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Mechanical properties and microstructure of advanced ferritic–martensitic steels used under high dose neutron irradiation

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Abstract

Some results of the study of mechanical properties and structure of ferritic–martensitic chromium steels with 13% and 9% chromium, irradiated in the BOR-60 reactor up to different damage doses are presented in this report. Results concerning the behaviour of commercial steels, containing to molybdenum, vanadium and niobium, and developed for the use in fusion reactors, are compared to low-activation steels in which W and Ta replaced Mo and Nb. It is shown that after irradiation to the dose of ~10 dpa at 400°C 0.1C–9Cr–1W, V, Ta steels are prone to lower embrittlement as deduced from fracture surface observations of tensile specimens. Peculiarities of fine structure and fracture mode, composition and precipitation reactions in steels during irradiation are discussed.

1. Introduction

Chromium ferritic–martensitic (FM) stainless steels with 10–13% Cr alloyed by Mo, V and Nb in the normalized and tempered condition have found wide application for fuel assembly (FA) and fuel element (FE) wrapper and cladding tubes for Liquid Metal Fast Reactor (LMFR) [1–5]. It is due to their high radiation swelling resistance and their withstandability to high non-stationary heat load [6]. Steels containing 9% Cr are more economic, easier for manufacturing (especially at welding), possess higher ductility, toughness, and show high-temperature strength, as good as steels with 12% Cr [7–13].

The experience accumulated on steel 0.1C–13Cr–2Mo–Nb, V, B could be profitable for the development of low-activation steels for DEMO. In the present work results on mechanical properties, microstructure and fracture mode of steel 0.1C–9Cr–1W–V, B, Ta irradiated in the Fast Experimental Reactor BOR-60 to 10 at 400°C are discussed.

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2. Experimental procedures

Table 1 shows the typical compositions of studied FM steels and their metallurgical conditions. Steels were melted in an electric arc furnace with clean charges and then electro-slag remelted. Such method of melting provided low-phosphorus and low-copper impurities (about 0.01% and 0.02%, respectively), high chemical homogeneity ingots with low inclusion contents.

Steels containing 12% Cr and relatively higher percent of Mo have two-phase structure which consists of tempered martensite and δ-ferrite with the ratio 1:1 as in steel 0.1C–13Cr–2Mo–Nb, V, B.

Steels with 9% Cr after normalization and tempering have a fully martensitic matrix (Fig. 1) with carbide precipitate (Fig. 2) $M_{23}C_6$, M_6C_3, MX [9].

Sheet specimens were used with thickness, width and length of the gauge Section 1, 5 and 25 mm, respectively. They were cut from the irradiated hexagonal wrapper tube by the electroerosion method. Tensile tests were conducted at 1 mm/min deformation rate in the range 20–500°C.

Fracture surface observations were carried out with the scanning electron microscope REM-100. Transmission electron microscopy was used to study neutron irradiation effects on fine structural changes of

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Table 1
Chemical composition of steels

Type of steel	Chemical elements content % (mass)													Heat treatment
	C	Si	Mn	Ni	Cr	P	S	W	Nb	Mo	V	Ta	B	
0.1C–9Cr–1W–V, B, Ta	0.1	0.15	0.24	–	9.2	0.012	0.003	1.2	–	–	0.29	0.1 calc.	0.006c calc.	Normalisation: 1050°C 5 min. Tempering: 790°C 1 h
0.11C–12Cr–2W–V, Ti, B	0.11	0.15	1.31	–	11.97	0.010	0.003	1.73	–	–	0.28	0.04 Ti	0.006 calc.	1070°C 20 min oil; 780°C 2 h air
0.12C–12Cr–2Mo–Nb, V, B	0.12	0.21	0.32	0.21	13.10	0.018	0.007	–	0.52	1.60	0.22	-	0.004	1050°C 0.5 h; 720°C 1 h
0.1C–9Cr–1Mo, V, Nb	0.10	0.17	0.39	0.33	10.2	0.006	0.003	–	0.12	0.67	0.15	-	-	1040–1050°C 40 min, air cooling; 770°C 5 h

x 20 000

Fig. 1. Microstructure of 0.1C–9Cr–1W, V, Ta in the unirradiated condition.

x 30 000

Fig. 2. Secondary phases precipitation in unirradiated steel.

