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Atom Probe Tomography of the Evolution of the Nanostructure of Oxide Dispersion Strengthened Steels under Ion Irradiation

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Abstract—The atom probe tomography of the nanostructure evolution in ODS[1] Eurofer, ODS 13.5Cr, and ODS 13.5Cr–0.3Ti steels under heavy ion irradiation at 300 and 573 K is performed. The samples were irradiated by 5.6 MeV Fe^{2+} ions and 4.8 MeV Ti^{2+} ions to a fluence of $\sim 10^{15}$ cm^{-2}. It is shown that the number of nanoclusters increases by a factor of 2–3 after irradiation. The chemical composition of the clusters in the steels changes after irradiation at 300 K, whereas the chemical composition of the clusters in the 13.5Cr–0.3Ti ODS steel remains the same after irradiation at 573 K.

Keywords: oxide dispersion strengthened (ODS) steels, nanostructure, irradiation, heavy ions, clusters, atom probe tomography

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INTRODUCTION

Oxide dispersion strengthened (ODS) reduced activation ferritic-martensitic steels with a high-temperature strength and, as expected, high resistance to radiation damage are developing for application in fission and fusion reactors [1]. They contain a large number of oxide nanoparticles, which ensure better service properties at elevated temperatures [2, 3]. The atom probe tomography (APT) study of ODS steels revealed a considerable number of nanoclusters (regions enriched in elements such as Y, O, V, and/or Ti), which is greater than the number of oxide particles. The influence of this clusters on the mechanical properties of the ODS steel, in particular, on their irradiation-induced change is poorly understood.

Our previous studies of the irradiation effect on the ODS Eurofer steel nanostructure revealed the exchange of chemical elements between oxide particles and clusters [4, 5]. For example, neutron irradiation at 603 K to a dose of 32 dpa causes a significant change in the nanocluster chemical composition: vanadium and nitrogen migrate from clusters into the matrix, while yttrium, oxygen, and manganese partially leave oxide particles to enrich nanoclusters [4]. Similar behavior of nanoclusters in ODS Eurofer steel was observed in APT samples irradiated by low-energy iron ions in the damage dose range up to 32 dpa at room temperature [5]. A significant change in the composition was observed at doses on the order of several displacements per atom.

The aim of the present work is to study 13.5Cr ODS, 13.5Cr–0.3Ti ODS, and ODS Eurofer steels after irradiation by atom probe tomography. The nanostructure evolution under irradiation by Fe^{2+} and Ti^{2+} ions with an energy of 100 keV/nucleon to fluences of $\sim 10^{15}$ cm^{-2} at 300 and 573 K is investigated.

EXPERIMENTAL

Materials

The following high-chromium ODS steels were the objects of study: 13.5Cr ODS, 13.5Cr–0.3Ti ODS (wt %) [6], and ODS Eurofer steels [3]. These steels were produced by mechanical alloying of initial base powders with the addition of yttrium oxide or 0.3 wt % titanium powder (in the case of 13.5Cr–0.3Ti ODS steel) in an attritor mill. The ground powders were encapsulated into steel for subsequent degassing and

[1] Oxide dispersion strengthened.

Table 1. Irradiation conditions for ODS steels

Irradiated steel	Energy, MeV	Type of ion	Fluence, $\times 10^{15}$ cm^{-2}	T, K
ODS Eurofer	5.6	Fe^{2+}	1	300
	4.8	Ti^{2+}	1	300
ODS 13.5Cr	4.8	Ti^{2+}	1	300
ODS 13.5Cr–0.3Ti	4.8	Ti^{2+}	1	300
	4.8	Ti^{2+}	1	573
	4.8	Ti^{2+}	3	573

pressing; then, after electron-beam welding of the capsule cap, they were compacted. The 13.5Cr ODS and ODS Eurofer steels were produced by hot isostatic pressing (HIP) at a pressure of 100 MPa and temperatures of 1100 and 1150°C, respectively. The 13.5Cr–0.3Ti ODS steel was compacted by hot extrusion at 1100°C. The ODS Eurofer steel was additionally heat-treated under the following conditions: annealing at 980°C for 30 min and tempering at 760°C for 2 h. The 13.5Cr ODS and 13.5Cr–0.3Ti ODS steels were subjected to no additional treatment after HIP and extrusion.

