might blur the sensitive NDT data or lead to results misinterpretation. Multi-technique approach will be essential here in order to utilize the strength of complementary NDT methods.

4. Conclusions

The presented experiments on VVER weld material show the evolution of radiation embrittlement up to half design fluence. The actual running development focused on increasing age of the European NPPs and envisaged lifetime extensions up to 80 years require an improved understanding of RPV irradiation embrittlement effects connected with long term operation. Phenomena which might become important at high neutron fluences (such as late blooming effects and flux effects) must be considered adequately in the safety assessments. Therefore the project LONGLIFE was initiated within the 7th Framework Programme of the European Commission [6].

The impact of individual lattice imperfections induced by radiation is changing with the neutron fluence. While the early stage of irradiation is characterized by formation of small open volume defects and dislocations, in the late stage of irradiation the role of dislocations in the embrittlement of the microstructure is dominant. It seems that above the fluence ~ $50x10^{22}$ cm^{-2} radiation induced vacancies are attracted and collapsed into dislocation loops, which can be seen in step decrease of thermoelectric (Seebeck) parameter and increase of hardness. Similar observations have been performed with positron annihilation techniques which we have used in previous period.

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5. References

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