0.1C–13Cr–2Mo, Nb, V, B and 0.1C–9Cr–1W, V, Ta, B steels. For this purpose discs have been cut from tensile specimen heads. They were mechanically and electrochemically thinned before being examined in the electron microscope EM-25 at 100 kV.

Auger analysis was used to determine the compositions of the precipitates, appearing in steel with tungsten and tantalum.

3. Results

3.1. Steel 0.1C–13Cr–2Mo, Nb, V, B

Experiments on specimens, manufactured from irradiated wrapper tube and fuel pin cladding show the following: the yield strength dose dependence and uniform elongation of steel 0.1C–13Cr–2Mo, Nb, V, B do not change at irradiation temperature of 320–350°C and at considerably higher doses (Fig. 3). At doses ~10 dpa the elongation is about 0.5–1.0% and has the tendency to slightly increase at doses higher than 50 dpa. Radiation hardening is maximum in the range of 10–40 dpa: yield strength and ultimate strength of the irradiated material are 1150–1350 and 1200–1400 Mpa, respectively. Increase of the irradiation temperature (or out of pile annealing at $T \geqslant 380$°C) leads to noticeable annealing of damages and recovery of ductility (Figs. 4 and 5). Figs. 6 and 7 show the dependencies of ductile-to-brittle transition (DBTT) temperature of irradiated 0.1C–13Cr–2Mo, Nb, V, B steel [4] on dose and irradiation temperature. Regions characterized by a decrease of ductility (Fig. 4) are related to the maximum DBTT shift as a result of irradiation (Fig. 6). Impact toughness at $T_{irr} < 350$°C passes through minimum when damage dose is about 20–30 dpa. This minimum value is correlated to a maximum of dislocation loops density [4,5] which decreases when the dose increases. Ageev and coworkers [5] showed that radiation hardening and embrittlement in temperature range lower than 350°C are caused by formation of dislocation loops and small radiation-induced defects Ø0.5–1.0 nm, which presumably are loops of interstitial or vacancy type.

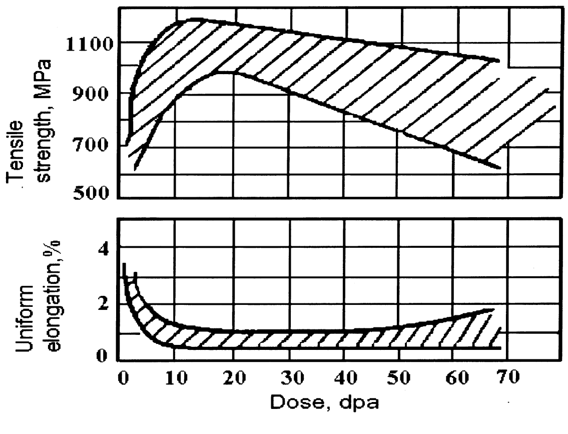

Fig. 3. Dependence of the mechanical properties for 0.1C–13Cr–2Mo, Nb, V, B on damage dose at $T_{irr} = 320$–350°C.

