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Contribution of thermal neutrons to radiation hardening of pure copper

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Abstract

The paper presents the results of an experiment the aim of which was to estimate directly the effect of the thermal neutron fluence on pure copper hardening. Identical specimens were irradiated in two reactors (SM-2 and RBT-6) in the dose range 10^{-3}–10^{-1} dpa at $T_{irr} = 80$ °C under substantially different, by a factor of 5, thermal neutron fluences, with other irradiation parameters being close. The results show that the elevated thermal fluence in the SM-2 reactor increases the radiation hardening of pure copper by 50% at a dose of about 10^{-3} dpa as compared with specimens irradiated in the RBT-6 reactor. The contribution of thermal neutrons proved to be much more considerable than the theoretical estimates.

1. Introduction

According to the present-day viewpoint the radiation hardening of metals under neutron irradiation at $T_{irr} < 0.3T_{melting}$ is determined by complexes of defects (interstitials and vacancies) [1–3] which are produced by agglomeration of point defects generated by neutrons displacing the metal atoms from the lattice positions, if the energy transferred by an incident particle is higher than the threshold energy E_d (for Cu ≈ 30 eV). The calculation of damage accumulation in metals is based on the Kinchin–Pease model [4], and the damage value is estimated in displacements per atom (dpa) [5,6]. Accordingly, the dose dependence of hardening and embrittlement is constructed currently as a function of dpa and not as a function of neutron fluence, as was the case 30 years ago. Though, in principle, the Kinchin–Pease model takes into account all neutrons in the reactor spectrum, the contribution to damage accumulation is determined up to 99% only by high-energy neutrons with $E > 0.1$ MeV. Although the spectra of the research reactors (ETR, SM-2, HFIR, HFR) contain 30–90% thermal neutrons ($E < 1$ eV), their contribution to the damage accumulation is considered equal to zero because of their low energy ($E \ll E_d$).

It is customary to associate the effect of thermal neutrons with the resultant transmutation which causes accumulation of helium and hydrogen in metals through the (n, p) and (n, α) reactions [7,8], Ni and Zn generation in Cu [9] or Si accumulation in Al [10]. It should be noted that the transmutation is capable of changing essentially the chemical composition of the metals only at sufficiently high irradiation doses >1 dpa.

Within the last 40 years the point of view is hotly debated whether thermal neutrons, despite their low energy, still can essentially contribute to the radiation damage [11,12]. This hypothesis is based on the observed accelerated embrittlement of reactor pressure vessel steels [12–14], where the thermal neutron fluence is much higher than the fast neutron fluence ($Ft_{thermal}/Ft_{fast} \approx 300$ to 600) compared with control specimens irradiated at $Ft_{thermal}/Ft_{fast} \approx 1$. Comparing the properties of specimens irradiated by such different fluences

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of thermal neutrons, one should take into account that reactor pressure vessel steels are irradiated at a low damage rate $\approx 10^{-11}$ dpa/s and the control specimens are irradiated at $\approx 10^{-8}$ dpa/s, i.e. the neutron flux will also affect the embrittlement [15].

As a rule, the role of the spectrum in experiments on surveillance steels is estimated by the shift of the ductile–brittle transition temperature (DBTT). The scatter in these data is wide. Steels are complicated systems with a high density of dislocations, they contain Cu and Sn atoms, which, while forming stable complexes with radiation defects, will considerably affect the strengthening and embrittlement [15,16].

In other words, up to now no direct experimental evidences of a considerable contribution of thermal neutrons to the radiation damage have been obtained. In principle, it is quite evident if neutrons of the thermal part of the spectrum do affect the process of primary damage, the most pronounced effect should exist in pure annealed metals. Such systems are practically defect-free. They have an extremely low yield strength in the initial state, i.e. 30–60 MPa and, hence, the radiation-strengthening effect caused by thermal neutrons will be more pronounced in these systems than in steels with a yield strength of $\approx$300 MPa. Nevertheless, no experiment has been yet undertaken to compare the strengthening of pure metals irradiated in the range of low doses at different $\mathrm{Ft}_{\mathrm{thermal}}/\mathrm{Ft}_{\mathrm{fast}}$. Our work presents the results of the like experiment made on pure annealed copper.

