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Journal of Nuclear Materials 258–263 (1998) 1675–1680

journal of nuclear materials

The structural evolution of new low-activation and chromium–nickel stainless steels under high-dose irradiation up to 200 dpa

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Abstract

This paper deals with the evolution of the dislocation structure, phase composition and vacancy voids in new reactor stainless steels over the temperature interval from 500°C to 700°C under irradiation with electrons, neutrons and krypton ions up to high damaging doses (200 dpa). It is shown that the amount of voids formed in stainless steels exposed to irradiation with high-energy particles can be reduced by producing a high-density of direct and indirect sinks of point defects in the form of α/γ phase boundaries and dispersed intermetallics (γ' and α' phases in FCC and BCC steels, respectively) formed under irradiation. Compositions of radiation-resistant alloys, including low-activation ones of the Cr13Mn7W2 type having an austenitic–martensitic lath structure, have been proposed.

1. Introduction

The radiation swelling resistance of stainless steels is known [1–7] to be largely determined by the evolution of the structural and phase compositions under irradiation. The formation of voids under irradiation can be retarded by producing a large number of point-defect sinks in the form of dislocations [1] and coherent and incoherent phases [5,6]. The appearance of the "point defect-impurity" complexes in stainless steels containing up to 0.5% Si or Ti [7] and also replacement of the lattice types in these steels (FCC by BCC) [2] alter the diffusion characteristics and frequently cause a decrease in the intensity of the radiation-induced swelling. This paper analyzes the structural evolution, including the void concentration variation, in special efficiently alloyed stainless steels having a large amount of point defect sinks in the form of α/γ and γ/γ' boundaries, when these steels are exposed to large doses (up to 200 dpa) of irradiation with high-energy particles.

2. Materials, heat treatment and methods

The subjects of study were two classes of stainless steels containing a high-plasticity FCC austenite in their structure: (1) austenitic-martensitic Cr16Ni9Mo3 and Cr13Mn7W2 steels having a lath α/γ structure; (2) Cr16Ni15Mo3 and Cr16Ni15Mo3Til austenitic steels. The radiation-induced precipitation of the phase γ'-phase (Ni_3Ti) is observed in the titanium-containing steel. The compositions of the steels at hand are shown in Table 1.

The samples were irradiated at 480–650°C with 1-MeV electrons (JEM-1000 electron microscope) [6], 1.5-MeV Kr^+ ions [4], and fast neutrons (BN-600 reactor) [3]. the structural evolution and phase transformations were studied using transmission electron microscopy. Accelerated ions were fed to the electron microscope [4], making it possible to analyze the same place of the foils during irradiation to 200 dpa.

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PII: S0022-3115(98)00401-2

Table 1
Chemical composition and thermal treatment conditions of the steels studied

No	Steel type	Thermal treatment conditions	Concentration of alloying elements, mass%						
			C	Cr	Ni	Mo	Mn	Ti	W
1.	Cr16Ni9Mo3	Quenching from 1050°C–80°C for 3 h, 560°C for 1h	0.02	15.8	8.9	2.7	–	–	–
2.	Cr13Mn7W2	Quenching from 1050°C–80°C for 3 h, 670°C for 1.5 h	0.06	12.5	–	–	7.0	–	2.0
3.	Cr16Ni15Mo3	Quenching from 1100°C	0.02	16.0	15.0	2.7	–	–	–
4.	Cr16Ni15Mo3Til	Quenching from 1100°C	0.03	15.9	15.0	2.5	0.38	1.0	–