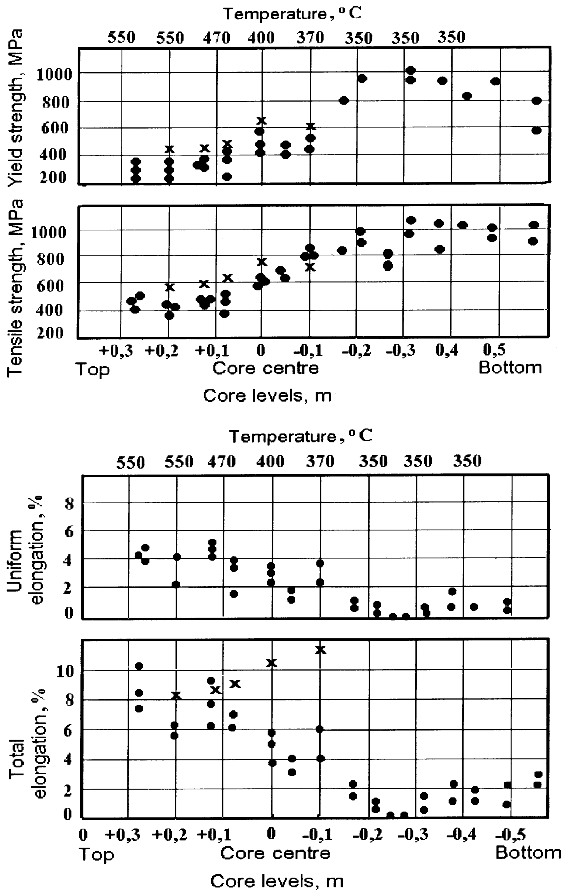

Fig. 4. Changes in mechanical properties for 0.1C–13Cr–2Mo–Nb, V, B of the FA wrapper tube irradiated in BOR-60 along the core height (where x means σ_0 (a), σ_B (b), δ_p (c) and δ_0 (d) before irradiation).

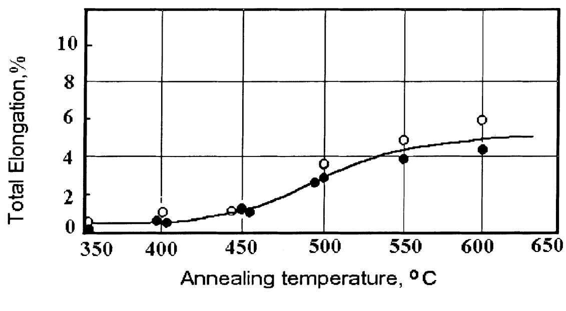

Fig. 5. Temperature and long-term annealing effect on the total percentage elongation for 13Cr–2Mo–Nb, V, B, irradiated at 320–350°C to 5 ×1 0^{26} m^{-2}, $E \geqslant 0.1$ MeV neutron fluence. $T_{test} = 350$°C. ((●) annealing time 1 h (○) annealing time 10 h).

As shown in Table 2 at high doses the main reason of 13% Cr steel higher radiation embrittlement is formation of fine-dispersion particles of irradiation-induced α′-phase in structure.

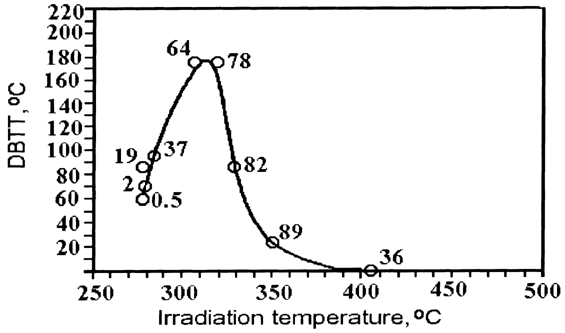

Fig. 6. Change of the DBTT of the wrapper tube material 0.1C–13Cr–2Mo–V, Nb, B with T_{irr} (O^N – damage dose) [4].

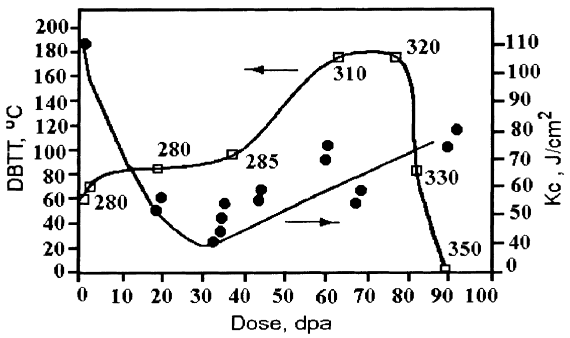

Fig. 7. Change of the DBTT and impact toughness of wrapper tube material 0.1C–13Cr–2Mo–V, Nb, B depending on dose [4] ($N - T_{irr}$).