Irradiation Conditions

The heavy-ion irradiations of the ODS steels were conducted using a HIP-1 spatially uniform quadrupole focusing linear accelerator [7, 8]. This linear accelerator can accelerate ions with the mass to charge ratio of ≤60 at an energy of 100 keV/nucleon. The ion beam density at a target was 3–6 mA/cm^2. The irradiation was pulsed at a repetition rate of 0.25 Hz. The ion beam pulse duration was 450 μs. The pressure during irradiation was lower than 0.2 mPa.

In this work, Fe^{+2} and Ti^{2+} ion beams at an energy of 5.6 and 4.8 MeV, respectively, were used to irradiate the samples. According to the calculations carried out with the SRIM software, the maximum number of radiation-induced defects in iron is generated at a distance of 1.4 and 1.25 μm for Fe^{2+} and Ti^{2+} ion beams, respectively, from the irradiated surface. Damage calculation (in displacements per atom) was carried out according to the recommendations given in [9].

The irradiated samples had the shape of disks 3 mm in diameter and a thickness of 0.1 mm. The samples were mechanically thinned to a thickness of 100 μm. The surface roughness of the samples was controlled by atomic force microscopy before and after irradiation. It was less than 50 nm for all samples. The samples of the ODS steels were irradiated up to a fluence of 3×10^{15} cm^{-2} at different temperatures (Table 1).

Atom Probe Tomography

The nanostructure examination of the ODS materials was performed at the Nano, Microfacility (KNMF) Center of the Karlsruhe Institute of Technology using an LEAP 4000X HR atom probe with a local electrode. All presented data were collected in the field evaporation mode. The sample temperature was 70–75 K, the repetition rate was 200 kHz, and the pulse fraction was 20% DC voltage. The samples to be irradiated were prepared in the following two stages: first, strips 0.3 × 0.3 × 10 mm in size were cut from a bulk workpiece using electroerosion cutting in water; second, they were thinned to the desired dimensions (tip radius of <50 nm and taper of less than 11°) using anodic etching in electrolyte. Samples from the irradiated materials were cut out at the desired distance from the irradiated surface using an FEI QUANTA 3D dual-beam system [10, 11]. The samples were cut out at different distances from the irradiated surface, near the region of the maximum damages.

Data processing included analysis of mass spectra and the reconstruction of the spatial distribution of chemical elements over the volume. For cluster analysis, the maximum separation method was used [12]. It allows identifying clusters and gathering information about their number, composition, and density. In this procedure, a sphere of radius $d_{\max}$ is constructed around every atom detected in the volume. If the number of atoms, which belong to a selected chemical group, in the sphere is greater than some value $N_{\min}$, the detected atom is considered to belong to the cluster. The parameters for the determination of clusters ($d_{\max}$ and $N_{\min}$) were the same for all samples (0.8 nm and 5 atoms, respectively). The groups of chemical elements used in the identification algorithm were as follows: Y, O, V, and N for the ODS Eurofer steel; Y, O, and V for the 13.5Cr ODS steel; and Y, O, V, and Ti for the 13.5Cr–0.3Ti ODS steel.

