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The effect of tritium and low-temperature neutron irradiation at 77 K on the structure and mechanical properties of reactor steels

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Abstract

The effect of tritium and deuterium (~0.03 at%) and also low-temperature (77 K) neutron irradiation on the physical and mechanical properties of stainless steels type Cr16Ni15Mo3Ti1 has been studied. Using an autoradiographic method, it was shown that tritium located mainly at dislocations, pinning the dislocations and slightly strengthening the steel. The resistance to small plastic deformations (the yield stress $\sigma_{0.2}$) was found to increase considerably when the fluence of fast neutrons was as high as 1.5×10^{19} n/cm^2. This is attributed to a large number of low-temperature clusters, which appear during the cascade-forming irradiation. A much lesser increase in the strength σ_B may probably be explained by dissolution of the strengthening clusters when they interact with dislocations as the test samples are being tensioned at 77 K. The degradation of the plastic characteristics was shown to be an order of magnitude larger in BCC steels and V alloys than in reactor materials possessing an FCC lattice.

1. Introduction

An ever growing interest has been shown recently to the study of the structure and physical-and-mechanical characteristics of reactor materials subject to loading with tritium and cascade-forming neutron irradiation at relatively low temperatures (77 K) and small fluences (10^{18}–10^{19} n/cm^2) [1]. This treatment permits limiting the migration of the vacancies and interstitials formed and allows one to directly observe the effect that point defects and their clusters (in cascade regions) have on the low-temperature mechanical properties of materials under fast-neutron irradiation. From a comparative study of BCC and FCC alloys, which represent candidate materials for fission and fusion reactors, it is possible to evaluate their practical significance, specifically for use in cryogenic systems of superconducting magnets, and analyze the reasons for degradation of their properties. This paper is concerned with variation of the mechanical properties of the Cr16Ni15Mo3Ti1 stainless steel when it is loaded with tritium or undergoes low-temperature (77 K) neutron irradiation.

2. Materials, thermal treatment and methods

The radiation-resistant Cr16Ni15Mo3Ti1 steel [2] had the following composition (wt%): 15.9 Cr, 15.0 Ni, 2.53 Mo, 1.02 Ti and 0.03 C, (Fe balance). The steel was examined in a single-phase FCC state after quenching from 1323 K. The mechanical properties of the steel (yield stress $\sigma_{0.2}$, tensile strength σ_B and plasticity or elongation δ) were studied during tension tests. The plasticity characteristics of the FCC steel in question were compared with those of the Fe–13Cr, V–4Ti–4Cr and V–10Ti–5Cr BCC alloys and the Cr16Ni9Mo3 steel having BCC + FCC lattices [3]. The samples were neutron-irradiated at the energy $E > 0.1$

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MeV and the temperature of 77 K in the low-temperature loop of the IVV-2M reactor. The break-test flat bars 0.3 × 2.2 mm in cross-section having the test part 10 mm long were placed in an aluminum container and were irradiated at a fluence of 1.5×10^{18}, 7×10^{18} or 1.5×10^{19} n/cm^2. The irradiated samples were transferred into a liquid-nitrogen Dewar and were allowed to stand for 2 months at 77 K to reduce the radioactivity. Then the mechanical properties of the samples were examined at the same temperature. Some of the irradiated samples were tested at 77 K after intermediate annealing at 298 K (24 h) and 473 K (1 h). Annealing of point defects was checked using the change in the electric resistivity $\Delta\rho/\Delta\rho_{77}$ (holding for 0.5 h at temperatures indicated in Fig. 3; subsequent testing at 77 K). Prior to irradiation, part of the thermally treated samples were loaded with tritium and other hydrogen isotopes from a gaseous mixture containing 40.4% T + 55.6% D + 4% H at the temperature of 873 K (3 h) and the gas pressure of 2 MPa. Subject to this treatment, the samples had ~0.03 at% hydrogen isotopes (the measurements were performed by the degassing method). Subsequent to loading with hydrogen isotopes, the samples were pressure-cooled and were held at 77 K to avoid outgassing [3]. An autoradiographic method was used to examine the distribution of tritium in the structure. The autoradiograms were prepared by a thin-film technique (the autoradiograms less than 1 μm thick) using a photoemulsion, which permits recording the soft β-radiation of tritium. A carbon replica ~25 nm thick served as the autoradiogram substrate. The structure was examined in the JEM-200CX electron microscope.