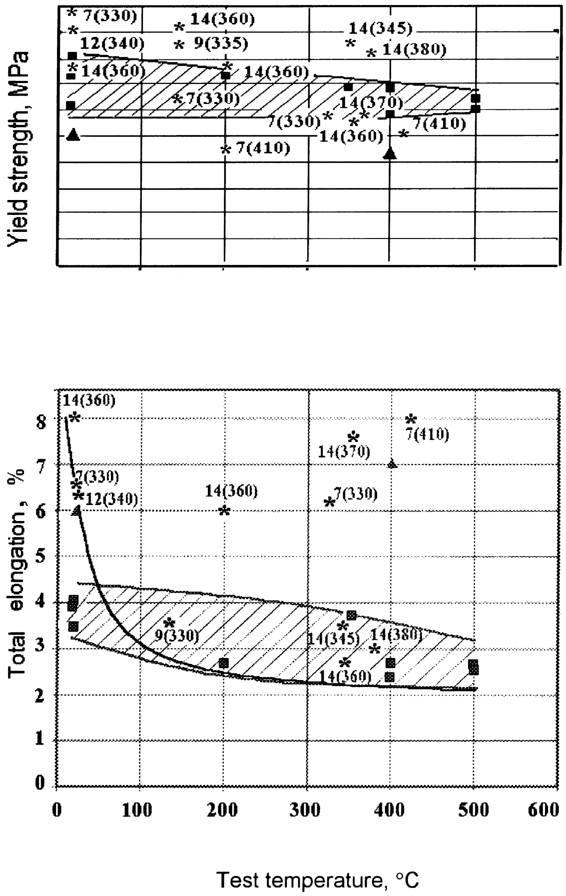

Fig. 8. Temperature dependence of 0.1C–9Cr–1W, V, Ta yield strength (a) and total elongation (b) after irradiation to 10 dpa at 400°C in the BOR-60 reactor. (■) 0.1C–9Cr–1W, V, Ta after irradiation; (▲) 0.1C–9Cr–1W, V, Ta unirradiated; (*) 0.1C–9Cr–1Mo, V, Nb after irradiation (Figures indicate irradiation dose and temperature, enclosed in brackets.).

Table 2
Microstructural parameters of 0.1C–13Cr–2Mo, Nb, V, B steel irradiated to high doses

T_{irr} (°C)	Dose Kt (dpa)	Ferrite							
		Voids				Dislocations $\times 10^{10}$ (cm^{-2})	α′-phase		
		d (A)	V $\times 10^{-18}$ (cm^3)	$p \times 10^{15}$ (cm^{-3})	S (%)		$p \times 10^{16}$ (cm^{-3})	d (A)	V/V (%)
460	110	204 ± 25	5.6 ± 0.8	1.7 ± 0.6	1.0 ± 0.3	7.5 ± 2.2	4.6 ± 1.4	∼80	1.2 ± 0.4
430	100	168 ± 21	3.1 ± 0.48	3.7 ± 1.2	1.2 ± 0.4	8.0 ± 2.4	12 ± 3,0	∼50	1.6 ± 0.5
420	100	206 ± 25	6.0 ± 0.8	1.9 ± 0.6	1.1 ± 0.4	9.6 ± 3.1	1.6 ± 0.5	∼75	1.3 ± 0.4
440	130	233 ± 27	8.7 ± 1.1	1.9 ± 0.6	1.6 ± 0.5	9.0 ± 3.0	0.07 ± 0.2	180	∼0.2
450	142	244 ± 28	10. ± 1.2	1.81 ± 0.6	1.9 ± 0.6	7.0 ± 2.1	0.4 ± 0.13	115	∼0.35
Tempered martensite									
460	110	265 ± 30	12.7 ± 1.5	0.9 ± 0.3	1.2 ± 0.4	9.5 ± 3.0	2.8 ± 0.8	∼100	1.4 ± 0.5
430	100	213 ± 27	6.1 ± 0.8	1.3 ± 0.4	0.8 ± 0.3	7.3 ± 2.2	7.6 ± 2.3	∼501	1.0 ± 0.4
420	100	237 ± 30	8.3 ± 1.2	0.9 ± 0.3	0.7 ± 0.3	12 ± 4.0	1.0 ± 0.3	∼1000	0.5 ± 0.2
440	130	298 ± 34	16.2 ± 2.0	0.6 ± 0.2	0.9 ± 0.3	6.0 ± 2.0	0.19 ± 0.6	∼70	∼0.003
450	142	345 ± 35	22.7 ± 2.5	0.6 ± 0.2	1.4 ± 0.4	4.3 ± 1.3	0.3 ± 0.1	∼100	∼0.16