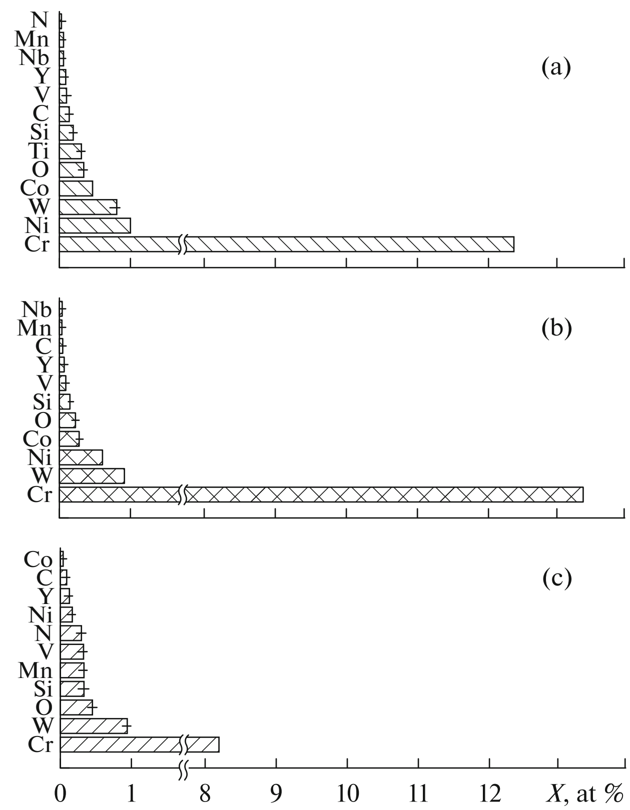

Fig. 1. Average concentrations of chemical elements (except iron) in the ODS steels in the initial state: (a) 13.5Cr–0.3Ti ODS, (b) 13.5Cr ODS, and (c) ODS Eurofer.

RESULTS AND DISCUSSION

Atom Probe Study of the Initial State

Three ODS steels with different compositions (Fig. 1) were examined. In addition to the elements mentioned above, other chemical elements were also detected in the steels (Si, Mn, V, Ni, Co, and others). This is most probably due to contamination during mechanical alloying [6]. The 13.5Cr ODS and 13.5Cr–0.3Ti ODS steels are different in the average chromium content. This can be caused by a nonuniform distribution of chromium in the steels, e.g., segregation at different sinks, diffusion of chromium atoms towards grain boundaries, and so on.

Analysis of 3D atomic distributions revealed a high density (~10^{23} m^{-3}) of nanoscale clusters (2–6 nm) enriched in a number of elements (V, N, O, Y, Si, and Cr in the ODS Eurofer; O, V, Y, Cr, and Mn in the ODS 13.5Cr steel). With Ti alloying, the composition of the clusters changes considerably (clusters enriched in Ti, O, Y, V, and Cr). Figure 2 shows a comparison of the average contents of the main chemical elements of clusters.

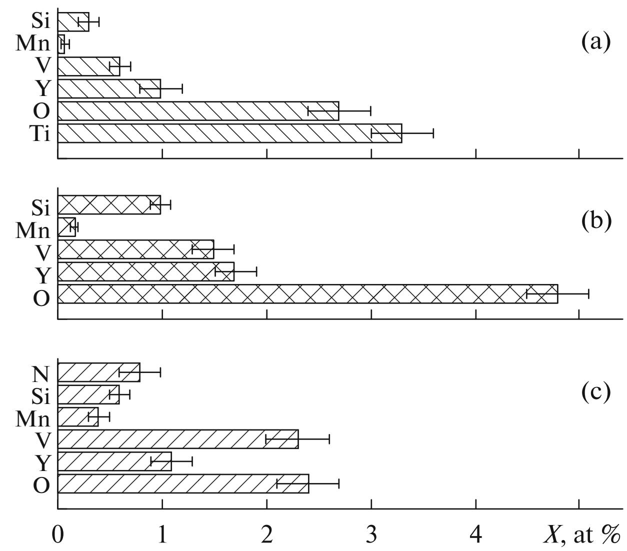

Fig. 2. Average contents of the main chemical elements in clusters in the ODS steels: (a) 13.5Cr–0.3Ti ODS, (b) 13.5Cr ODS, and (c) ODS Eurofer.

Atom Probe Study of the Irradiated States

The irradiated conditions for the materials are listed in detail in Table 2. As noted above, the samples to be studied in an atom probe tomography were cut at various distances from the irradiated surface. Clusters were detected in all the samples after irradiation. Irradiation did not change their sizes (2–6 nm).

