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Non-equilibrium intragrain concentration redistribution of the alloying elements in austenitic steels under irradiation

V.V. Sagaradze [a,*], S.S. Lapin [a], M.A. Kirk [b]

[a] *Institute of Metal Physics, Ural Branch RAS, 18 S. Kovalevskaya Str., 620219 Ekaterinburg, Russian Federation*
[b] *Argonne National Laboratory, Argonne, USA*

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Abstract

Radiation-induced and thermally activated decomposition of austenitic 16Cr15Ni3Mo1Ti, 32Ni, 34Ni steels at high temperature (500–650°C) were examined. High doses (up to 10–200 dpa) in 16Cr15Ni3Mo1Ti stainless steel with 1.5 MeV Kr ions and 450 keV Fe ions at 550–650°C lead to the appearance of relatively large regions (up to 200–400 nm) of concentration-oscillations with 'mosaic' dark–white diffraction contrast in TEM images. The radiation-induced redistribution of alloying elements takes place thanks to inverse Kirkendall effect and, in particular, removal of Cr to cell volume from boundaries of coarse cellular structure. The competing formation of ultrafine subgrains and grains 10–50 nm in size structure in Ti-free steel (16Cr15Ni3Mo) impedes the development of large ingrain segregations. The Mössbauer investigations showed that the 32Ni and 34Ni steels with purposefully produced concentration-oscillations were fully homogenised in that high-temperature region. This fact indicated the absence of the thermal decomposition dome in the Fe–Ni equilibrium diagram.

1. Introduction

Formation of radiation-induced segregations at 'stable' sinks (grain- and subgrain-boundaries) of point defects is a widely occurring phenomenon. It is known [1], in particular, that grain-boundaries are enriched in Ni and depleted of Cr as a result of the inverse Kirkendall effect in Cr–Ni stainless steels exposed to irradiation with fast neutrons. Calculations of radiation-induced segregations [2] are important for estimating proneness of steels to swelling, since segregations can alter diffusion characteristics of point defects. Radiation-induced microredistribution of Ni and Cr in the Fe–Ni and Fe–Cr–Ni solid solutions [3] can be classified as a certain type of segregation phenomena. This microredistribution is not associated with grain-boundary sinks and gives rise to composition oscillations in the grain (with respect to Cr, Ni, etc.) having the period of 100–200 nm. These processes can fundamentally change diffusion of point defects in the volume of irradiated metals and, consequently, alter physical properties of alloys and their tendency to void formation and corrosion. This study was aimed at ascertaining the conditions of radiation-induced microredistribution of alloying elements in austenitic steels. It also deals with the time–temperature stability of the segregations formed during irradiation.

2. Materials and methods

Samples of the reactor steel type 16Cr15Ni3Mo1Ti (containing, mass%, 15.9 Cr, 15.0 Ni, 2.5 Mo, 1.02 Ti, 0.03 C, the balance, Fe), Ti-free steel type 16Cr15Ni3Mo of the similar composition, and FCC alloys Fe–34Ni and Fe–32Ni (mass%) were irradiated. The samples were exposed to irradiation with 1.5 MeV

* Corresponding author. Tel.: +7-3432 744 214; fax: +7-3432 740 003.
E-mail addresses: rdnr@neutron.e-burg.su, vsagaradze@imp.uran.ru (V.V. Sagaradze).

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Kr ions at 500–650°C to the damaging dose of 200 dpa in an accelerator or directly in an electron microscope coupled with the accelerator [4]. For comparison, some samples were irradiated with Fe ions having the energy of ≈450 keV. Irradiated foils were examined in an electron microscope. Concentration changes were determined using a microprobe 30 nm in size (EDAX-9900) in a Philips CM-30 electron microscope.