3. Results and discussion

3.1. Cr–Ni–Mo stainless steels having a martensitic–austenitic lath structure

Ferritic, martensitic and ferritic–martensitic stainless steels having a BCC lattice have been widely used recently as reactor materials. These steels are highly resistant to radiation swelling but are prone to be a strong embrittlement under irradiation. The plasticity and the toughness of steels with dominating BCC lattice may be considerably improved if a sufficient amount of a high-plasticity austenite is produced in the structure [8]. To this end, it is necessary [6] that the two-phase steel contains martensite instead of ferrite as the BCC structure and the transformation-hardened FCC austenite with a high density of dislocations (this austenite is the product of the reverse martensitic $\alpha \rightarrow \gamma$ transformation). A lamellar austenitic-martensitic structure having a high density of sinks in the form of closely spaced α/γ phase boundaries and intralath dislocations was produced in the Cr16Ni9Mo3 steel with the martensite start temperature of $\sim$0°C. This structure appears as a result of the $\gamma \rightarrow \alpha$ transformation (−80°C, 3h) and a partial reverse $\alpha \rightarrow \gamma$ transformation during heating to 560°C. Thin plates of reverse austenite are formed between martensitic lath α-crystals. In addition to the austenitic-martensitic laths, the structure contains large regions of the retained austenite. Thus, two modifications of the austenite were irradiated: an ordinary polyhedral austenite produced in quenched austenitic steels and a thin-plate austenite located between laths of the α-martensite. Both austenitic components large light-colored fields of the retained austenite (40%) and thin oblong crystals of the reverse austenite (30%) between martensitic laths (30%) – are seen in Fig. 1(a). The Cr16Ni9Mo3 steel possesses rather high properties: $\sigma_{0.2} = 700$ MPa, $\sigma_B = 886$ MPa, $\delta = 27\%$, and $\psi = 70\%$ ($T_{test} = 20$°C).

A 6-h electron irradiation of the samples in the JEM-1000 microscope at 500°C and the dose of 20 dpa [6] does not cause any void formation in the lamellar α/γ structure (Fig. 1(b)). Swelling of the polyhedral retained austenite exposed to the same irradiation conditions is considerable ($\Delta V/V = 0.2\%$), Fig. 1(b). Voids up to 15 nm in diameter appear in the areas of the retained austenite already after 30 min of electron irradiation (fluence $F = 1 \times 10^{23}$ e/cm^2, dose of 1.7 dpa). The mean dimension of the voids increases to 18 nm after a 1-h irradiation. The variation of the mean dimension d of the voids, their density ρ, and swelling $\Delta V/V$ of the Cr–Ni–Mo austenite having different morphologies under exposure to an electron fluence at 500°C are shown in Fig. 2. The main reasons for the different behaviour of the polyhedral austenite and the lath α/γ structure are as follows: (1) Numerous α/γ phase boundaries between alternating austenite and martensite laths (spaced $\sim$100 nm) represent closely spaced sinks of point defects and suppress the void formation. (2) A high density of dislocations in the martensite (up to 10^{11} cm^{-2}) and the transformation-hardened austenite (up to 5×10^{10} cm^{-2}) [8] inhibits swelling too.

Moreover, the reverse austenite in the structure of the martensitic-austenitic stainless steel provides for a higher plasticity and improved toughness compared to those of martensitic or ferritic steels.

The lath α/γ structure remains stable at 400–550°C and no void formation is observed. The $\alpha \rightarrow \gamma$ transformation takes place, the lath phase becomes coarser, and the density of dislocations in the reverse austenite decreases, when the irradiation temperature is raised to 600–650°C. As a result, voids are formed in the γ-phase plates, although a rate of voids formation is smaller than in the massive fields of the retained austenite. Large (40 nm) and small ($\sim$10 nm) voids are seen in the structure of Cr16Ni9Mo3 steel after 200 dpa irradiation with 1.5-MeV Kr^+ ions at 650°C (Fig. 1(c)).

3.2. Low-activation stainless steels with a lath α/γ structure

The development of low-activation reactor steels and alloys where only "short-lived" isotopes having a short half-life period are formed under neutron irradiation is very important from the ecological viewpoint. These materials would not present any hazard and could be used again, in particular, after they have been stored for 100 years [9]. Manganese could serve as the austenite-forming element in low-activated steels. The Fe–Cr, Fe–V and Fe–Cr–V(W) BCC systems and the Fe–Mn and Fe–Cr–Mn–W FCC systems may be used for develop-