However, irradiation at 300 K increased the number density of clusters in all samples that were cut at a 1.2 μm distance from the irradiated surface (Table 2). This distance corresponds to the peak of the radiation damage dose (0.8 dpa). At this distance, the cluster volume density increased by a factor of about two for the ODS Eurofer and 13.5Cr ODS steels, and by a factor of about three for the 13.5Cr–0.3Ti ODS steel. However, this effect was less pronounced at a distance of 1.4–1.5 μm from the surface and there is no effect at a distance of ≤1 μm. The increased number density of clusters can be explained by the dissolution of coarse oxide inclusions (Y_2O_3, $Y_2Ti_2O_7$, and others) observed by TEM in these materials [13, 14] and the formation of new nanoclusters. A similar increase in the number density of clusters was observed in the ODS Eurofer steel irradiated in a BOR-60 reactor up to 32 dpa [4].

Chemical analysis showed a change in the chemical composition of clusters (Fig. 3) at a distance of 1.2 μm from the irradiated surface in the steels after irradiation up to 0.8 dpa at 300 K: the content of yttrium, oxygen, and manganese in the ODS Eurofer steel, the content of titanium and oxygen in the 13.5Cr–0.3Ti ODS steel, and the content of yttrium in the 13.5Cr ODS steel increased. This seems to be associated with the dissolution of coarse oxide particles and the supply

Table 2. Number density of clusters N_{clust} in the ODS steels in the initial state and after ion irradiation at 300 K to a fluence of 1×10^{15} cm^{-2} at various distances l from the irradiated surface

Steel	Irradiation: type of ion	Irradiation: energy, MeV	l, μm	Dose, dpa	N_{clust}, $\times 10^{23}$ m^{-3}
ODS Eurofer	Initial state		–	–	4.0 ± 1.0
	Fe^{2+}	5.6	1.0	0.6	3.0 ± 2.0
	Fe^{2+}	5.6	1.2	0.8	9.0 ± 2.0
	Ti^{2+}	4.8	0.7	0.4	4.0 ± 1.0
	Ti^{2+}	4.8	1.2	0.8	7.4 ± 0.8
	Ti^{2+}	4.8	1.4	0.7	6.0 ±0.7
ODS 13.5Cr	Initial state		–	–	1.3 ± 0.2
	Ti^{2+}	4.8	1.0	0.6	2.0 ± 0.6
	Ti^{2+}	4.8	1.2	0.8	2.8 ± 0.6
	Ti^{2+}	4.8	1.5	0.4	1.2 ± 0.3
ODS 13.5Cr–0.3Ti	Initial state		–	–	1.9 ± 0.2
	Ti^{2+}	4.8	1.0	0.6	2.7 ± 0.5
	Ti^{2+}	4.8	1.2	0.8	6.0 ± 1.0
	Ti^{2+}	4.8	1.5	0.4	5.3 ± 0.8

Table 3. Number density of clusters N_{clust} in the 13.5Cr–0.3Ti ODS steel in the initial state and after Ti^{2+} ion irradiation at various temperatures T at a distance of 1.2 μm from the irradiated surface

Irradiation: type of ion	Irradiation: energy, MeV	Irradiation: T, K	Fluence, $\times 10^{15}$ cm^{-2}	Dose, dpa	N_{clust}, $\times 10^{23}$ m^{-3}
Initial state		–	–	–	1.9 ± 0.2
Ti^{2+}	4.8	300	1	0.8	6.0 ± 1.0
Ti^{2+}	4.8	573	1	0.8	7.0 ± 1.0
Ti^{2+}	4.8	573	3	2.4	6.0 ± 1.0

