MICROSTRUCTURAL ANALYSIS OF IRRADIATED MARTENSITIC STEELS -- J.J. Kai (National Tsing Hua University, Hsinchu, Taiwan) and R.L. Klueh (Oak Ridge National Laboratory)

OBJECTIVE

The goal of this study is the development of reduced-activation ferritic steels.

SUMMARY

Four martensitic steels were examined by transmission electron microscopy after irradiation in the Fast Flux Test Facility (FFTF). Irradiation in FFTF was at 420°C to about 7.8×10^{26} n/m^2 (E>0.1MeV), which gave a displacement damage of about 35 dpa. The steels were those of interest for fusion applications and included two commercial steels, 9Cr-1MoVNb (modified 9Cr-1Mo) and 12Cr-1MoVW (Sandvik HT9), and two experimental reduced-activation steels, 9Cr-2WV and 9Cr-2WVTa. Before irradiation, the tempered martensite microstructures of the four steels contained a high dislocation density, and the major precipitate was $M_{23}C_6$ carbide, with lesser amounts of MC carbide. Irradiation caused only small changes in these precipitates. Voids were found in all irradiated specimens, but swelling remained below 1%, with the 9Cr-1MoVNb having the highest void density. Although the 12Cr-1MoVW steel showed the best swelling resistance, it also contained the highest density of radiation-induced new phases, which were identified as chi-phase and possibly α'. Radiation-induced chi phase was also observed in the 9Cr-1MoVNb steel. The two reduced-activation steels showed very stable behavior under irradiation: a high density of dislocation loops (average diameter of 50 nm) replaced the original high dislocation density; moderate void swelling occurred, but no new phases formed. The differences in microstructural evolution of the steels can explain some of the mechanical properties observations made in these steels.

PROGRESS AND STATUS

Introduction

Reduced-activation or fast-induced radioactivity decay (FIRD) martensitic steels are one of the major candidate materials for the first wall and blanket structures for future fusion reactors. A FIRD alloy cannot contain molybdenum and niobium, important constituents in conventional Cr-Mo steels of interest for fusion. Previous publications on the FIRD steels developed at Oak Ridge National Laboratory [1-3] reported on microstructure, tempering and tensile behavior [2], and Charpy impact behavior [3] in the unirradiated condition. Results were also reported on the tensile and Charpy properties of neutron-irradiated specimens [4-6].

Ferritic/martensitic steels containing 7-9 wt% Cr are favored for fusion. FIRD 9Cr alloys were patterned after the composition of conventional 9Cr-1MoVNb (modified 9Cr-1Mo) steel, with molybdenum replaced by tungsten and niobium replaced by tantalum. A 9Cr-2W-0.25V (9Cr-2WV) and this nominal composition with 0.07% Ta (9Cr-2WVTa) were irradiated. In order to compare these steels with the conventional Cr-Mo steels of interest for fusion, both 12Cr-1MoVW (Sandvik HT9) and 9Cr-1MoVNb steels were also included in this study. In this paper, the effect of neutron irradiation on the microstructural evolution of the four martensitic steels irradiated to 35 dpa at 420°C in the FFTF is presented. The microstructural evolution affects the mechanical property