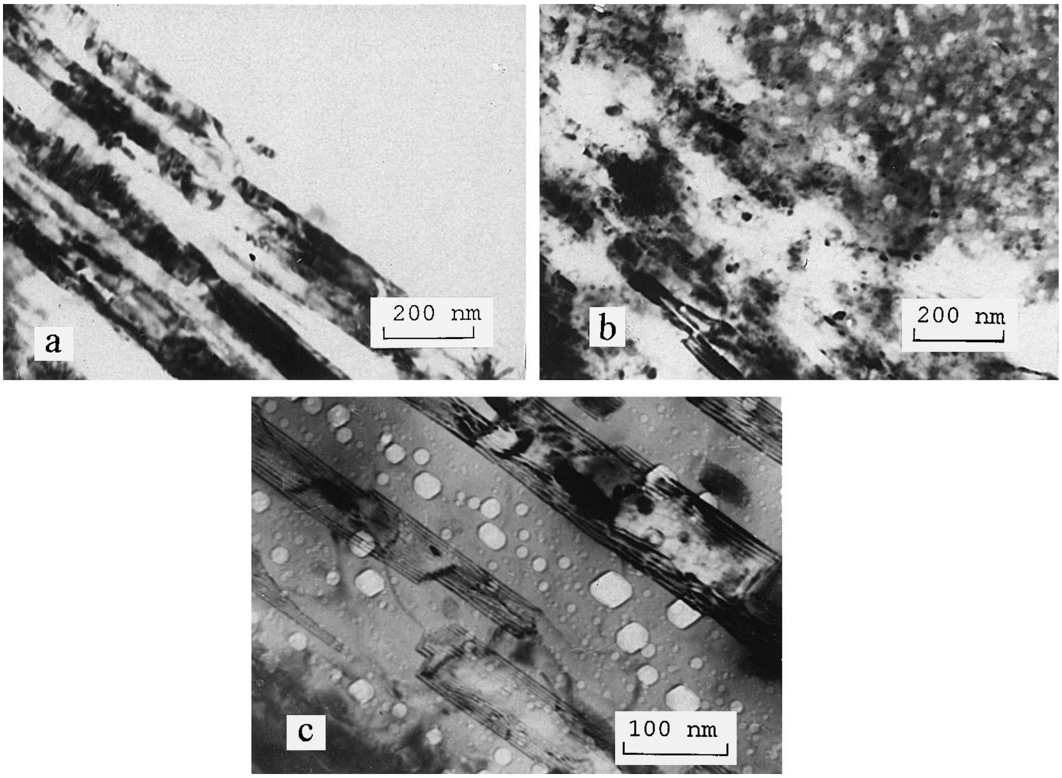

Fig. 1. Lath austenitic-martensitic structure and retained austenite of the Cr16Ni9Mo3 steel in the initial state (a) and after irradiation with electrons (~1 MeV) up to the dose of 20 dpa at 500°C (b) and Kr^+ ions (~1.5 MeV) up to the dose of 200 dpa at 650°C (c). The preliminary treatment included quenching from 1100° C, the γ→α transformation at −80°C for 3 h, and a partial α→γ transformation at −560°C for 1 h.

ment of low-activation steels. The low-activation Cr12Mn20W steel, which was chosen as the prototype [9], contains a large amount of manganese (~20%). If a martensitic-austenitic lath structure having 15–30% plastic γ-phase is used, the manganese content of the steel may be decreased to 6–8 mass%. The composition of the low-activation Cr13Mn7W2 steel is given in Table 1. The steel containing 12.5 mass% chromium and 0.06 mass% C (Cr13Mn7W2) is virtually a martensitic steel ($M_s \approx 170$°C, content of δ-ferrite ⩽ 5%). Nearly 75% α-matensite is formed in this steel after quenching and cold treatment (−80°C, 3 h). Note that for the Cr13Mn7W2 steel the α→γ transformation range corresponds to the temperatures of 640–720°C. This is almost 100°C higher than for the Cr16Ni9Mo3 steel. Therefore the temperature stability region of the lath structure is larger for the low-activation steel than for the Cr–Ni–Mo steel. A lamellar α/γ structure was produced in the Cr13Mn7W2 steel thanks to the reverse α → γ transformation during heating to 670°C (holding for 1.5 h). Under these thermal conditions the lath γ-phase is stabilized, because it is enriched in austenite-forming elements (Mn,C). Voids are not formed when the austenitic-martensitic structure is irradiated with 1-MeV electrons up to the dose of 150 dpa at 600°C (Fig. 3(a)). Voids are not formed in the δ-ferrite either. Small voids up to 10 nm in dimension appear in the lath structure of the Cr13Mn7W2 steel exposed to irradiation with 1.5-Me V Kr ions up to the dose of 200 dpa at 650°C (Fig. 3(b)). Thus, the thin-plate martensitic-austenitic structure of the low-activation Cr13Mn7W2 steel resists radiation swelling up to the temperature of 600°C.