3. Results and discussion

3.1. Radiation-induced redistribution of alloying elements in 16Cr15Ni3Mo1Ti steel irradiated with Kr^+ ions

Fig. 1(a), (b) and 6(a)–(d) from our earlier paper [4] illustrates structural changes, which occur in the radiation-resistant steel type 16Cr15Ni3Mo1Ti during irradiation with Kr^+ ions to the damaging dose of 10–200

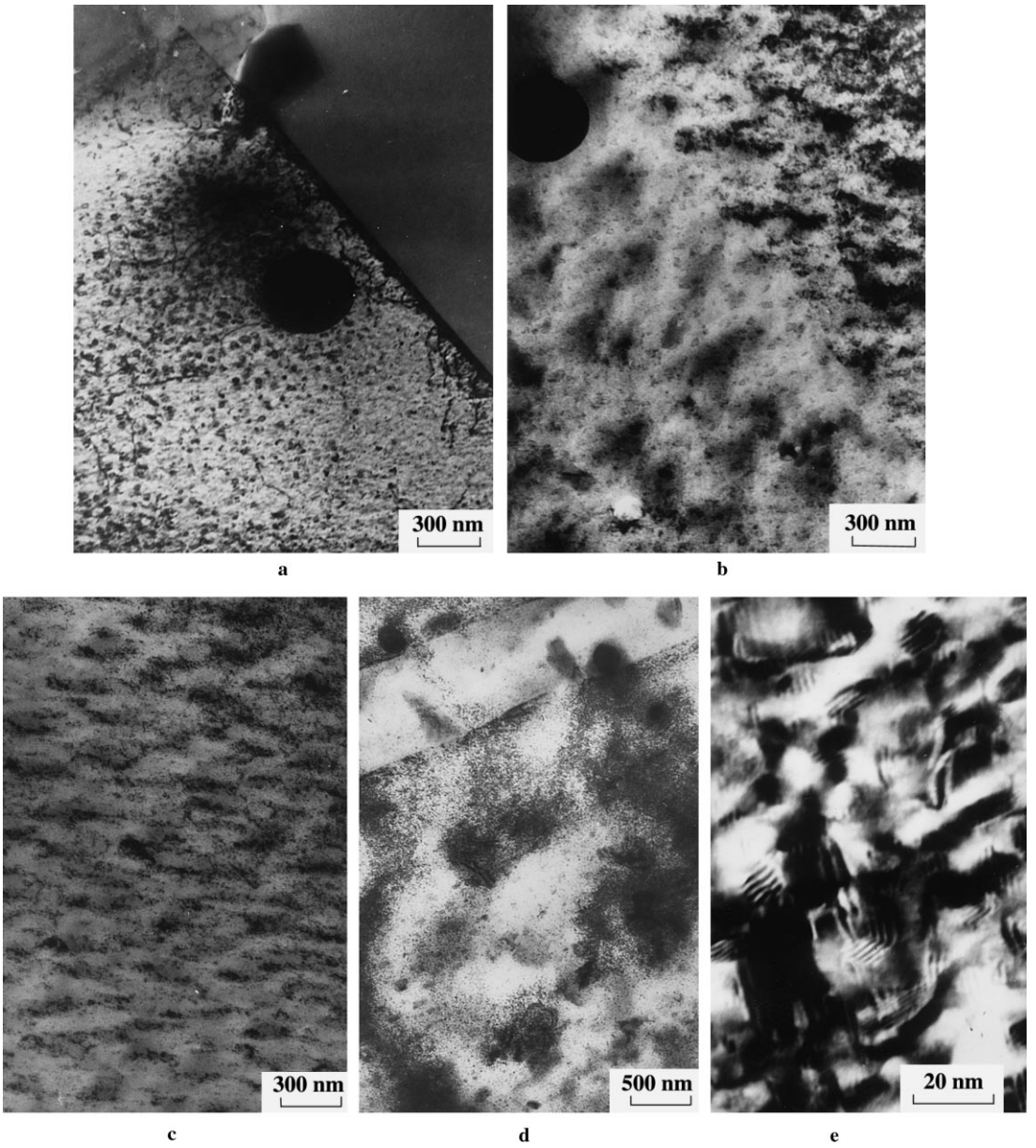

Fig. 1. Structural inhomogeneous regions in the 16Cr15Ni3Mo1Ti steel irradiated with Kr^+ ions ($E = 1.5$ MeV) at 550°C, dose 10 dpa (a); 550°C, 30 dpa (b); 500°C, 100 dpa (c); 650°C, 200 dpa (d) and (e).