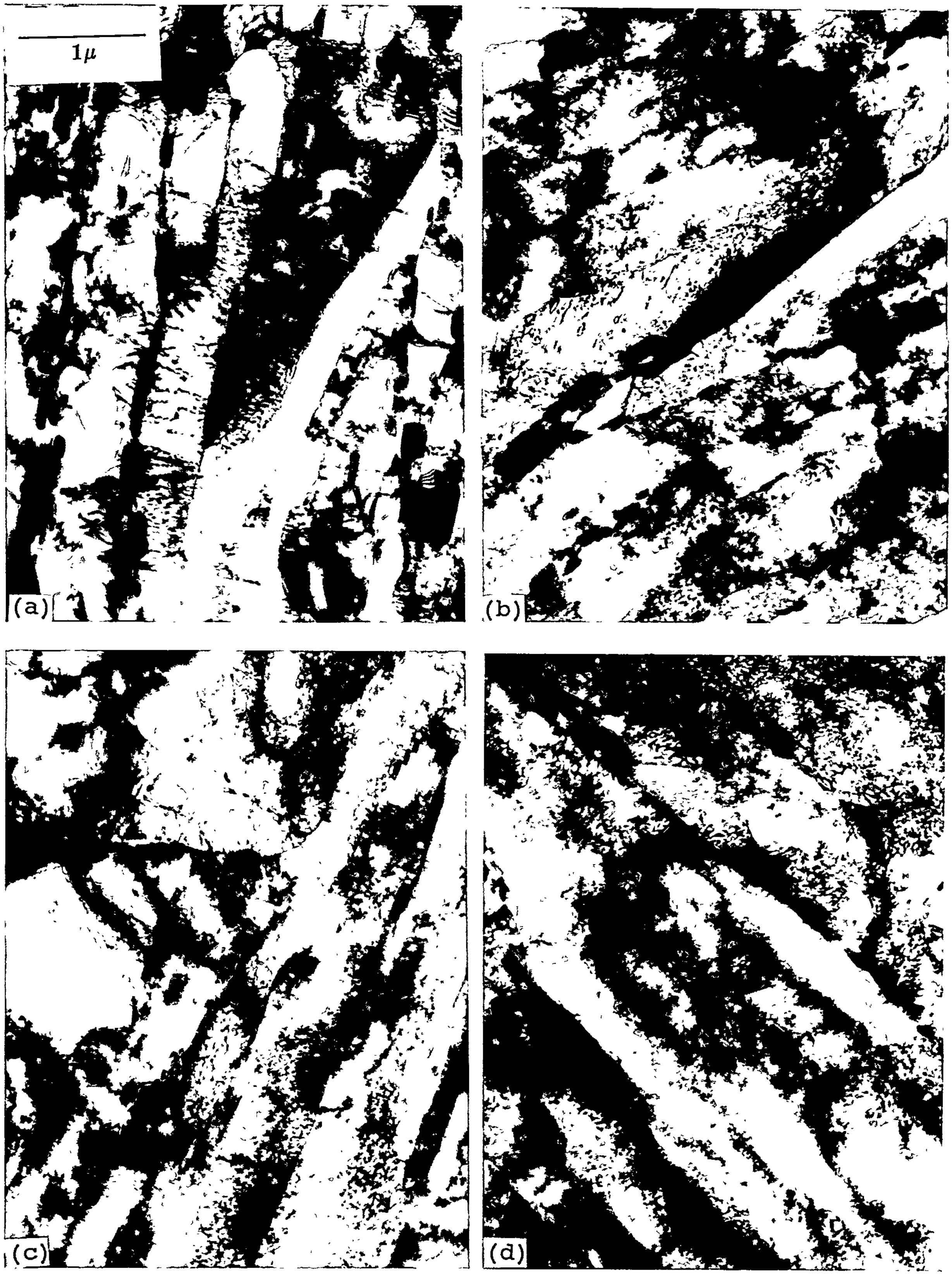

Fig. 1. Microstructures of (a) normalized-and-tempered 12Cr-1MoVW, (b) irradiated 12Cr-1MoVW, (c) normalized-and-tempered 9Cr-1MoVNb, and (c) irradiated 9Cr-1MoVNb.

changes, which under a fusion environment will determine the applicability of these steels for future fusion power plants.

Experimental Procedure

Four martensitic steels were used in this study: the commercial steels 12Cr-1MoVW and 9Cr-1MoVNb and the experimental steels 9Cr-2WV and 9Cr-2WVTa. In addition to nominal compositions of Cr, V, W, C, and Ta in the experimental steels, concentrations of elements normally found in commercial steels, such as Mn, P, Si, etc., were added in the levels typical of commercial practice. Chemical compositions are given in Table 1.

Table 1. Chemical Composition of Four Steels Tested

Steel	Fe	Cr	Mo	C	V	W	Nb	Ta	Si	Mn	P	S	N
12Cr–1MoVW	bal.	12.1	1.04	0.2	0.29	0.61	—	—	0.17	0.57	0.016	0.003	0.027
9Cr–1MoVNb	bal.	8.32	0.86	0.092	0.2	—	0.06	—	0.15	0.48	0.012	0.004	0.054
9Cr–2WV	bal.	8.73	—	0.12	0.25	2.09	—	—	0.25	0.51	0.014	0.005	—
9Cr–2WVTa	bal.	8.72	—	0.1	0.23	2.09	—	0.07	0.23	0.43	0.015	0.005	—

Specimens from each steel were irradiated in the Materials Open Test Assembly (MOTA) of the Fast Flux Test Facility (FFTF) at 420°C. Irradiation was to about 7.8×10^{26} n/m^2 (E>0.1 MeV), which produced a damage dose of about 35 dpa.

Microstructural examinations were performed on a Philips CM-30 scanning transmission electron microscope operating at 300 keV and equipped with an EDAX 9900 X-ray energy dispersive spectroscopy system.

Results

Microstructural examination indicated that irradiation caused basically three types of microstructural changes, which involved voids, dislocations and dislocation loops, and precipitates. Figures 1 and 2 show the unirradiated and irradiated microstructures of the two Cr-Mo and two Cr-W steels, respectively. Before irradiation, all specimens were 100% tempered martensite with a lath width of about 0.5 micron. Neutron irradiation produced micro features in the matrix and caused some coarsening of lath width.

Void swelling

Figure 3 shows the void morphology in the four irradiated steels. The 9Cr-1MoVNb steel showed the highest void density with a relatively larger average void diameter. Table 2 contains the estimated void density, average void diameter, and total swelling of the four different materials. Swelling values for all four steels are less than 1%.

The 9Cr-1MoVNb developed the largest amount of swelling (0.85%), with the 12Cr-1MoVW showing the best swelling resistance (<0.01%). The two tungsten-containing alloys also showed good swelling resistance, with the swelling about 3 to 4 times better than 9Cr-1MoVNb. The 9Cr-2WV performed slightly better than the 9Cr-2WVTa. Therefore, the FIRD steels are highly swelling resistant and better than conventional 9Cr-1MoVNb steel.