3.3. The behaviour of radiation-ageable stainless steels

The radiation-induced precipitations of γ′-intermetallics of the Ni_3Al type was found [2] to suppress radiation swelling. However, this phenomenon applies primarily to FCC steels and alloys containing a high concentration of nickel (40–80%) and a sufficient amount of intermetallic-forming elements (Ti,Al). The austenitic Cr16Ni15Mo3Ti1 steel containing 1.0 mass% Ti was studied [3]. The intermetallic γ′-phase of Ni_3Ti is formed in this steel under irradiation with fast neutrons at 480–500°C, which are the temperatures of the

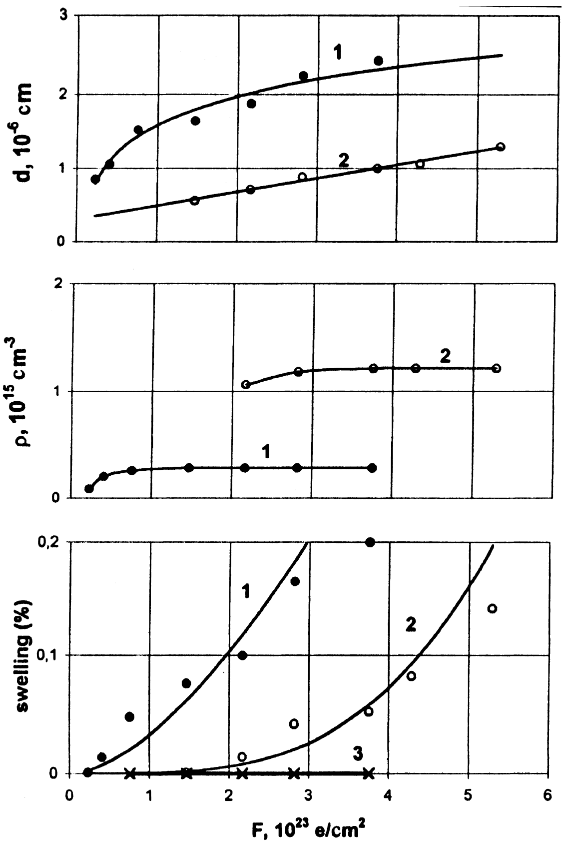

Fig. 2. Mean dimension of the voids, d, their density ρ and the specific volume $\Delta V/V$ in different morphology austenites depending on the electron fluence ($E = 1$ MeV) at 500°C: 1-Cr16Ni9Mo3; 2-06CrNi15Mo3B, polyhedral austenitic; 3-Cr16Ni9Mo3, lath austenite.

maximum swelling rate. At 480°C swelling of the quenched steel with 1 mass% Ti was 0.6% (the dose of 60 dpa). This value is 7 times as low as that ($\Delta V/V \approx 3.9\%$ or more) for other quenched stainless steels of the Cr16Ni15Mo3 type, which did not contain titanium or contained 0.3 mass% Ti, 0.6 mass% Al or Si. The steel with 1 mass% Ti had the void concentration $\rho = 0.25 \times 10^{20}$ m^{-3}, which is several times lower than in other steels. The dimensions of the voids differed insignificantly (78–100 nm).

To determine the temperature dependence of swelling of FCC stainless steels exposed to a high damaging dose (up to 200 dpa), the samples were irradiated with 1.5-MeV Kr^+ ions at 500–700°C [4]. Fig. 4 illustrates the temperature dependence of swelling $\Delta V/V$ of the steels studied. The Cr16Ni15Mo3 steel irradiated with Kr^+ ions has the swelling peak at 650°C, which is nearly 150°C higher than in the case of fast-neutron irradiation. This phenomenon has been known before [2] and constitutes a specific feature of the ion irradiation. The