2. Experimental procedure

Channel 6 on the periphery of the SM-2 reactor (SRIAR) and Channel 2 in the active zone of the RBT-6 reactor (SRIAR) were chosen for the experiment. Fast neutron fluences in both reactors, as follows from Table 1, are close in value making it possible to provide a sufficiently close rate of radiation damage, i.e. 3.1×10^{-8} dpa/s in SM-2 and 1.6×10^{-8} dpa/s in RBT-6. In this case the average values of the thermal fluence amounted to $F_{\mathrm{thermal}} \approx 4.91 F_{\mathrm{fast}}$ for SM-2 and $F_{\mathrm{thermal}} \approx 1.03 F_{\mathrm{fast}}$ for RBT-6.

Three irradiation facilities with flat samples for tension were sequentially inserted into each reactor. The irradiation devices were installed in one and the same cell of the reactor, thus providing the identity of the neutron spectrum for all irradiation doses. The value of the accumulated irradiation dose was defined by the irradiation time varying from 12 to 1200 h in SM-2 and from 24 to 1563 h in RBT-6 providing dose variations as high as 100. The specimens were placed in vacuum-tight capsules filled with helium. The irradiation temperature was controlled by thermocouples. According to the measurement data the average irradiation temperatures amounted to (80 ± 5) °C in the SM-2 reactor and (75 ± 5) °C in RBT-6. Note that a difference of 5 °C in T_{irr} is negligible regarding the embrittlement effects.

A batch of about 200 specimens of pure copper (99.997%) made from one piece of material was investigated in the annealed state (550 °C, 2 h). The grain size in copper was 35 μm. Specimens with 10 mm gauge length were tested at $T_{\mathrm{test}} = 80$ °C and a strain rate of 1.66×10^{-3} s^{-1}. The fast and thermal neutron fluence accumulated on specimens was estimated by readings of fluence monitors located in three positions of the height and cross-section of each irradiation device.

3. Results

Fig. 1 shows the dose dependence of the yield strength change $\Delta\sigma_{\mathrm{Y}} = \sigma_{\mathrm{Y}}(\mathrm{irr}) - \sigma_{\mathrm{Y}}(\mathrm{unirr})$ of pure copper after irradiation in the SM-2 and RBT-6 reactors. As it is evident, the radiation hardening of specimens irradiated in the SM-2 reactor is distinctly higher, especially at the lowest irradiation dose 10^{-3} dpa, where pure copper is strengthened by 50 MPa more than in the RBT-6. The uniform elongation of the materials at high thermal fluence is decreased (Fig. 2). At the lowest irradiation dose of $\approx 10^{-3}$ dpa the uniform elongation of pure copper irradiated in SM-2 amounts to $\approx$20% and in RBT-6 to $\approx$30%. Thus, at low irradiation doses a five-fold increase in the thermal neutron fluence results in an

Table 1
Irradiation conditions in irradiation facilities of SM-2 and RBT-6 reactors

Reactor/irradiation facility	Irradiation time (h)	T_{irr} (°C)	$\mathrm{Ft}_{\mathrm{fast}}$, $E > 0.1$ MeV (n/m^2)	$\mathrm{Ft}_{\mathrm{thermal}}$, $E < 0.67$ eV (n/m^2)	$\mathrm{Ft}_{\mathrm{thermal}}/\mathrm{Ft}_{\mathrm{fast}}$ ratio	Radiation damage (dpa)	Displacement damage rate (dpa/s)
SM-2/1	12	80	1.89×10^{22}	9.30×10^{22}	4.92	1.32×10^{-3}	3.05×10^{-8}
SM-2/2	120	80	1.93×10^{23}	9.48×10^{23}	4.91	1.35×10^{-2}	3.12×10^{-8}
SM-2/3	1200	80	2.25×10^{24}	1.10×10^{25}	4.89	1.57×10^{-1}	3.63×10^{-8}
RBT-6/1	24	75	2.03×10^{22}	2.1×10^{22}	1.03	1.59×10^{-3}	1.62×10^{-8}
RBT-6/2	253.7	75	2.2×10^{23}	2.3×10^{23}	1.04	1.54×10^{-2}	1.68×10^{-8}
RBT-6/3	1563.3	75	1.22×10^{24}	1.3×10^{24}	1.06	8.54×10^{-2}	1.52×10^{-8}