3. Results and discussion

3.1. Strengthening of the steel under neutron irradiation

Fig. 1 (curves 1 and 3) shows the experimental data and the approximating dependences, which reflect the effect of the fluence of fast neutrons on the incremental yield stress $\Delta\sigma_{0.2}$ and the incremental tensile strength $\Delta\sigma_B$ of the quenched Cr16Ni15Mo3Ti1 stainless steel having an FCC lattice. The observed strengthening is due to the fact that neutrons whose energy exceeds 0.1 MeV form small defect regions (clusters) in displacement cascades. These regions impede the movement of dislocations and strengthen the steel as in the case of precipitation hardening. Therefore the dependence of $\Delta\sigma$ on the neutron fluence F was approximated by a power function [1,4], which determines the effect of the cluster concentration on strengthening. The cluster concentration is directly proportional to the neutron fluence (see Eqs. (1) and (2)). A remarkable point is an extremely large increase in the resistance to small plastic deformations at 77 K under low-temperature neutron irradiation: $\sigma_{0.2}$ changes from 530 to 1097 MPa. This phenomenon occurs at a fluence of 1.5×10^{19} n/cm^2 and a small damaging dose of ~0.005 displacements per at-

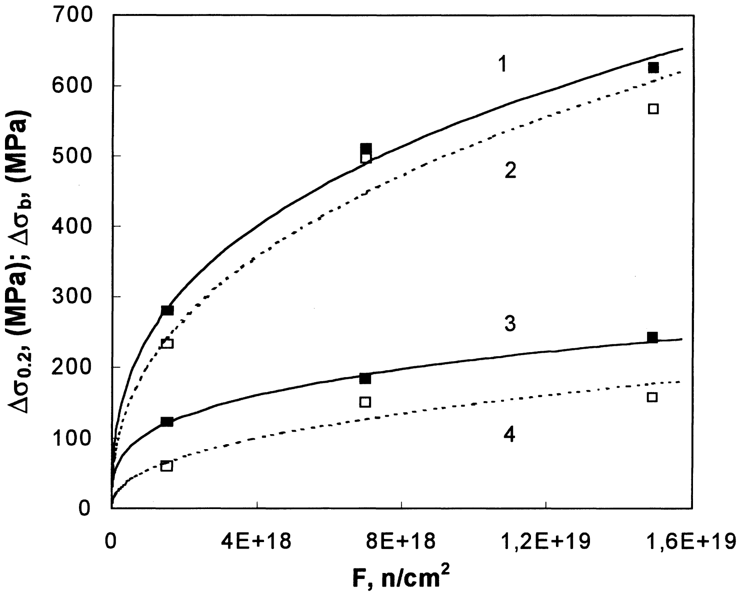

Fig. 1. Dependence of the incremental yield stress $\Delta\sigma_{0.2}$ (1, 2) and the incremental tensile strength $\Delta\sigma_B$ (3, 4) on the fast neutron fluence F for the Cr16Ni15Mo3Ti1 steel in the initial quenched state (2, 4) and after loading with tritium and deuterium (1, 3). The irradiation and test temperature are 77 K.

om (dpa). At fluences (1.5–15) × 10^{18} n/cm^2 the dependences of the incremental yield stress and the incremental tensile strength are given by the expressions $\Delta\sigma_{0.2} = 1 \times 10^{-5}\ F^{0.4}$ and $\Delta\sigma_{\mathrm{B}} = 7 \times 10^{-7}\ F^{0.44}$.

If the concentration and dimensions of the clusters are known, it is possible to calculate the variation of the yield stress in terms of the Orowan or Nabarro models correspondingly for by-passing or cutting the clusters by dislocations. The concentration of the clusters, n, formed under irradiation is directly proportional to the fluene F, depends on the neutron elastic scattering cross-section $\sigma_n(E_n)$, and is determined by the following expression [5]: $n = N_0\sigma_n(E_n)F = \lambda F$, where N_0 stands for the total number of atoms per irradiated unit volume. With the elastic scattering cross-section $\sigma_n(E_n) = 2.1 \times 10^{-32}$ n/cm^2 (^{56}Fe core, the neutron energy $E_n = 1$ MeV) [5] and the fluence $F = 7 \times 10^{18}$ n/cm^2, rough calculations give the cluster concentration $n \approx 10^{18}$ cm^{-3}. n is overestimated considering possible overlapping of part of the clusters during irradiation and the approximate character of the calculations.