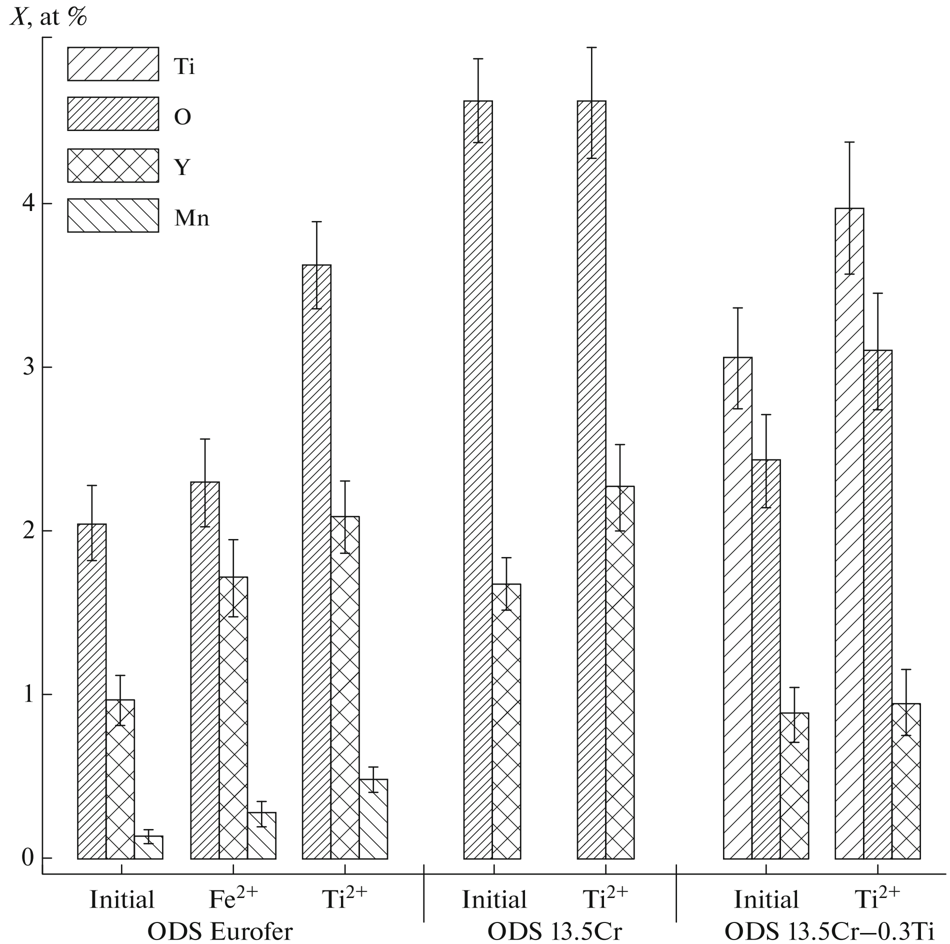

Fig. 3. Average concentrations of chemical elements in the clusters in the ODS steels in the initial state and after irradiation with Fe^{+2} (energy of 5.6 MeV) or Ti^{+2} (energy of 4.8 MeV) ions at 300 K up to 0.8 dpa.

of clusters with elements comprising oxides under irradiation. It should be noted that, despite the increased number of clusters, there was no significant difference in either size or composition: each state is characterized by one type of clusters. A similar increase in the content of yttrium, oxygen, manganese in the ODS Eurofer steel was observed in samples after neutron irradiation to a dose of 32 dpa [4], but a less pronounced increase was observed in the yttrium content in samples after 150 keV iron ion irradiation to a dose of about 30 dpa [5].

In addition, samples of the 13.5Cr–0.3Ti ODS steel were studied after irradiation with 4.8 MeV Ti^{2+} ions to fluences of 1×10^{15} and 3×10^{15} cm^{-2} at 573 K.

Samples were cut at a distance of 1.2 μm from the irradiated surface. APT analysis showed that the chemical composition of the clusters remained the same after irradiation at 573 K (Fig. 4). It can be assumed that the microstructure of the 13.5Cr–0.3Ti ODS steel is stable due to a large number of oxide inclusions with the sizes that are smaller than those observed in the ODS Eurofer and 13.5Cr ODS steels [13–15]. The increase in the number density of clusters in these samples is similar to that observed in the samples irradiated at 300 K (Table 3).

CONCLUSIONS

(1) ODS Eurofer and 13.5Cr–(0–0.3)Ti ODS steels were irradiated with heavy Fe^{2+} and Ti^{2+} ions (energy of 100 keV/nucleon) at temperatures of 300 and 573 K, to fluences of 1×10^{15} and 3×10^{15} cm^{-2} (corresponds to the maximum damage doses of ~0.8 and ~2.4 dpa, respectively). Irradiation at 300 K increased the number of clusters by a factor of 2–3.