3.2. Steels 0.1C–9Cr–1Mo, Nb, V, B and 0.1C–9Cr–1W, V, Ta, B

Fig. 8 shows the comparative temperature dependences of yield strength and total elongation at correlated conditions of 0.1C–9Cr–1Mo, Nb, V, B and 0.1C–9Cr–1W, V, Ta, B steel specimens. On the average lesser ductility values (Fig. 8(b)) for steels in which W and Ta replaced Mo and Nb are the most evident irradiation effect. At the same time the radiation hardening (the dose and irradiation temperature scattering for steel 9Cr–1Mo, Nb, V, B having place) is correlated (Fig. 8(a)).

Dislocation loops at lower average size (10–15 nm) are also present in the structure of irradiated 0.1C–9Cr–1W, V, Ta, B steel (Fig. 9). Voids were not detected in structure, that testifies the absence of this steel swelling at 400°C to a dose of $\sim$10 dpa. During irradiation certain decrease of rod-like particles of M_2X type took place although their amount compared with the initial state was invariable. No new phases formed during irradiation.

Klueh and coworkers [14] point out the strong dependence of dislocation loops formation and annealing in ferritic–martensitic steels on alloying manner. So, at comparable irradiation condition 9Cr–2W, V, Ta steels have much higher dislocation loops density than steels 9Cr–1Mo, Nb, V. It occurs as a consequence of great difference in Mo and W diffusion coefficient in ferritic steels at 400°C (D_{mo} is 1000 times higher than D_W).

Information about failure mode was obtained from examinations of fracture surface after tensile tests of irradiated 9Cr–1W, V, Ta, B and 13Cr–2W, V, Ti, B. Fig. 10 shows the examples of non-irradiated fracture surface specimens (room-temperature test) and irradiated to 10 dpa at 400°C. The fracture mode in both cases is ductile and transgranular.

Studies have shown two types of micro-voids, most of them contains globular precipitates of from 2 to 10 μm size. In the irradiated specimen at much more greater magnification there were noticed sections with quasi-brittle (Fig. 10(d)) cleavage surfaces containing precipitates. By means of Auger-spectral analysis there was taken an attempt to define particle elementary composition near which microcrack formation was noticed. Besides tungsten and oxygen it was found sulphur, its segregation could bring to the noted cracking effect near precipitation (Fig. 10(d)).

4. Discussion

The results of the performed studies may be used for the development of reduced-activation ferritic–martensitic steels and more precise definition of their composition. The preference should be given to steels 9% Cr, containing tungsten and tantalum to provide the