The concentration of radiation-induced vacancies is high at the center of the low-temperature cluster, while the number of interstitials increases at its periphery. When the sample is heated from 77 to 298 K, more mobile interstitials leave and the cluster dimension decreases. According to the calculations [1], subsequent to irradiation in the IVV-2M reactor the dimensions of the low-temperature (77 K) and ordinary vacancy clusters (298 K) in the steel equal 8 and 4 nm, respectively. Microscopic observation with the method given in Ref. [6] showed that at 298 K the diameter d of vacancy clusters in the Cr16Ni15Mo3Ti1 steel irradiated with fast neutrons (77 K, fluence 1.5 × 10^{-19} n/cm^2) equals ~6 nm (Fig. 2(a)), while the cluster-to-cluster spacing $1 \approx 15$ nm, a value which corresponds to the cluster concentration $n \approx 1.6 \times 10^{17}$ cm^{-3} and the cluster volume fraction $f = 3.4\%$.

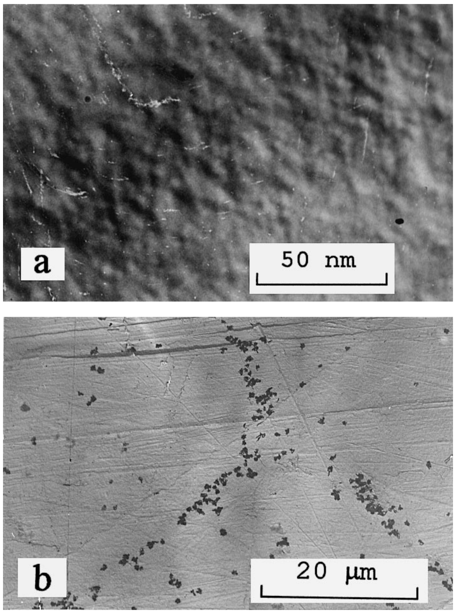

Fig. 2. Structure of the irradiated ($F = 1.5 \times 10^{19}$ n/cm^2) Cr16Ni15Mo3Ti1 steel (a) and a microautoradiogram (b) characterizing the distribution of tritium in the structure of the quenched Cr16Ni15Mo3Ti1 FCC steel.

Given $F = 7 \times 10^{18}$ n/cm^2, $n = 5 \times 10^{17}$ cm^{-3} and $d = 8$ nm, the calculated strengthening [4] (in terms of the model when dislocations by-pass clusters) $\Delta\sigma_{0.2} = 409$ MPa, which is close to $\Delta\sigma_{0.2} = 496$ MPa observed experimentally in the Cr16Ni15Mo3Ti1 steel (see Fig. 1). It is however more probable that low-temperature and vacancy clusters are cut rather than by-passed by dislocations because of their small dimensions (4–8 nm), close spacing and a low binding energy of atoms in the clusters. In particular [7], even coarse coherent or semi-coherent γ'-particles of the Ni$_3$Al intermetallic 100 nm in size are cut by dislocations in FCC alloys, despite large elastic distortions arising near the γ'-particles. Strengthening $\Delta\sigma_{0.2}$ of the irradiated steel in terms of the model when clusters are cut by dislocations considerably depends not only on the dimension d and density n of the particles but also on the elastic distortions ε near the particles [8]

$$\Delta\sigma_{0.2} = \beta m G \varepsilon^{1.5}\left(\frac{fd}{2b}\right)^{0.5}, \qquad (1)$$

where $G = 70\,000$ MPa is the shear modulus of the FCC austenite; $b = 0.25$ nm is the Burgers vector, which is typical of the $a/2\ \langle 1\ 1\ 0\rangle$ dislocation in FCC steels; β is the coefficient characterizing the type of dislocations (1 – screw dislocations, 3 – edge dislocations, 2 – mixed dislocations); $m = 3.1$ denotes the orientation factor of the FCC matrix; $f = n\frac{4}{3}\pi(d/2)^3 = \pi n(d^3/6)$ is the volume fraction of the clusters. Considering $n = \lambda F$, then

$$\Delta\sigma_{0.2} = \beta m G \varepsilon^{1.5} d^2\left(\frac{\pi}{12b}\right)^{0.5}(\lambda F)^{0.5}. \qquad (2)$$