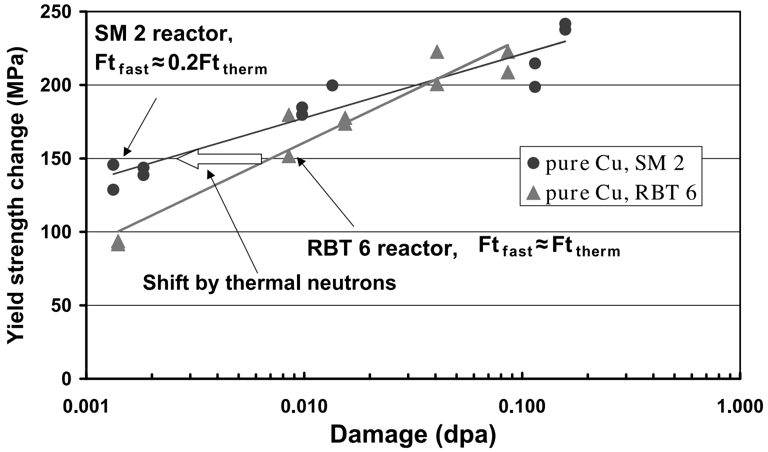

Fig. 1. Change in the yield strength $\Delta\sigma_Y = \sigma_Y(\text{irr}) - \sigma_Y(\text{unirr})$ of pure copper plotted versus the neutron damage, calculated according to the NRT standard (disregarding the thermal neutron contribution), $T_{irr} = T_{test} = 80$ °C, irradiated in the SM-2 and RBT-6 reactors.

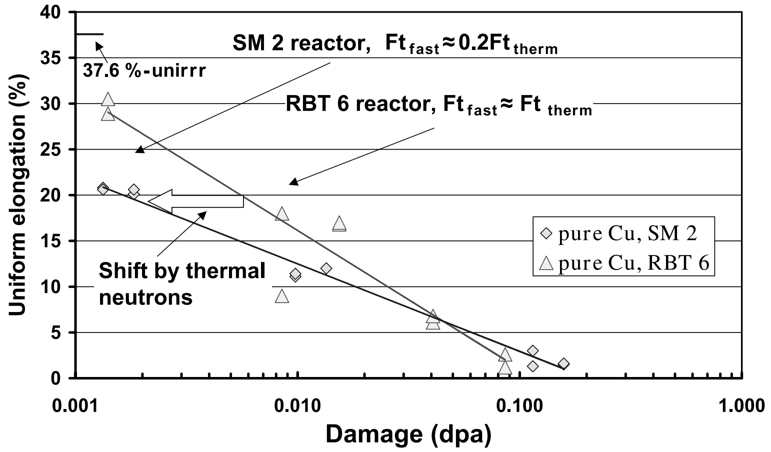

Fig. 2. Change in the uniform elongation of pure copper plotted versus neutron damage, calculated according to the NRT standard (disregarding the thermal neutron contribution) $T_{irr} = T_{test} = 80$ °C, irradiated in SM-2 and RBT-6 reactors.

increase in $\Delta\sigma_Y(\text{irr})$ by 50% and decreases in the uniform elongation $\delta_{unif}(\text{irr})$ by 30% of the absolute values. The observed effect of thermal neutrons is considerably higher than the spread in the data and in the measurement inaccuracy, which amounts to ≈7 MPa for the yield strength and ≈3% for the uniform elongation. The total elongation of the specimens irradiated in SM-2 and RBT-6 practically coincides. The ultimate strength of specimens irradiated in SM-2 is slightly higher (by 10 MPa) at low irradiation doses and this difference is negligible at doses of ≈0.1 dpa. Thus, an increase of the thermal neutron fluence increases the yield strength, reduces the uniform elongation and hence, as follows from the stress–strain curves of irradiated specimens, decreases the strengthening coefficient, i.e. the capability of pure copper for strengthening.

4. Discussion

Pure copper is the model material sufficiently well studied in radiation materials science. In particular, the data have been obtained from the effect of the irradiation dose on strengthening [1,2,17] and the defect structure development in pure copper [18–20]. In the dose range of interest to us the TEM investigations of pure copper specimens irradiated by 14 MeV neutrons in RTNSII at 90 °C [19] and by fission neutrons in the DR-3 reactor at 47 °C [20] showed that a rise in the defect complex density occurs in the dose range of 10^{-4}–10^{-2} dpa (Fig. 3).