dpa at 550°C. One and the same place of the foil (near a round inclusion) was examined. It is seen that a host of dislocation loops is formed uniformly during irradiation up to 10 dpa (Fig. 1(a)). Most of the pre-irradiation dislocations are preserved in the structure, but their location is slightly changed. Starting from 30 dpa [4] (Fig. 6(c) and Fig. 1(b)) one can see a 'mosaic' dark–white diffraction contrast, which looks like a sequence of dark spots against a light background. Dark areas are 200–400 nm in size and are spaced nearly the same distance. The spots go in certain directions. It is seen that direction of the spots is different in adjacent grains. At large magnification the extinction contours show that the dark areas and the light-fields between them are filled with a multitude of dislocation loops and other dislocations. Diffraction from the whole mosaic field is as from monocrystalline. This is evidence that the fragmentation of grains is inconsiderable after such irradiation. When the dose is increased to 100 dpa, the size of the 'spots' changes little, but the density of dislocations in the structure is enhanced and individual dislocation loops are difficult to perceive. At the dose of 160–200 dpa separate precipitates and ultrafine subgrains 10–50 nm in size [4] (Fig. 6(d)), whose reflections are extended in the azimuthal direction, are observed inside blocks of the dark–white mosaic pattern. When the dose exceeds 200 dpa, separate fine grains are seen. Their orientation largely deviates from the orientation of the initial grain.

Similar dark–white contrasts appear after irradiation of another foil at 500°C (Fig. 1(c)) and 650°C (Fig. 1(d), (e)). When the 16Cr1Ni3Mo1Ti steel is aged beforehand (650°C, 8000 h) and then is exposed to ionic irradiation up to the dose of 200 dpa, a sequence of dark smeared regions 200–400 nm in size appear in addition to subgrains, particles of second phases σ, χ, G, TiC and γ'-cuboids, which precipitated during aging [4].

Examination of the composition using the microprobe (EDAX-9900) showed that the concentration of alloying elements changed in the areas with the mosaic structure of the foil. The analytical probe 30 nm in size moving in the steel irradiated at 650°C up to the dose of 200 dpa revealed that the dark areas were strongly enriched in Cr (Fig. 2). Such area 300–400 nm in size was Cr-enriched up to 17.5 mass%. But the region adjacent to this area was depleted of Cr to 12.5 mass%. The Ni concentration of the Cr-depleted zone increased a little (by $\approx$1 mass%).

The mosaic dark–light structure closely resembles radiation-induced regions with Cr and Ni oscillations of the composition in Fe–35Ni and Fe–35Ni–15Cr austenitic steels [3]. Irradiation of the Fe–35Ni–15Cr steel with neutrons up to 13 dpa at 510°C causes formation of 100 nm regions, which are depleted of Cr to 8% and enriched in Ni up to 40–45%. These regions are spaced 200 nm one from the other. This brings up the question: What is the cause of appearance of such local intragrain entities with an altered composition? These entities may be represented by radiation-induced segregations. But then, what is unclear is their large dimensions and periodic arrangement, which is not connected with usual sinks of point defects (grains, subgrains, uniformly distributed dislocations, etc.). Probably, they are the product of radiation-accelerated precipitation of austenite. Decomposition of austenite probably takes place in the absence of radiation as well, but its kinetics are much higher under irradiation. A detailed substantiation can be found in Garner's paper [3]. He plotted two domes of spinodal-like precipitation (redistribution) – thermal and radiation-induced ones – in the high-temperature range (over 500°C) of the Fe–Ni diagram (Fig. 3).