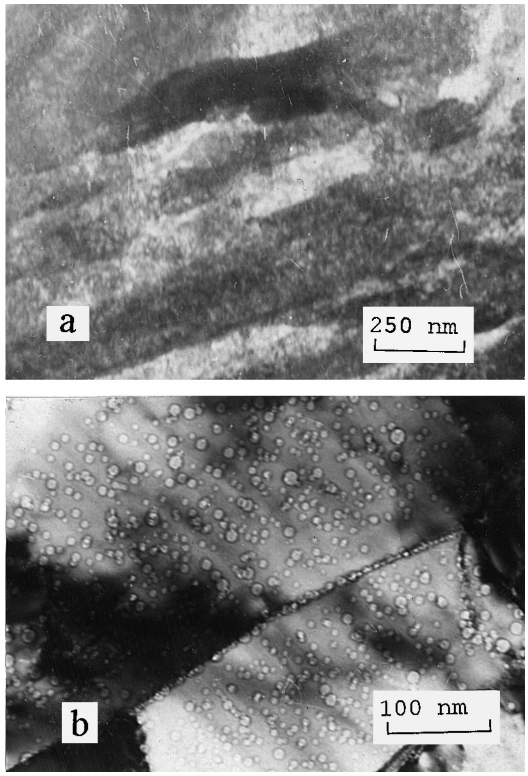

Fig. 3. Structure of the Cr13Mn7W2 steel after irradiation with 1-MeV electrons up to the dose of 150 dpa at 500°C (a) and 1.5-MeV Kr^+ ions up to the dose of 200 dpa at 650°C (b).

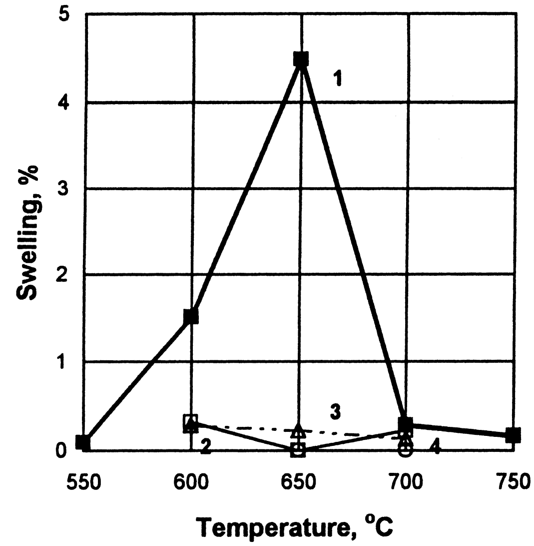

Fig. 4. Vacancy swelling $\Delta V/V$ of the austentic steels types Cr16Ni15Mo3 (1) and Cr16ni15mo3til (2–4) as a function of the temperature of irradiation with 1.5-MeV Kr^+ ions (200 dpa). Treatment:1,2-quenching from 1050°C; 3-quenching + aging at 650°C for 8000 h; 4-quenching+20-% cold deformation.

Cr16Ni15Mo3Ti1 steel irradiated with 1.5-Mev Kr^+ swells considerably less (~0.2%) both in the quenched and annealed (8000 h at 650°C) states. No vacancy voids were detected in the cold-deformed steel with 1 mass% Ti under Kr^+ irradiation up to 200 dpa. The last fact attests to a considerable increase in the radiation swelling resistance under the combined effect of cold deformation and radiation-induced intermetallic aging. The structural evolution was studied in one and the same area of a foil exposed to a high-dose ion irradiation in an electron microscope [4]. It was found that some dislocations pinned by fine particles during irradiation are preserved. However, the main reason for the swelling suppression is probably the fact that γ'-particles of Ni_3Ti, which precipitate under irradiation, represent effective "indirect" sinks of point defects [3]. Precipitation of Ni_3Ti in a Cr–Ni–Mo Ti steel requires that nickel and titanium atoms are supplied to the nucleation sites of this phase and "excess" atoms of iron, chromium and molybdenum are removed from these zones. In the case of the vacancy mechanism of diffusion, radiation vacancies will be "involved" in diffusion flows of substitutional elements until austenite precipitates. The larger the number of the precipitating particles, the greater the number of vacancies engaged in diffusion processes. If the precipitation kinetics of fine γ'-particles (6–8 nm in dimension, the concentration of ~3% [3]) is slow (which is the case at 500–600°C in stainless steels of the Cr16Ni15Mo3Ti1 type with a small titanium supersaturation), the aging process takes a long time before it is complete. This is also due to the fact that the aging process is accompanied by the dissolution of γ'-particles in displacement cascades. Under these conditions swelling may be suppressed for a very long time. The suppression of swelling does not require that the precipitating particles and high elastic distortions about these particles are necessarily coherent. What counts is that the particles contain substitutional elements (diffusion of interstitials does not require movement of vacancies) and are spaced close to one another.