The calculated low-temperature strengthening due to the clusters ($d \approx 8$ nm, $l = 15$ nm, $f = 8.1\%$, $n = 1.6 \times 10^{17}$ cm^{-3}) under neutron irradiation in terms of the model when the clusters are cut by mixed dislocations will be equal to the experimental strengthening $\Delta\sigma_{0.2} = 560$ MPa (fluence 1.5 × 10^{19} n/cm^2, $T = 77$ K) if the elastic distortions near the clusters $\varepsilon \approx 1\%$. This value of ε is much lower than the one observed in austenite during precipitation of coherent VC carbide particles [8] but is higher than ε observed during precipitation of the γ'-particles of the Ni$_3$Ti or Ni$_3$Al phase [9]. It is worth noting that the incremental yield stress is preserved at the level $\Delta\sigma_{0.2} \approx 270$ MPa when the Cr16Ni15Mo3Ti1 steel irradiated at 77 K is heated to room temperature. Given the dimensions and the number of clusters ($d = 6$ mm, $l = 1.5$ nm, $n = 1.6 \times 10^{17}$ cm^{-3}, $f = 3.4\%$) observed at 298 K, the calculated $\Delta\sigma_{0.2} \approx$ 300MPa approximates the experimentally observed strengthening when $\varepsilon \approx 1\%$ (fluence 1.5×10^{19} n/cm^2).

The incremental tensile strength ($\Delta\sigma_B = 60$–158 MPa) under irradiation is several-times lower than the incremental yield stress (see Fig. 1, curves 3 and 4). The fact that σ_B is similar in irradiated and nonirradiated samples of the Cr16Ni15Mo3Ti1 steel may be attributed, along with other reason, to dissolution of fine clusters as a result of their interaction with moving edge dislocations when the deformation increases during tension to 30–60%. Low-mobile point defects do not move to sinks during cold deformation at 77 K while sinks such as edge dislocations approach the point defect clusters and absorb the point defects. By the moment the sample breaks, the structure of the irradiated steel will contain little, if any, clusters and become similar to the structure of the deformed nonirradiated steel. This situation is observed when γ'-particles of Ni_3Ti or Ni_3Al dissolve in aged austenitic alloys during cold deformation at 77 and 298 K. Dissolution of Ni_3Ti particles comprising substitutional elements requires that dislocations cut these particles and Ni and Ti atoms drift to the γ matrix for one interatomic distance after every dislocation emitted from a particle [9]. If edge dislocations cut low-temperature or ordinary vacancy clusters, dissolution of these clusters is facilitated, because each edge dislocation crossing a cluster is capable of absorbing a great number of point defects.

3.2. The effect of tritium on the steel strengthening

When the Cr16Ni15Mo3Ti1 steel was preloaded with deuterium and tritium from a gaseous phase up to 0.03 at%, $\Delta\sigma_{0.2}$ and $\Delta\sigma_B$ increased slightly by ~35 MPa at 77 K. This small increment in yield and tensile strength agrees with the previously obtained results [3]. The autoradiographic studies showed that tritium is located mainly at dislocations, grain boundaries and subgrain boundaries and some were found at interphase between coarse inclusions and matrix. Fig. 2(b) gives a microradiogram of the quenched and tritium-loaded Cr16Ni15Mo3Ti steel. The silver crystals, which appear in the treated photoemulsion as a result of the tritium disintegration, indicate the position of the tritium atoms. It is seen from Fig. 2(b) that predominantly the grain boundaries and their triple junctions are decorated. The silver crystals often from chains inside grains, a fact which attests to the location of tritium at subboundaries. The formation of the tritium atmospheres at dislocations should lead to a decrease in the dislocation mobility even if the tritium concentration is small. As a result, the steel strength should be enhanced. This supposition has been confirmed experimentally.

The combined effect of the tritium and deuterium loading (up to 0.03%) and subsequent neutron irradiation on $\sigma_{0.2}$ and σ_B is shown in Fig. 1 (curves 2 and 4). The strength characteristics of the austenitic Cr16Ni15-Mo3Ti1 steel with and without tritium differ little ($\Delta\sigma = 20$–85 MPa) after low-temperature neutron irradiation too. For the tritium- and deuterium-loaded FCC steels (compared to their untreated state), the dependence of the increase in the strengthening characteristics on the fast neutron fluence is $\Delta\sigma_{0.2}^{T+D} = 6 \times 10^{-4} F^{0.29}$ and $\Delta\sigma_B^{T+D} = 7 \times 10^{-7} F^{0.44}$.