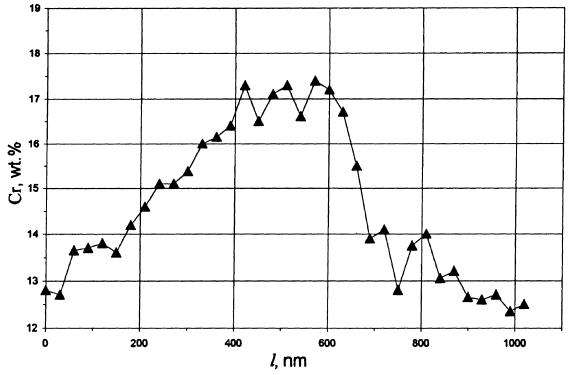

Fig. 2. Variation of Cr-concentration in the inhomogeneous area of the Kr^+ ions irradiated 16Cr15Ni3Mo1Ti steel (650°C, 200 dpa).

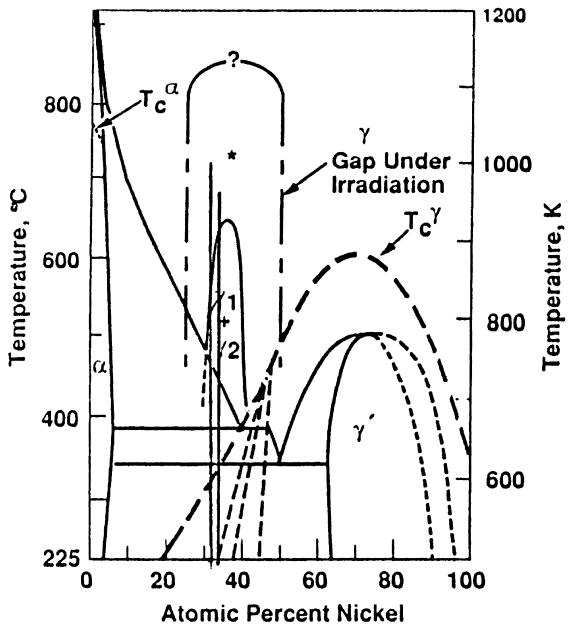

Fig. 3. Fe–Ni phase diagram by Russell and Garner [3].

Finally, these areas may be due to specific alloying of samples with Kr or a nonuniform distribution of liquating elements in steels (for example, Ti, Cr). Let us verify these suppositions.

3.2. Radiation-induced redistribution in Ti-free stainless steels

Large regions of the dark–white contrast with concentration-oscillations are not selected when the Ti-free 16Cr15Ni3Mo steel is irradiated with Kr^+ ions at 600°C even to a small dose (10–30 dpa). The irradiated Ti-free steel has an unstable dislocation structure, because dislocations are not pinned by Ti carbides and intermetallics. Dislocation loops with stacking faults turn into defectless loops, which are transformed to ordinary dislocations [5]. This is accompanied by appearance of misoriented subgrains. Fig. 4(a) and (b) give dark- and bright-field images of ultrafine subgrains up to 10–50 nm in size. These subgrains are formed even at the damaging dose of 10–30 dpa. When the ionic dose is increased to 80–100 dpa, the subgrains grow in size and their misorientation is enhanced. This is attested to by smearing of reflections in the electron diffraction patterns.

A large number of closely spaced sinks of point defects in the form of subgrain dislocations probably precludes a large-scale (to the distance of 300–400 nm) redistribution of alloying elements under irradiation. The increase in the fluence (160–200 dpa) leads to formation of fine grains having different orientations. Despite a rapid dispersion of the matrix, which represents a competing process, it is possible, on occasion, to realize the radiation-induced redistribution of alloying elements in the Ti-free steel at other temperatures. Intragrain concentration-oscillations were detected [3,6] in samples of Ti-free Fe–Ni and Fe–Ni–Cr FCC alloys exposed to irradiation. Thus, kinetics of the intragrain radiation-induced redistribution depends on whether austenitic steels and alloys contain or do not contain Ti.