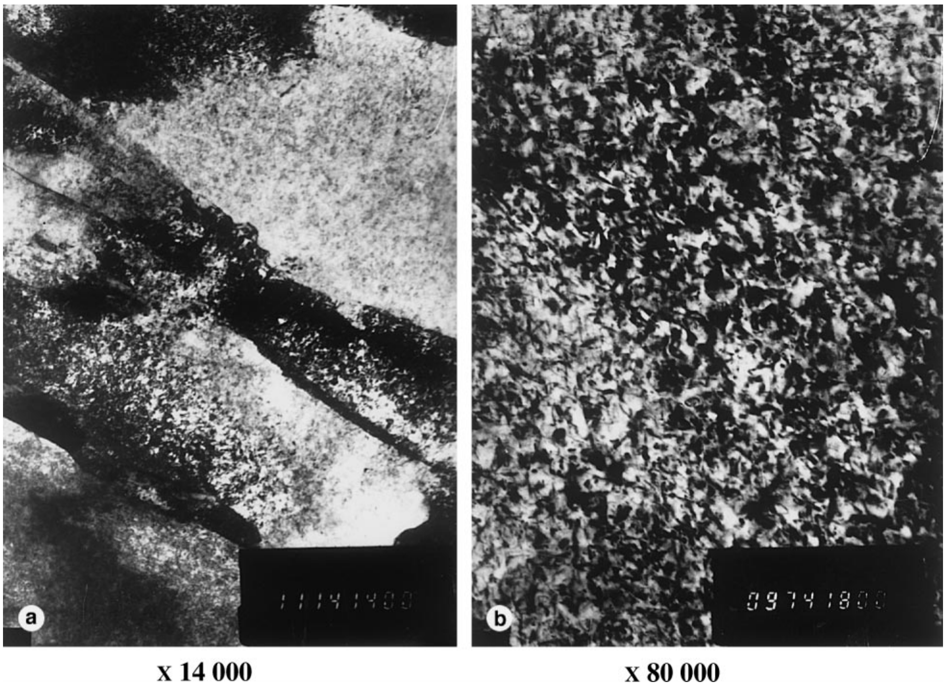

Fig. 9. Steel 0.1C–9Cr–1W, V, Ta microstructure after irradiation to 10 dpa at 400°C in the BOR-60 reactor.