(2) The radiation-induced change in the chemical composition of the clusters seems to be caused by the dissolution of coarse oxide inclusions (Y_2O_3, $Y_2Ti_2O_7$, and others), which are observed by TEM in the steels.

(3) A similar increase in the number density of clusters and an increase in the content of chemical elements in the clusters were observed in the ODS Euro-

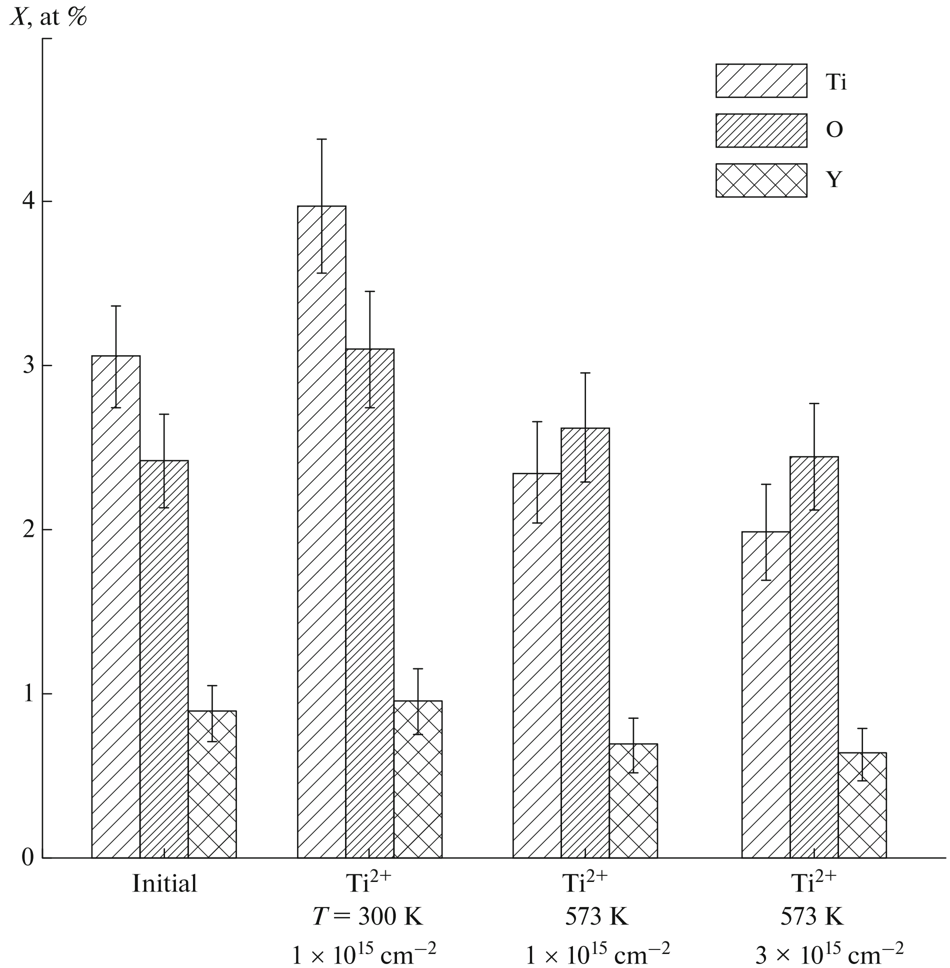

Fig. 4. Average concentrations of chemical elements in the clusters in the 13.5Cr–0.3Ti ODS steel in the initial state and after irradiation with Ti^{+2} (energy of 5.6 MeV) at 300 and 573 K to a maximum dose of 2.4 dpa.

fer steel after neutron irradiated in a BOR-60 reactor to 32 dpa. The chemical composition of the clusters in the 13.5Cr–0.3Ti ODS steel remains the same after irradiation to doses of ~0.8 and ~2.4 dpa at 573 K. It was assumed that an increase in the temperature stabilized the oxide inclusions. The microstructure of the 13.5Cr–0.3Ti ODS steel seems to be more stable due to a large number of oxide inclusions with the sizes that are smaller than those observed in the ODS Eurofer and 13.5Cr ODS steels.

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