3.3. Comparison of structural changes in steels irradiated with Fe and Kr ions

Kr can dissolve in foils, form gas cavities and 'vacancy–Kr atom' complexes, change the diffusion rate of point defects, and alter formation conditions of segregation regions. Therefore Kr was replaced by Fe as the damaging element. Fe ions accelerated to 450 keV do not implant additional alloying elements in the irradiated steel, but produce analogous structural and concentration changes as Kr does. Fig. 5(a) illustrates an ordered arrangement of alternating dark and white areas

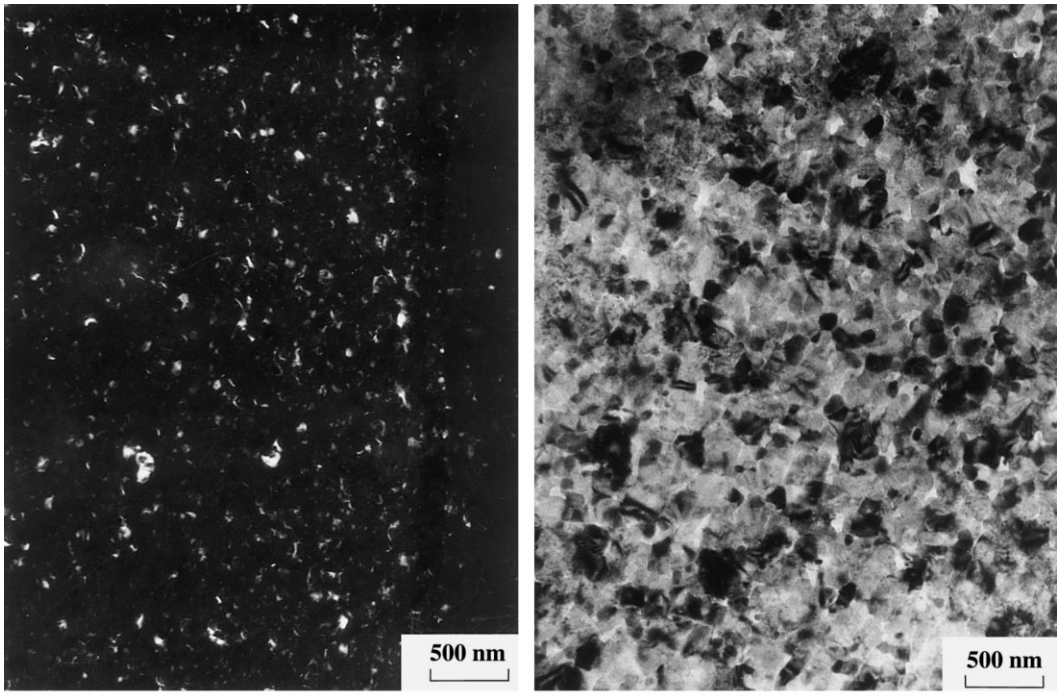

Fig. 4. Structural evolution of the 16Cr15Ni3Mo steel irradiated with Kr^+ ions ($E = 1.5$ MeV, 600°C) up to dose 30 dpa (a) and 100 dpa (b); (a) dark-field image in the γ-reflex.

having the size of 200–400 nm in the structure of the 16Cr15Ni3Mo1Ti steel irradiated to 30 dpa at 550°C. This mosaic structure differs little from the structure formed under irradiation with Kr ions and connected with radiation-induced redistribution of alloying elements. A disperse dislocation structure dominated by dislocation loops is well seen between dark areas, especially in the dark-field and extinction contours (Fig. 5(b) and (c)). If the foil is tilted in the microscope through 0.5° to 10° and the extinction contour is displaced (Fig. 5(c)), dark (Cr-enriched) regions remain in place and the reflecting position is occupied by dislocation loops and dislocations having a higher density at the boundaries of dark areas with concentration-inhomogeneities. If the fluence of irradiating ions is increased, thin particles of $Cr_{23}C_6$ and TiC carbides appear in the structure of stainless steels. Note that pileups of dislocations and loops can be seen occasionally at the boundaries of dark areas of the 'mosaic' pattern. This is similar to a cellular structure, which is formed during deformation of Cr–Ni stainless steels with low-energy stacking faults.

Thus, alloying of steels with Kr under irradiation is not responsible for concentration-oscillations.