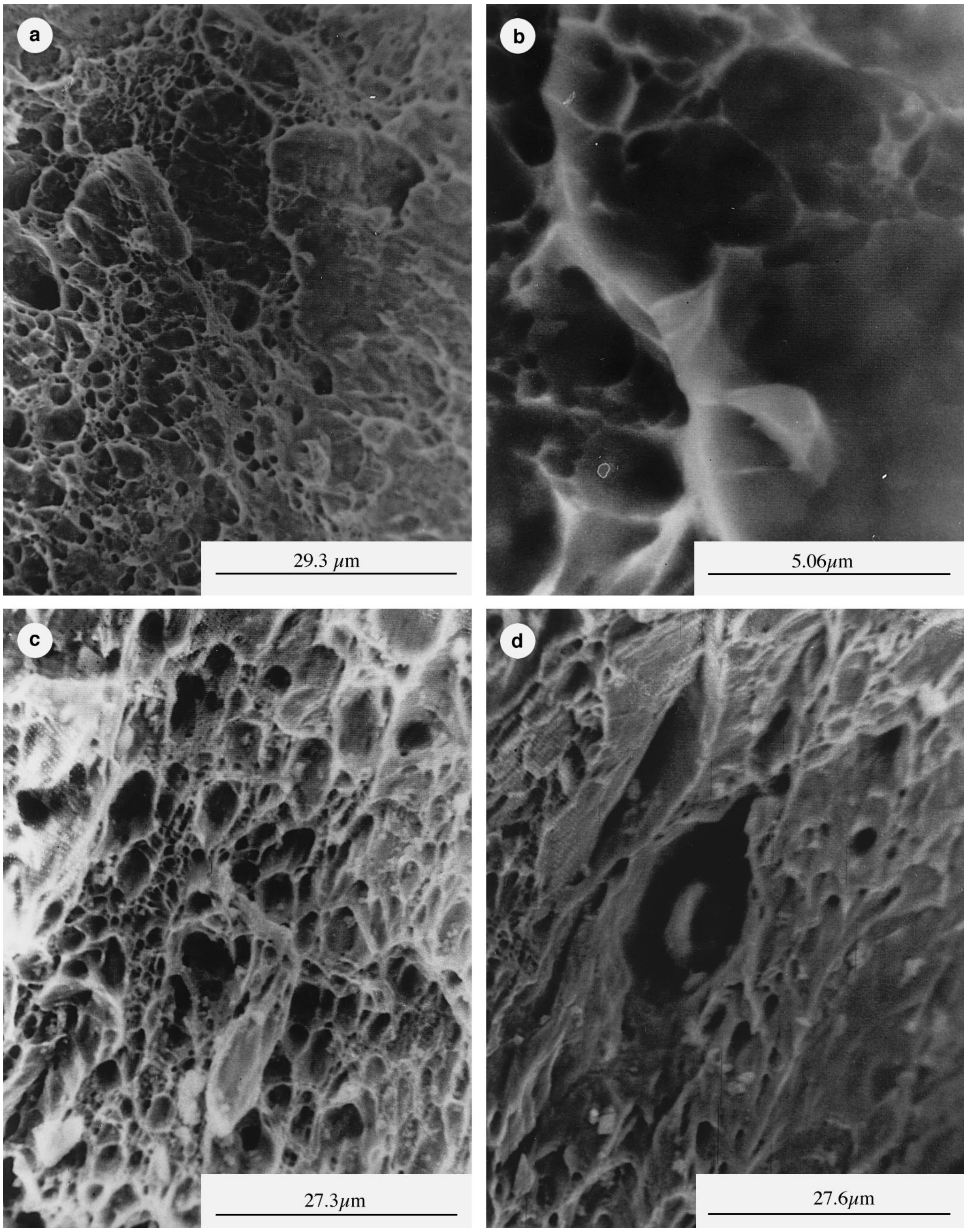

Fig. 10. Failure mode of the 0.1C–9Cr–1W, V, Ta steel, unirradiated (a,b,) and irradiated (c,d) to 10 dpa at 400°C in the BOR-60 reactor after tensile test at 20°C (a,b) and 400°C (c,d).

requirements of the low-level induced activity and its decrease with time.

Low temperature radiation embrittlement of ferritic–martensitic steels is accompanied by at least four processes:

- embrittlement because of radiation defects-dislocation loops [4,5,14];
- embrittlement because of radiation-induced α'-phase [11–13,15] and χ-phase precipitation [14] in 9CrMoNbV steels;
- loss of strength because of radiation-stimulated martensite tempering;
- loss of strength because of radiation-stimulated decay of second phases, in first turn $M_{23}C_6$.

The role of those processes appears in varying degrees in chromium steels with variable alloying. For instance, radiation-induced α'-phase precipitation is typical of 12–13% Cr steels and is absent in steels with 9% Cr.

Replacement of Mo by W and Nb by Ta leads to another quantitative effect after irradiation from the point of view of dislocation loops formation, development and their behaviour at annealing.

However, there are data [14] that DBTT for steels with tungsten and tantalum is noticeably lower in the initial state and its shifts after irradiation are smaller than in steels with molybdenum and niobium. As a result an effect of DBTT reduction in steel and its shift after irradiation is achieved.

The results of fracture surface studies obtained on irradiated 9Cr1WVTaB specimens are in qualitative agreement with the result of Klueh [14] and demonstrate that brittle-to-ductile temperature of this material should be lower than room temperature.

5. Conclusion

Basing on the results of the present study and data obtained before it is possible to make the following conclusions:

1. Characteristics of ductility and impact toughness of 0.1C–13Cr–2Mo–Nb, V, B in the normalized and tempered condition decrease up to minimal value at irradiation temperatures 320–350°C and doses ~30 dpa.
2. The main contribution to radiation hardening and embrittlement at 280–350°C and doses up to 70 dpa is due to dislocation loops of the size ~20–60 nm and other radiation defects of 0.5–1.0 nm size. At temperatures higher than 350°C the process of radiation-induced α'-phase also contributes to embrittlement, that is typical for steels with 13% Cr.
3. For irradiation temperatures higher than 380°C the increase of ductility well correlates with decreasing of dislocation loops concentration.
4. For low-activation ferritic–martensitic 0.1C–9Cr–1W, V, Ta, B steel, radiation hardening is comparable to commercial steels containing Mo and Nb (ductility of W, Ta steels is in the low region of data scattering zone for steels with Mo and Nb).
5. The irradiation with the dose 10 dpa at 400°C did not change the fracture mode of 0.1C–9Cr–1W, V, Ta, B at room temperature and at 400°C.

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