Ferritic and ferritic–martensitic BCC stainless steels are known [2,10,11] to have a higher resistance to the vacancy void formation than austenitic FCC steels. BCC Fe alloys containing 12.5 or 18 mass% chromium possess a high resistance to swelling ($\Delta V/V \leqslant 0.5\%$) up to the dose of 140 dpa at 425°C. The swelling resistance of their low-chromium (6–9%) counterparts in the same conditions is lower: $\Delta V/V \approx 1.5$–2.3% [10]. Note that the study of ferritic-martensitic steels containing over 12% chromium revealed a redistribution of Cr in the α solid solution under irradiation with fast neutrons. That was accompanied by the isomorphous precipitation of the dispersed high-chromium BCC α'-phase whose parameters were similar to those of the α-matrix. In ordinary thermal conditions (w/o irradiation) the α'-phase appears in high-chromium BCC steels and causes a considerable embrittlement (at 475°C). It may be assumed that the formation of the α'-phase in irradiated ferritic-martensitic steels, where the content of Cr and other ferrite-forming elements (Mo,W) is about 12% or higher, suppresses the radiation-induced void formation in a way similar to the precipitation of the γ'-phase in austenitic stainless steels having a FCC lattice [3,4]. The α'-phase does not precipitate in low-chromium Fe–Cr alloys under irradiation and therefore these alloys experience an active vacancy swelling [10]. Radiation point defects involved in diffusion flows of Fe, Cr and other substitutional elements during a uniform precipitation of a large amount of the α'-phase prevent the vacancies from uniting into voids. However, the α'-phase and the γ'-phase have a largely different effect on the steel properties: the γ'-phase in FCC alloys does not embrittle the material, while the α'-phase causes a severe embrittlement of the BCC ferrite and martensite.

4. Conclusions

1. It is shown that at 500°C the radiation swelling resistance of the thin-plate transformation-hardened austenite is higher than the radiation swelling resistance of the ordinary equiaxial polyhedral austenite. Certain compositions have been developed for radiation-resistant stainless steels of the Cr16Ni9Mo3 type having a lamellar thin-plate structure, which comprises alternating laths of martensite and transformation-hardened austenite with numerous point-defect sinks in the form of α/γ phase boundaries and dislocations. Low-activation stainless steels of the Cr13Mn7W2 type have been proposed. These steels are highly resistant to the vacancy void formation under a large-dose irradiation with high-energy particles (150 dpa at 500°C).

2. Alloying of the Cr16Ni15Mo3 type steel with 1 mass% titanium is shown to re-assign this steel to the precipitation-hardening steels, lead to the radiation-induced precipitation of the coherent γ'-phase, and sharply decrease the vacancy swelling. A high radiation resistance of the aging austenitic steels is explained by pinning of dislocations and the formation of a large number of uniformly distributed neutral "indirect" point-perfect sinks represented by fine (up to 8 nm) γ'-phase particles (Ni_3Ti).

3. It is conjectured that the high resistance to a vacancy swelling has a similar origin in ferritic (ferritic-martensitic) chromium BCC stainless steels and aging austenitic FCC steels. In both cases the high resistance to the void formation is attributed to the radiation-induced precipitation in the matrix, which is accompanied by appearance of uniformly distributed fine coherent particles of the γ'-phase (austenitic steels) or a high-chromium α'-phase (ferritic steels). These phases serve as effective "indirect" sinks of point defects.

Acknowledgements

This study has been financially supported by the IPP, USA (Agreement No. 942492402) and the Russian Fundamental Research Foundation (Projects No. 95-02-03539a and No. 96-15-96515).

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