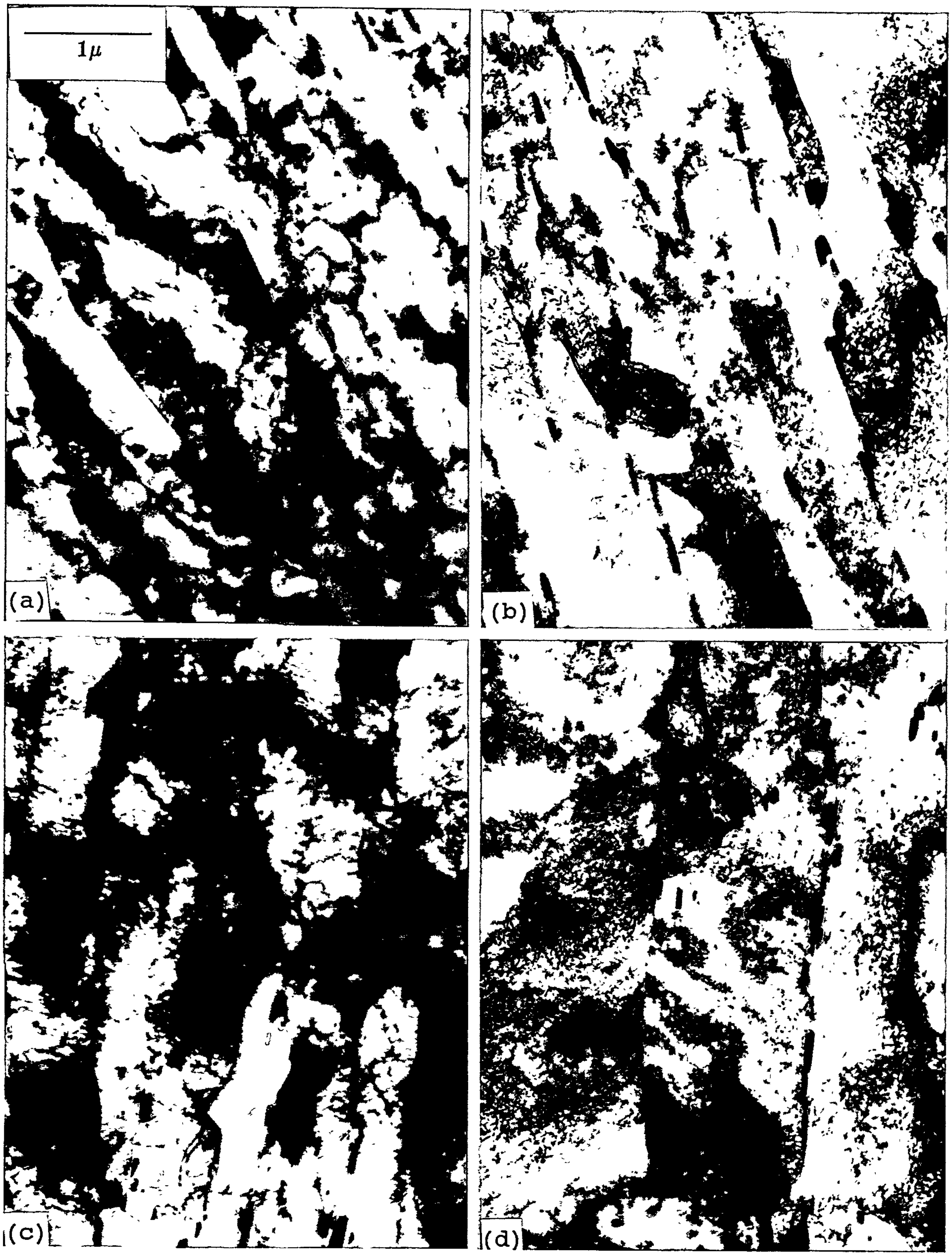

Fig. 2. Microstructures of (a) normalized-and-tempered 9Cr-2WV, (b) irradiated 9Cr-2WV, (c) normalized-and-tempered 9Cr-2WVTa, and (c) irradiated 9Cr-2WVTa.