3.3. Annealing of point defects and changes in the strength characteristics of the tritium- and deuterium-loaded irradiated steel

Fig. 3 depicts some curves showing the relative variation of the electroresistivity $\Delta\rho/\Delta\rho_{77}$ and the yield stress $\Delta\sigma_{0.2}/\Delta\sigma_{0.2(77)}$ at 77 K, which characterize the strength properties of the irradiated Cr16Ni15Mo3Ti1 steel as a function of the annealing temperature (77–625 K). From the $\Delta\rho/\Delta\rho_{77}$ curves it is seen that a marked annealing of the point defects (interstitials) starts at temperature below 100 K. A complete annealing of the "radiation" interstitials and vacancies, which leads to the restoration of electroresistivity, is observed at 525 K ($F = 1.5 \times 10^{18}$ n/cm^2) and 625 K ($F = (7$–$15) \times 10^{18}$ n/cm^2). The mechanical properties of the irradiated steel are restored much slower. When the T- and D-loaded irradiated Cr16Ni15Mo3Ti1 FCC steel is subject to intermediate heating up to 473 K (curve 3), the yield stress $\sigma_{0.2}$ is regained only by ~10% in the samples irradiated with the maximum fluence and by 37% in the samples receiving the minimum irradiation dose. The plasticity characteristics δ are poorly restored too (by 10–37%). Given the same conditions, the point defects are annealed to 73–87% (see Fig. 3). It was shown in the foregoing (see Section 3.1) that vacancy clusters ~6 nm in diameter are preserved when the samples are annealed to 298 K. This results in a high yield stress. Probably, the mechanical properties of irradiated FCC and BCC steels will be restored completely by recrystallization, which eliminates vacancy clusters and dislocation loops.

3.4. Variation of the plasticity characteristics

Low-temperature irradiation of steels and alloys with fast neutrons reduces plasticity properties, such as uniform δ_u and total δ specific elongation. When the Cr16Ni15Mo3Ti1 steel is exposed to the neutron fluence $F = 1.5 \times 10^{19}$ n/cm^2, the decrease in plasticity at 77 K is nearly two-fold: from 65–73% to 32–38%. If the steel is preloaded with tritium and deuterium up to 0.05 at%, the loss in plasticity is somewhat enhanced (by 2–7%) at

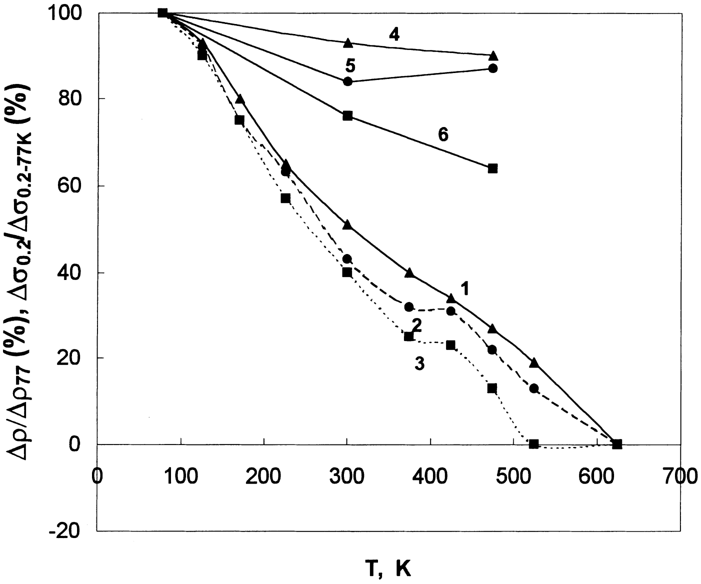

Fig. 3. Effect of the intermediate annealing temperature on the relative variation of the electroresistivity $\Delta\rho/\Delta\rho_{77}$ (1, 2, 3) and the yield stress $\Delta\sigma_{0.2}/\Delta\sigma_{0.2(77)}$ (4, 5, 6) for the Cr16Ni15Mo3Ti1 steel loaded with tritium and deuterium (~0.05 at%). The test temperature is 77 K. Irradiation at 77 K with the fluence (n/cm^2): 1.5×10^{19} (1, 4); 7.0×10^{18} (2, 5); 1.5×10^{18} (3, 6).