Singh and Zinkle [21], while comparing the data on defect density in copper obtained during irradiation by fission neutrons, 14 MeV neutrons, spallation neutrons

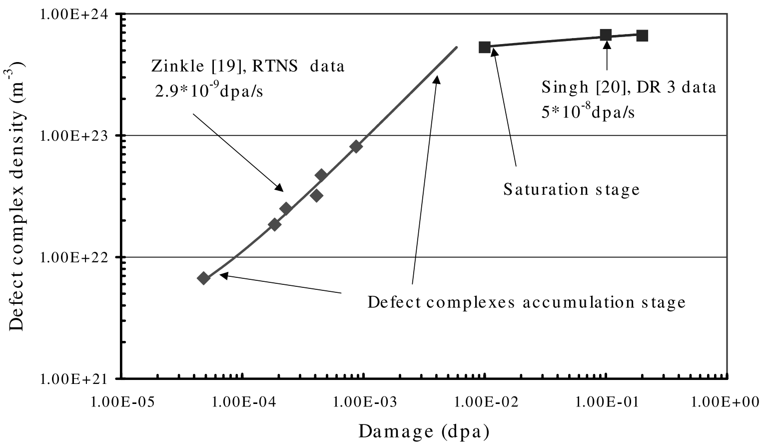

Fig. 3. Dose dependence of defect complex density of MARZ Cu, $T_{irr} = 90$ °C, 14 MeV neutrons, (RTNS II) [19]; and OFHC Cu, $T_{irr} = 47$ °C, fission neutrons, (DR-3 reactor) [20].

and 800 MeV protons, came to the conclusion that the fluence dependence of the defect complex density at doses of 10^{-4}–10^{-2} dpa corresponds to the linear or square root relation. At doses of 10^{-2}–10^{-1} dpa the complex density is saturated (Fig. 3). According to the change in the defect complex density, in our case both in SM-2 and RBT-6, the strengthening at small doses is increased with damage dose, and strengthening saturation is observed at doses higher than 0.05 dpa (Fig. 1). Therefore, when associating the strengthening with the radiation defect complex density, a distinction needs to be drawn between the strengthening saturation stage and strengthening gain stage, as it is done in Fig. 4.

Fig. 4 is supplemented by the data on irradiation of annealed MARZ Cu obtained by Heinish [2] during irradiation in the OWR reactor at $T_{irr} = 90$ °C. In this experiment the ratio $F_{fast}/F_{therm} \approx 1$ [22], i.e. close to RBT-6. Obviously the data obtained in the OWR and RBT-6 reactors in dose ranges, where strengthening gain is observed, practically coincide. Moreover, irradiation in RTNS by 14 MeV neutrons [23] also yielded the gain rate $\Delta\sigma_Y(\mathrm{irr})/\ln(\mathrm{dpa}) \approx 40$ close to that in OWR and RBT-6. Thus, the rate of yield strength gain with dose $\Delta\sigma/\ln(\mathrm{dpa})$ is at maximum, i.e. ≈40, when irradiated by 14 MeV neutrons. After irradiation by fission neutrons (in OWR and RBT-6) at $F_{fast} \approx F_{therm}\,\Delta\sigma/\ln(\mathrm{dpa})$ is 35