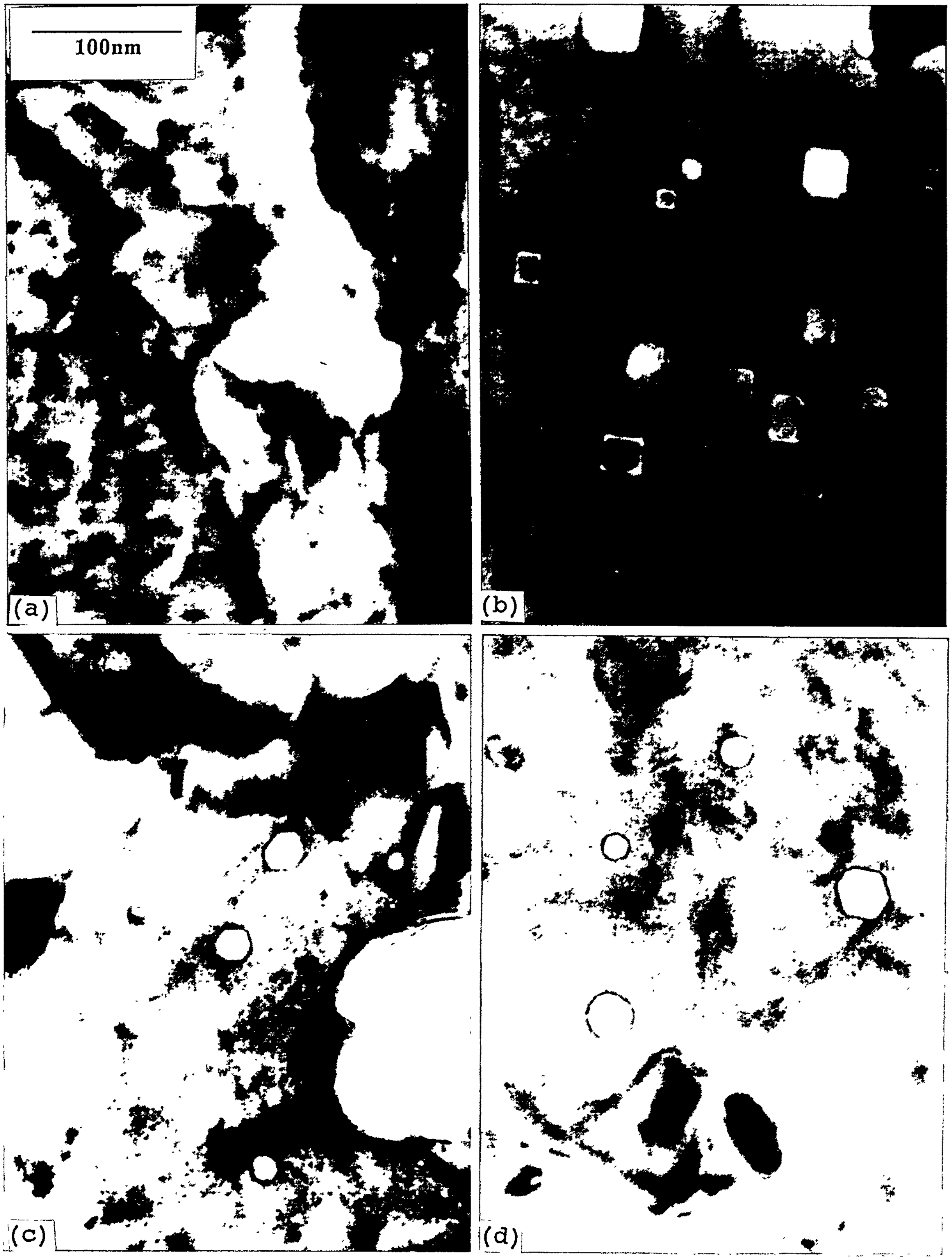

Fig. 3. Voids in (a) 12Cr-1MoVW, (b) 9Cr-1MoVNb, (c) 9Cr-2WV, and (d) 9Cr-2WVTa.

Dislocations and dislocation loops

Before irradiation, all four steels had a very high density of dislocations (about 10^{15} m^{-2}). Figure 4 shows the dislocation segments and loops of specimens after neutron irradiation. A quantitative summary of the dislocation loop density and total dislocation density is given in Table 2. It was observed that the 12Cr-1MoVW and 9Cr-1MoVNb steels contained a lower density of loops but with larger average diameter (about 100 nm) than the two tungsten-containing steels. The 12Cr-1MoVW and 9Cr-1MoVNb also contained some dislocation segments. On the other hand, the 9Cr-2WV and 9Cr-2WVTa alloys contained only loops and at a much higher density (around $3x10^{21}$ m^{-3}) and relatively smaller diameter (about 50 nm).

Table 2. Dislocation and Void Statistics For Four Steels Tested

Steel	Void density	Void mean diameter (nm)	void swelling (%)	dislocation loop diameter (nm)	loop density (m^{-3})	total dislocation density (m^{-2})
12Cr–1MoVW	5×10^{18}	30	0.007	100	5×10^{20}	*5×10^{14}
9Cr–1MoVNb	6×10^{20}	30	0.85	100	5×10^{19}	*2×10^{14}
9Cr–2WV	2.5×10^{19}	25	0.2	50	3×10^{21}	5×10^{14}
9Cr–2WVTa	4×10^{19}	25	0.33	50	3×10^{21}	5×10^{14}

*9Cr-1MoVNb and 12Cr-1MoVW had fewer loops but some dislocation lines

After irradiation, all of the specimens still contained a high density of dislocations (if the loop density is converted into dislocations). In 12Cr-1MoVW, the dislocation density was about $5x10^{14}$ m^{-2}. The loops in 9Cr-1MoVNb grew to a much larger size and looked like dislocation segments; the dislocation density of this steel was the lowest of the four steels at about $2x10^{14}$ m^{-2}. Both tungsten-containing alloys were similar and contained medium-sized loops and a dislocation density of about $5x10^{14}$ m^{-2}.

Precipitate evolution

It is well known that the majority of precipitates in these steels in the normalized-and-tempered condition are $M_{23}C_6$ carbides. It was observed that there was little difference in the $M_{23}C_6$ of the four steels in terms of size and distribution before and after irradiation. Nevertheless, the internal microstructure of the $M_{23}C_6$ particles did show some change after neutron irradiation. Figure 5 shows the microstructural features of $M_{23}C_6$ carbides after irradiation. The nature of this internal microstructural change was not identified.

Quantitative observations on the size and distribution of the precipitates are given in Table 3. The data indicate that the amount of $M_{23}C_6$ carbide in 12Cr-1MoVW is about twice as much as in the other three steels, which is understandable because there is twice as much carbon in the 12Cr-1MoVW (0.2 wt%) than in the other three steels (0.1 wt%).