small neutron fluences, while plasticity remains almost unchanged at $F = 1.5 \times 10^{19}$ n/cm^2. When the test temperature was reduced from 298 to 77 K, the elongation δ of the nonirradiated Cr16Ni15Mo3Ti1 steel increased from 45% to 73%. This is due to the γ→α martensitic transformation, which develops during low-temperature experiments. This transformation causes relaxation of peak stresses and prevents premature failure (TRIP-effect [10]). Low-temperature irradiation of the BCC steels and alloys with fluences of $(7–15) \times 10^{18}$ n/cm^2 decreases the total elongation δ from 20% to 2–6% and the uniform elongation δ_u to 1–2% in the V–4Ti–4Cr, V–10Ti–5Cr alloys and 0% in the Fe–13Cr steel. The strong deterioration of plasticity in the BCC steels and alloys exposed to a relatively small damaging dose of low-temperature neutron irradiation represents a serious drawback of these materials. Intermediate annealing of the irradiated BCC alloys restores their plasticity insignificantly when experiments are performed at 77 K.

The experiments showed that the deterioration of low-temperature plasticity of irradiated BCC stainless steels can be avoided if additional FCC austenite is introduced in the structure as a result of a partial α→γ transformation. The Cr16Ni9Mo3 steel whose structure consists of alternating thin laths of BCC martensite and transformation-hardening FCC austenite possesses not only a high resistance to void formation at 450–550°C, but also retains a rather high plasticity ($\delta = 19–20\%$) at 77 K after tritium loading and low-temperature irradiation at $F = 1.5 \times 10^{19}$ n/cm^2 [4].

4. Conclusion

1. Low-temperature (77 K) fast neutron irradiation ($F = (1.5–15) \times 10^{18}$) more than doubles the yield stress $\sigma_{0.2}$ (up to 1100 MPa) of the Cr16Ni15Mo3Ti1 FCC steel at 77 K. This is explained by the formation of low-temperature clusters (in displacement cascades), which retard movement of dislocations. The strengthening is given by the power function $\Delta\sigma_{0.2} = A \times F^x$. Rough calculations show that strengthening of steels can be realized through the Nabarro mechanism, which allows for the resistance of the clusters to cutting by dislocations. A much lesser incremental strength ($\Delta\sigma_B = 60–158$ MPa) observed under irradiation may be attributed to dissolution of the strengthening radiation-induced clusters as they are cut by dislocations during a strong plastic deformation of samples subject to mechanical tests.

2. Initial T- and D-loading of the Cr16Ni15Mo3Ti1 steel up to 0.03 at% leads to strengthening, which is preserved almost at the same level ($\Delta\sigma_{0.2} = 20–85$ MPa) during low-temperature (77 K) neutron irradiation, compared to the tritium-free irradiated steel. Proceeding from our microautoradiographic data, this strengthening is explained by the formation of tritium atmospheres on dislocations.

3. Intermediate heating of the irradiated Cr16Ni15Mo3Ti1 steel up to 473 K leads to a considerable annealing of point defects (the relative electroresistivity $\Delta\rho/\Delta\rho_{77}$ is regained by 73–87%). However, the mechanical properties (tests at 77 K) are restored insignificantly,

especially after the maximum irradiation dose: $\Delta\sigma_{0.2}/\Delta\sigma_{0.2(77)}$ decreases by 10% only.

4. Low-temperature neutron irradiation causes a strong degradation of plasticity in the Fe–13Cr, V–4Ti–4Cr and V–10Ti–5Cr alloys having a BCC lattice: the specific elongation δ decreases from 20% to 2–6%, while the uniform elongation drops to 0–2%. However, elongation is preserved at a high level ($\delta = 32$–38%) for the irradiated Cr16Ni15Mo3Ti1 FCC steel, even after loading with tritium and deuterium. The Cr16Ni9Mo3 steel was taken as an example to show that a high plasticity ($\delta = 19$–20%) can be preserved at 77 K after irradiation ($F = 1.5 \times 10^{19}$ n/cm^2) if a mixed structure of thin laths of martensite and austenite (BCC + FCC) is formed in the steel.

Acknowledgements

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