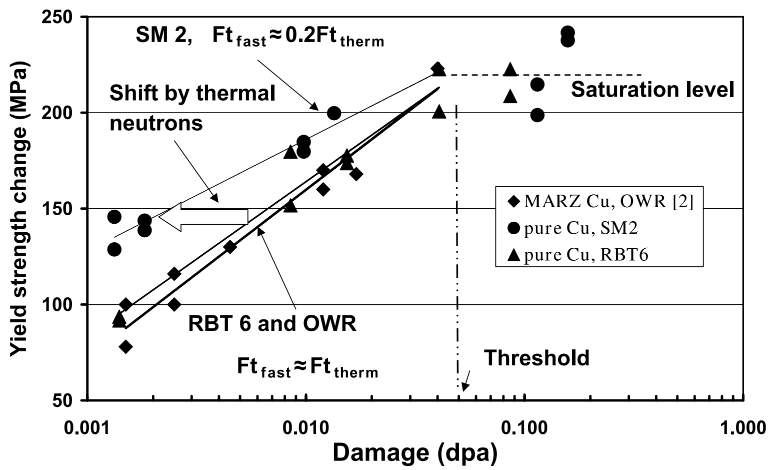

Fig. 4. Change in the yield strength of pure Cu and MARZ Cu plotted versus neutron damage, calculated according to the NRT standard (disregarding the thermal neutron contribution), with the hardening gain stage and the gain saturation stage being separated. Pure Cu (ann. 550 °C, 2 h), $T_{irr} = T_{test} = 80$ °C (SM-2 and RBT-6 reactors); MARZ Cu, (ann. 450 °C, 0.25 h), $T_{irr} = 90$ °C, $T_{test} = 20$ °C (OWR reactor) [2].

to 38. When irradiated by high fluences of thermal neutrons (in SM-2) the gain rate is reduced to ≈25.

An important point is that the maximum difference in the strengthening of pure copper specimens irradiated in SM-2 and RBT-6 is observed at the lowest dose of $\approx 10^{-3}$ dpa. This means that the contribution of thermal neutrons is at maximum at the lowest irradiation doses of 10^{-3}–10^{-2} dpa and is decreased with rising dose nearly to zero at a dose of ≈0.05 dpa. The strengthening saturation level in both reactors is very close (214 MPa for RBT-6 and 223 MPa for SM-2).

According to the present-day concepts the strengthening of neutron-irradiated materials is determined by the density and size of radiation defect complexes, which retain the dislocation motion. If irradiated copper contains N defect complexes of size d, the gain in yield strength, according to [1,18], will amount to

$$\Delta\sigma = \alpha\mu Mb(Nd)^{1/2}, \tag{1}$$

where α – the constant describing the complex strength; μ – the shear module; M – Taylor factor; b – Burgers vector.

The TEM investigations of pure copper specimens irradiated at 50–100 °C in the dose range 10^{-5}–10^{-2} dpa revealed [19–21] that the size of complexes varies only slightly with the dose and amounts to 2–3 nm. The density of the defect complexes grows, i.e. at low doses linearly with rising the dose, at higher doses (10^{-3}–10^{-2} dpa) either linearly or with the square root of the dose; the square root dependence is observed as a rule when copper contains impurities [21]. We have plotted the hardening as a function of $(\mathrm{Ft_{fast}})^{0.5}$ and $(\mathrm{Ft_{fast}})^{0.25}$. We have found out that the dependence $(\mathrm{Ft_{fast}})^{0.25}$ yields the best approximation for specimens irradiated in RBT-6 (Fig. 5). It is more difficult to judge the character of the dependence for specimens in SM-2, as in the low dose range the number of experimental points is not sufficient. Still even in this case the law $(\mathrm{Ft_{fast}})^{0.25}$ describes the data better. It is obvious that the density of produced defect complexes should be proportional to $(\mathrm{Ft_{fast}})^{0.5}$ in our irradiation, as only in this case it is possible to obtain the dependence $\Delta\sigma = \alpha\mu Mb(\mathrm{Ft_{fast}})^{0.25}$, which means that the impurities effectively capturing the free migrating defects also play a role in strengthening. The TEM investigations of specimens are under way, and only after their completion it will be possible to say with confidence, with which microstructure component (α or N or d) the effect of thermal neutrons on strengthening is associated.

Now let us examine how the obtained data correspond to the theory of the thermal neutron contribution to strengthening. At present the (n,γ) reactions in the matrix atoms (Fe for steels) and in the impurity B are considered as the major cause of an additional radiation damage produced by thermal neutrons [11,12]. The defects produced by thermal neutrons appear at a low energy, and due to it the fraction of surviving defects in this case, as theoretically predicted in [24], is much higher than for high-energy neutrons, which produce cascades. For the latter the fraction of surviving defects is small because of the recombination effectively proceeding in a cascade. Thus, an increase in the thermal neutron fluence should increase, according to the theory [12], the amount of surviving defects and complex density of defects responsible for embrittlement. The empiric estimate of a higher efficiency, by a factor of 1.7, of