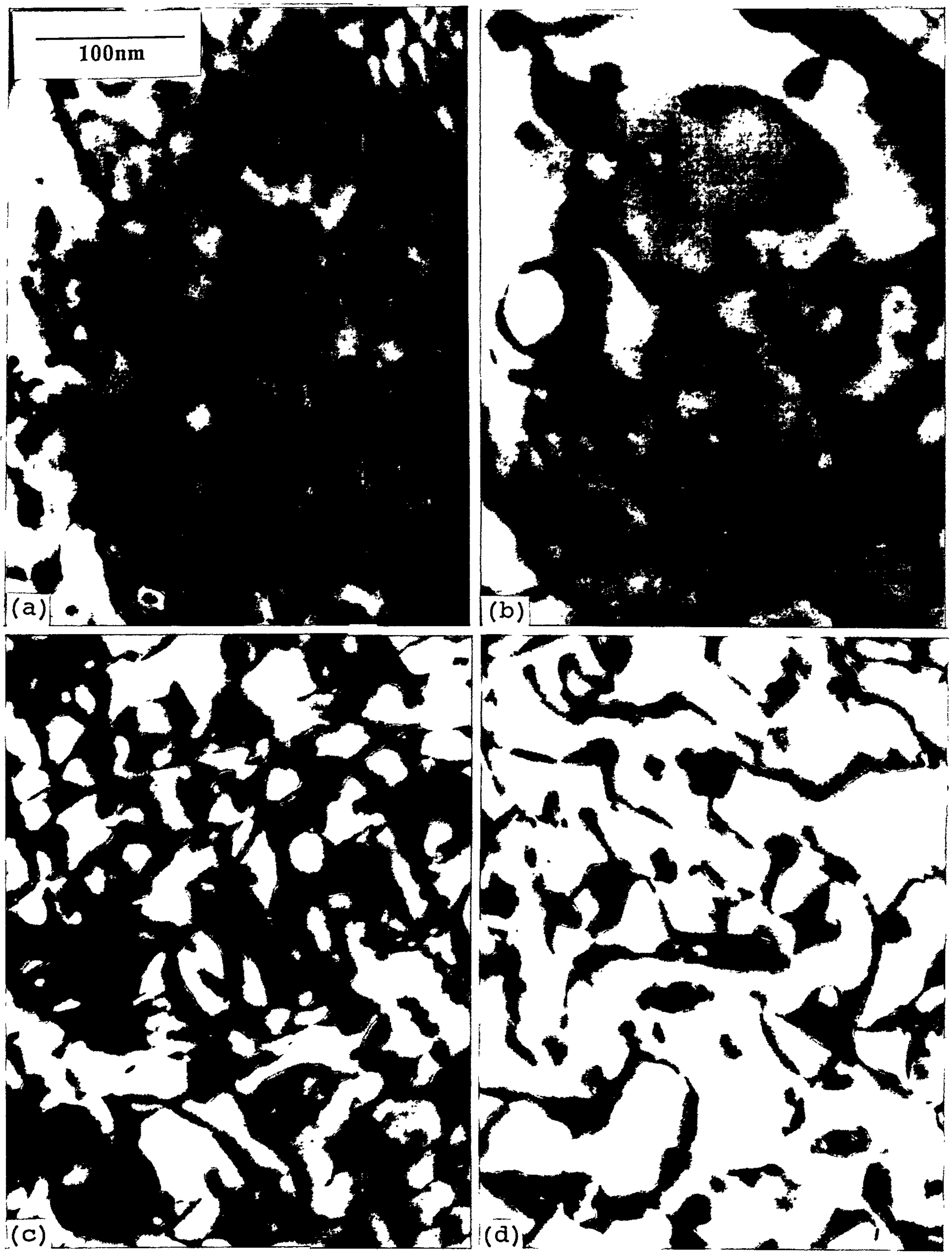

Fig. 4. Dislocation and dislocation loop structures in irradiated specimens of (a) 12Cr-1MoVW, (b) 9Cr-1MoVNb (c) 9Cr-2WV, and (d) 9Cr-2WVTa.

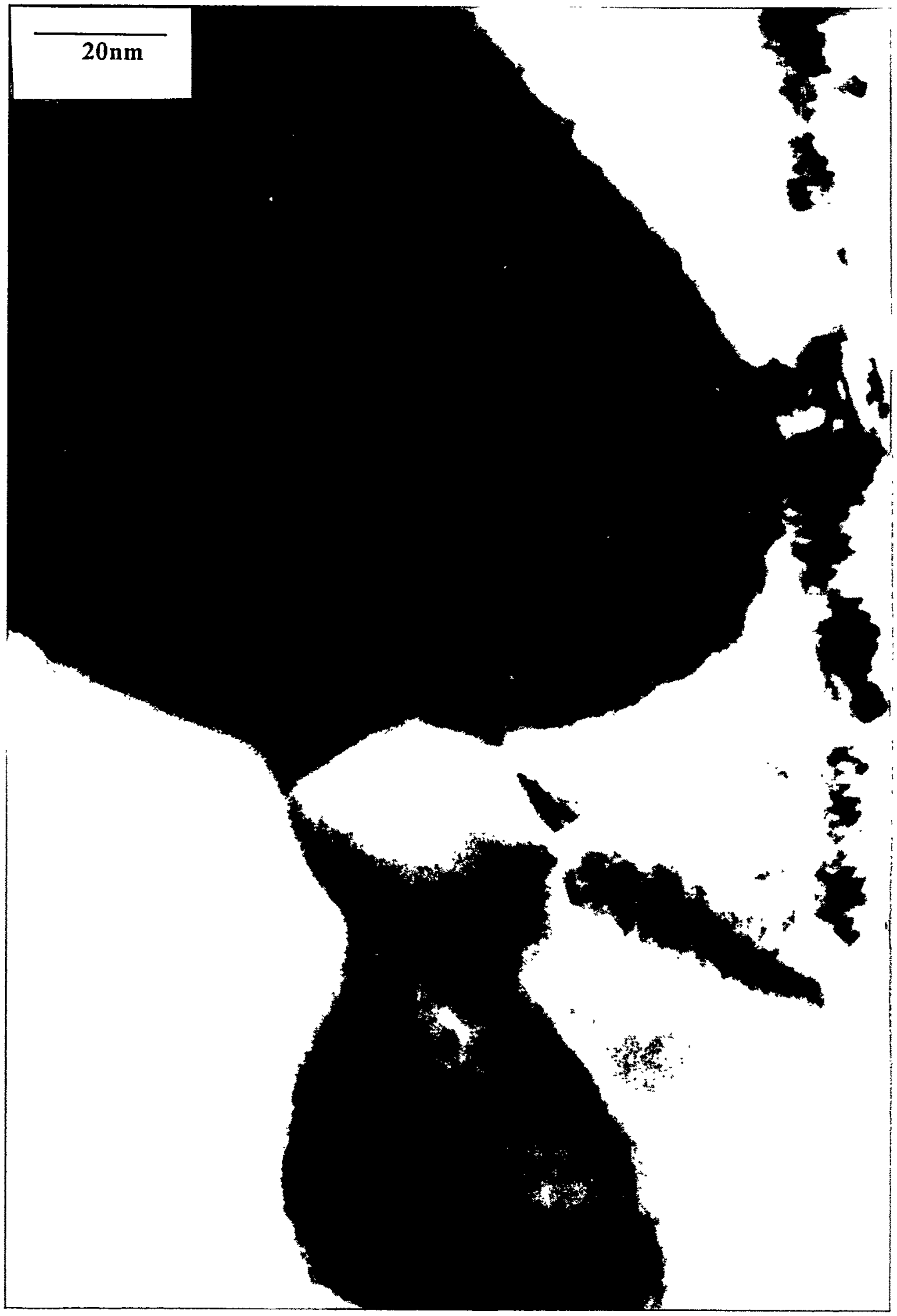

Fig. 5. Microstructure of $M_{23}C_6$ carbide in 9Cr-1MoVNb after neutron irradiation.