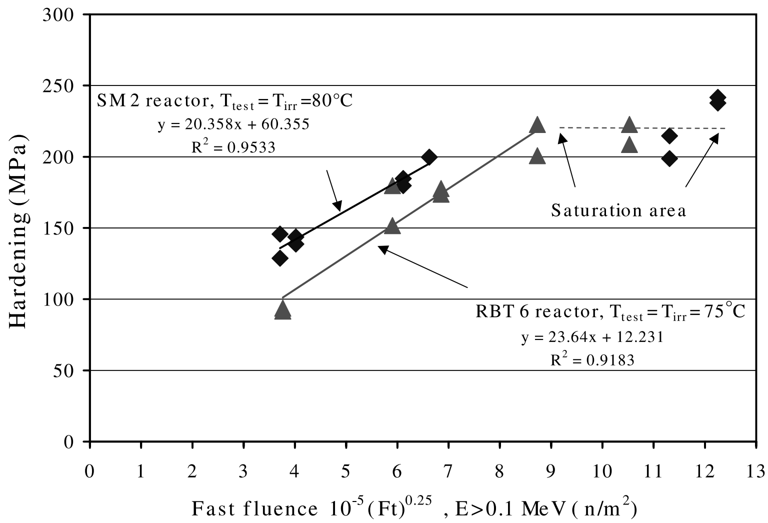

Fig. 5. Radiation hardening (change in the yield strength) of pure Cu plotted versus the one-fourth root of fast neutron fluence ($\mathrm{Ft}^{0.25}$), with the hardening gain-stage and the gain saturation stage being separated. Pure Cu (ann. 550 °C, 2 h), $T_{irr} = T_{test} = 80$ °C (SM-2 and RBT-6 reactors).

thermal neutrons in their contribution to damage is also proposed [14]. It is assumed [14] that such additional radiation damage is additively summed up with the radiation damage caused by fast neutrons and it shifts the curves of DBTT to the area of lower irradiation doses.

When the thermal neutron contribution to damage is estimated quantitatively by the methodology proposed in [14], the total contribution of fast and thermal neutrons to dpa at the lowest irradiation doses appears as follows:

$$\text{in SM-2} \quad \text{Sum (damage)} = (1.32 \times 10^{-3})_{\text{fast}} + (1.5 \times 10^{-4})_{\text{thermal}}, \tag{2}$$

$$\text{in RBT-6} \quad \text{Sum (damage)} = (1.59 \times 10^{-3})_{\text{fast}} + (2 \times 10^{-5})_{\text{thermal}}, \tag{3}$$

i.e. in RBT-6 the fraction attributed to thermal neutrons amounts to $\approx 2\%$, and hence it cannot actually affect the gain in dpa. This fraction amounts to $\approx 11\%$ in SM-2. This value, even though doubled (because of a higher efficiency of thermal neutrons in generation of surviving defects), is also insufficient for the data from two reactors to coincide.

The gain in dpa caused by thermal neutrons, even though being more appreciable, would result in a parallel shift of the strengthening curve along the dpa axis. Thermal neutrons affect the strengthening curve inclination in our experiments. This means that the thermal neutron contribution to radiation damage is more complicated than it is described by the theory and is not limited only to addition of dpa.

Copper is characterized by a high rate of Ni and Zn accumulation through the (n, γ) reaction in Cu^{63}. But at a dose of 0.001 dpa, about 4×10^{-5} Ni and Zn are accumulated in SM-2 and about 8×10^{-6} in RBT-6, i.e. at the level of the impurity content in the initial material. Certainly this amount cannot affect the strengthening, since even higher concentrations of Ni and Zn do not affect the copper yield strength [25]. The measured amount of boron in copper specimens amounted to <1 ppm, hence, an additional damage caused by the (n, α) reaction in B^{10} could also not affect the damage.

5. Conclusions

The experiment performed allowed to obtain direct experimental evidences of the substantial contribution of thermal neutrons to the radiation hardening of pure copper. The comparison of the effect of the low-temperature (80 °C) irradiation by different thermal neutron fluences on the properties of pure copper showed that an increase of the thermal neutron fluence at low ($10^{-3} \ldots 10^{-2}$ dpa) irradiation doses causes a yield strength increase and a uniform elongation decrease. It is shown that the contribution of thermal neutrons observed in the experiment is substantially higher than that predicted by the theory. Analyzing the effects of neutron irradiation in reactors ($F_{\text{fast}}/F_{\text{thermal}} \ll 1$) it is necessary to take into account the substantial contribution of thermal neutrons to radiation damage, especially at low doses.

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