Table 3. Precipitate Statistics for Four Steels Tested

steel	before irradiation			after irradiation		
	ppt.	density (m^{-3})	average diameter (nm)	ppt.	density (m^{-3})	average diameter (nm)
12Cr–1MoVW	$M_{23}C_6$	7.1×10^{19}	155	$M_{23}C_6$	5.6×10^{19}	164
	MC	1.6×10^{18}	50	MC	1.0×10^{18}	55
				α'	1.5×10^{22}	5
				χ	6.1×10^{20}	13
9Cr–1MoVNb	$M_{23}C_6$	2.8×10^{19}	151	$M_{23}C_6$	2.6×10^{19}	155
	MC	7.9×10^{18}	32	MC	6.8×10^{18}	40
				χ	8.6×10^{20}	10
9Cr–2WV	$M_{23}C_6$	5.9×10^{19}	125	$M_{23}C_6$	3.2×10^{19}	160
	MC	1.2×10^{18}	54	MC	1.1×10^{18}	160
9Cr–2WVTa	$M_{23}C_6$	4.5×10^{19}	136	$M_{23}C_6$	4.1×10^{19}	143
	MC	7.5×10^{18}	29	MC	5.6×10^{18}	36

MC carbides are the other type of precipitate commonly found in these steels (Fig. 6). In 12Cr-1MoVW, the MC carbides are usually vanadium rich with some exceptions, which were chromium rich. The number density of MC carbides in 12Cr-1MoVW was small compared to $M_{23}C_6$. The MC carbides in 9Cr-1MoVNb are usually enriched in niobium and/or vanadium rich, with a number density $\approx 7x10^{18}$ m^{-3} and an average diameter of 40 nm. In the tungsten-containing steels, the number density and diameter are $1x10^{18}$ m^{-3} and 60 nm for the 9Cr-2WV steel and are $6x10^{18}$ m^{-3} and 36 nm for 9Cr-2WVTa steel. These MC carbides are either vanadium rich (in 9Cr-2WV) and/or tantalum rich (in 9Cr-2WVTa). Table 3 also summarizes the quantitative data of these carbides.

A high density of small precipitates in the matrix of the neutron-irradiated 12Cr-1MoVW steel specimen was tentatively identified as α' phase [see Fig. 7(a)]. The number density is about $1.5x10^{22}$ m^{-3} and the size varied from 4 to 6 nm in diameter. No similar precipitates were observed in the other three steels irradiated to similar conditions.

Another type of small precipitate was observed in neutron-irradiated 12Cr-1MoVW. These precipitates have a number density of $\approx 6.1x10^{20}$ m^{-3} and an average diameter of 13 nm. It was identified with the lattice fringe image as chi phase (Fig. 7). This phase was also found in neutron-irradiated 9Cr-1MoVNb steel, where the number density was $8.6x10^{20}$ m^{-3} and the size about 10 nm in diameter. No such precipitate was found in the two tungsten-containing steels.

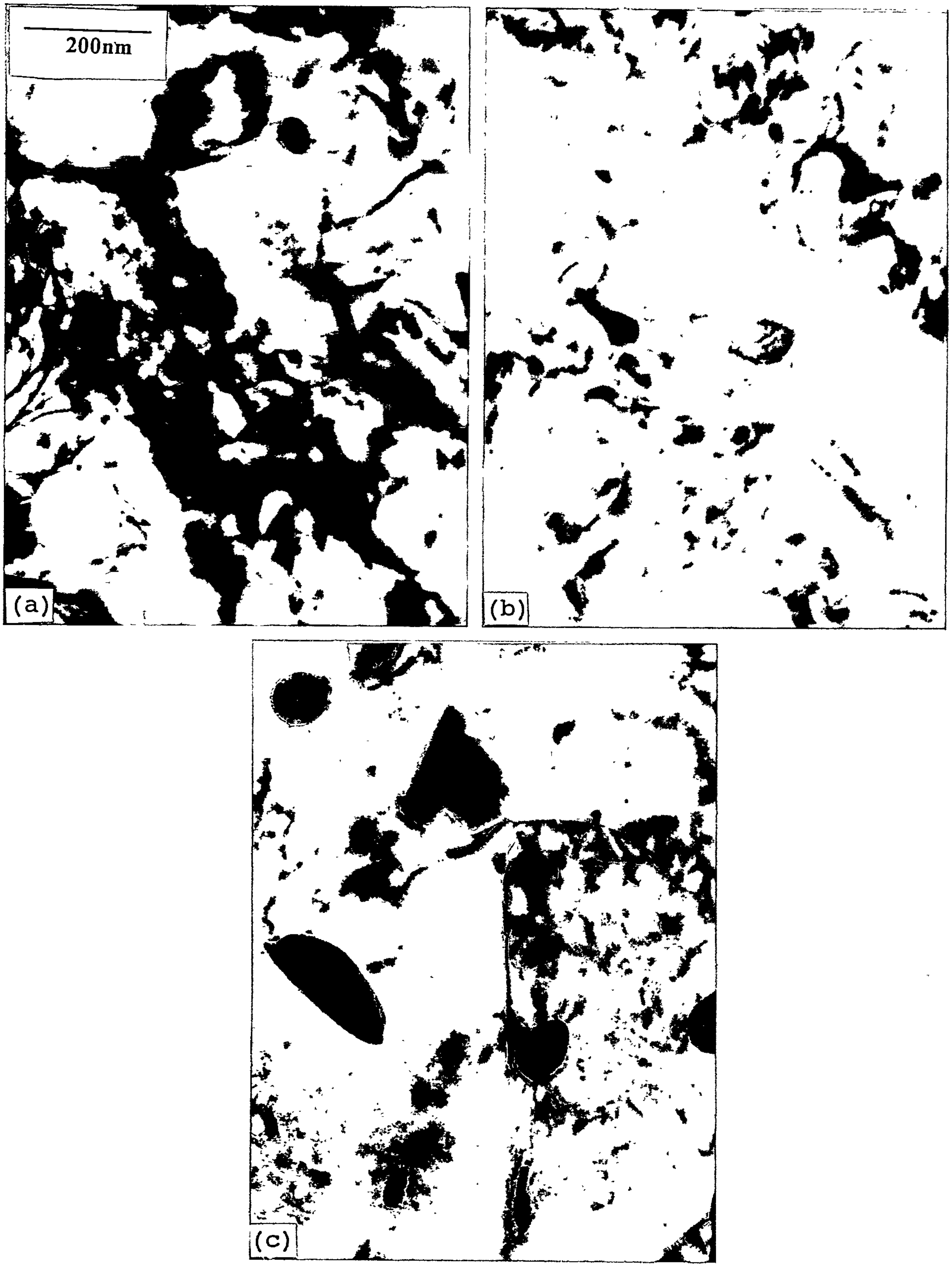

Fig. 6. Microstructures showing the MC carbides in (a) 9Cr-1MoVNb, (b) 9Cr-2WV, and (c) 9Cr-2WVTa.

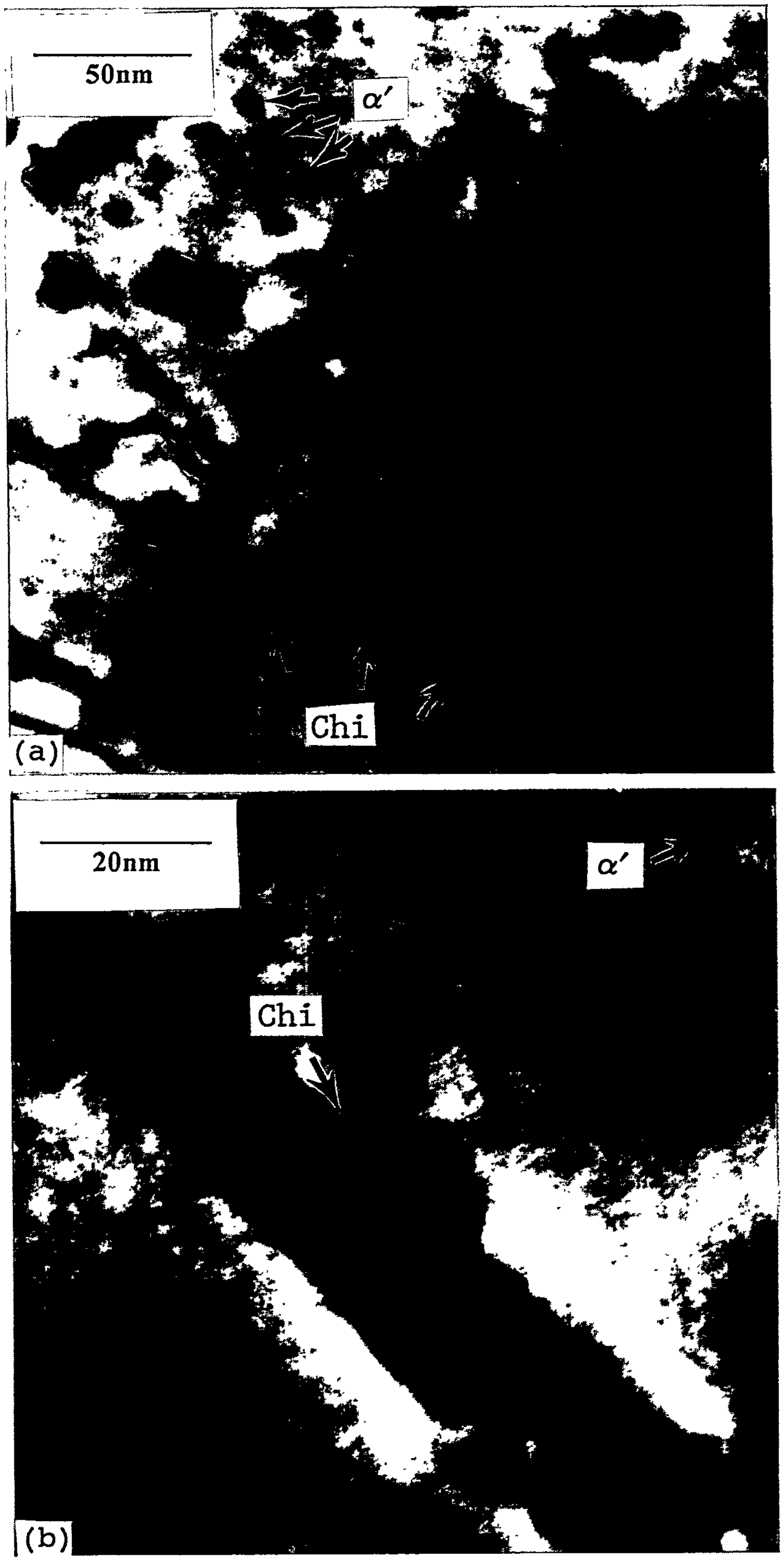

Fig. 7. The α′ and chi phases in 12Cr-1MoVW specimen after neutron irradiation.

Discussion

The difference in microstructure among the four unirradiated steels was minimal. In the normalized-and-tempered condition, all four steels contained 100% tempered martensite. The only significant difference was that the 12Cr-1MoVW steel contained twice the amount of carbides as were in the 9Cr steels, which was attributed to twice as much carbon in the 12Cr-1MoVW steel. The 9Cr steels with Nb or Ta contained small amounts of MC carbides enriched in either Nb or Ta, respectively. Despite these small differences before irradiation, the microstructural evolution during neutron irradiation caused significant differences among the four steels. In the following discussion, void swelling resistance, dislocation loop formation, and precipitate modification will be compared for the four steels.

It is well known that ferritic steels have excellent swelling resistance among the alloys considered for fusion structural applications. For the four steels, the 12Cr-1MoVW steel showed the best swelling resistance during neutron irradiation to 35 dpa, the total swelling being around 0.01%. Although the 9Cr-1MoVNb steel showed the most swelling among the four steels, swelling was still less than 1% at 35 dpa. Previous studies of several research groups showed similar results [8-12]. The void swelling behavior of the two tungsten-containing steels was similar that of the molybdenum-containing steels with the measured values falling between that of the two molybdenum-containing steels, around 0.2% to 0.3% at 35 dpa. The difference in void swelling among the four steels may be explained by the observations on the microstructural evolution. During irradiation of the 12Cr-1MoVW specimen, a very high density of small precipitates, both α' and chi phase, formed in the matrix, which served as sinks for vacancies and interstitials to recombine (it is known that coherent precipitates are sinks for recombination only), therefore suppressing the void nucleation and growth. A similar observation was found in proton-irradiated Inconel 600 alloy [13]. Although there were no such precipitates in the tungsten-containing steels, the high density of dislocation loops formed during irradiation served the same purpose with less effectiveness. In the irradiated 9Cr-1MoVNb specimen, there were fewer irradiation-induced precipitate particles compared to the 12Cr-1MoVW steel, and this steel also contained a lower dislocation density compared to that of the tungsten-containing steels. Therefore, it showed the highest void swelling during neutron irradiation.

Neutron-irradiation-induced precipitates were found in 12Cr-1MoVW steel. Chi phase particles were positively identified through the lattice image technique in both molybdenum-containing steels. The formation of this phase is believed to be due to the molybdenum content in the matrix or from decomposed $M_{23}C_6$ carbides which segregated during irradiation. However, no such phase formed in the two tungsten-containing steels. This observation agrees with other experimental evidence and thermodynamic calculations on the Fe-Cr-Mo [20] and on the Fe-Cr-W [21] ternary systems, which indicated that a higher concentration of chromium is required to form chi phase in the Fe-Cr-W system than in the Fe-Cr-Mo system.

Another type of very small precipitates was found in the 12Cr-1MoVW steel but not in the other three steels, and it was tentatively identified as α'. From Fig. 7(b), it is seen that these smaller particles are not chi phase, because although they were in the same matrix, they displayed a different orientation. It is generally believed that in high-chromium ferritic steels (>15%wt.), there is a possibility of aging embrittlement due to the formation of α' phase through either spinodal decomposition or nucleation and growth, depending on the aging temperature [15]. Under irradiation, however, the critical chromium content necessary to form α' phase may be lower than that during thermal aging. Previous studies of irradiated 12Cr steel [16-18] also reported the similar particles and identified them as chromium-enriched α′ phase. Mechanical property studies of the four steels indicated that of the four steels, the 12Cr-1MoVW steel showed the highest shift in ductile-brittle transition temperature (DBTT) and the most hardening after neutron irradiation. As discussed in a companion paper [19], it is believed that both new phases formed in 12Cr-1MoVW may contribute to the increase in strength and decrease in toughness.

It was observed that in 9Cr-2WV and 9Cr-2WVTa steels, a relatively high density of dislocation loops formed during irradiation at 420°C, which was not found in the molybdenum-containing steels (12Cr-1MoVW and 9Cr-1MoVNb). This observation has not been reported in the literature. It is believed that during neutron irradiation, the pre-existing dislocations gradually recovered and were replaced by dislocation loops (average size around 50 nm). These loops could then serve as the point defect sinks that suppressed the void swelling below that observed in 9Cr-1MoVNb, where no such loops formed.

Conclusions

An examination of the microstructural evolution of four martensitic steels before and after neutron-irradiation at 420°C to about 7.8×10^{26} n/m^2 leads to the following conclusions:

(a) Before irradiation, the microstructures of the four steels were tempered martensite containing $M_{23}C_6$ and a few MC carbides. Due to the higher carbon concentration, the 12Cr-1MoVW steel contained twice as much $M_{23}C_6$ carbides than the other three 9Cr steels.

(b) During irradiation of the 12Cr-1MoVW steel, a very high density of small precipitates formed, which were identified as chi phase (13 nm in diameter and 6.1×10^{20} m^{-3}) and α′ phase (5 nm in diameter and 1.5×10^{22} m^{-3}). These radiation-induced precipitates may be the reason for the large increase in DBTT of this steel after irradiation. The α′ phase forms because of the higher chromium content in this steel.

(c) In irradiated 9Cr-1MoVNb steel, the only radiation-induced phase observed was chi phase. The formation of chi phase in both 9Cr-1MoVNb and 12Cr-1MoVW steels and not in the 9Cr-2WV and 9Cr-2WVTa steels is believed to be due to the molybdenum in these steels.

(d) Irradiation caused no new phases to form in the 9Cr-2WV and 9Cr-2WVTa steels; however, a relatively high density of dislocation loops formed (the dislocation density is around 5×10^{14} m^{-2}).

(e) The 12Cr-1MoVW showed the best swelling resistance among the four steels irradiated, and the 9Cr-1MoVNb had the highest void swelling. The difference in void swelling behavior was attributed to the microstructural variations, including the radiation-induced precipitates and dislocation loops.

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