3.4. On the causes of formation of intragrain segregations

We have been unaware of any literature data concerning the causes of formation of intragrain segregations. Radiation-induced redistribution of alloying elements is probably due to segregations at sinks in the form of coarse dislocation boundaries. Dislocation loops, which are distributed relatively uniformly in the grain, are formed at the beginning of irradiation (Fig. 6(a)

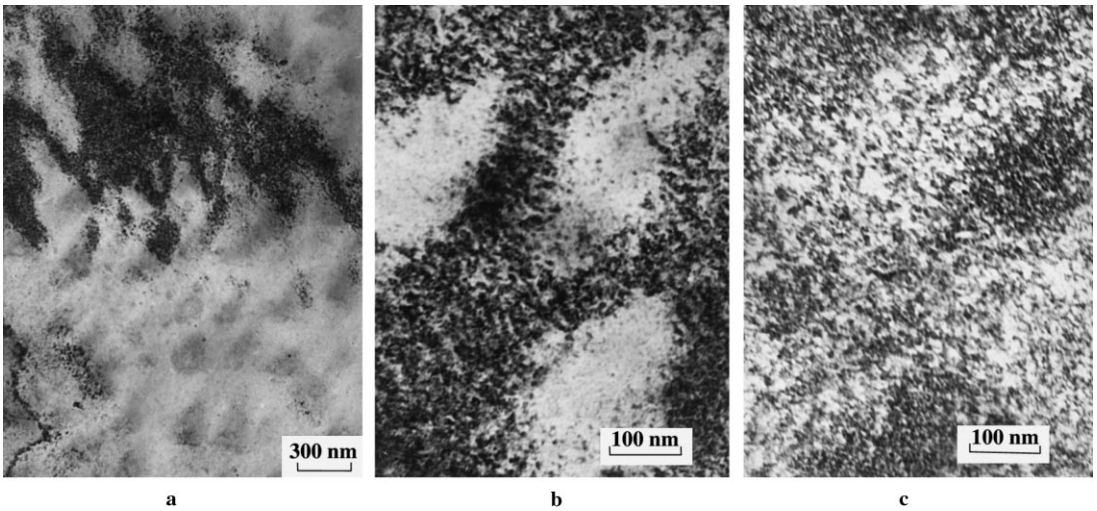

Fig. 5. Concentration-inhomogeneous regions (a) and dislocation structure (bright (b) and dark (c) image) of 16Cr15Ni3Mo1Ti steel irradiated with Fe^+ ions ($E = 400$ KeV, 550°C) up to dose 30 dpa.

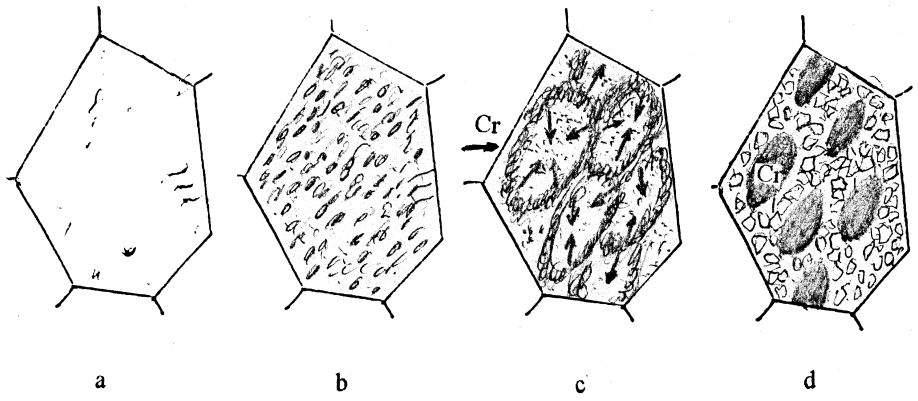

Fig. 6. The formation scheme of radiation-induced inhomogeneous regions in the austenitic steel.

and (b)). Subsequently they turn into ordinary dislocations and, finally, transform into boundaries of cells and subgrains. If the process of the subgrain formation is fast (dislocations are not pinned by Ti carbides, disperse intermetallics, for example, in Ti-free steels), an ultrafine subgrain structure with subgrains 10–20 nm in size appears readily (16Cr15Ni3Mo steel). Boundaries of disperse subgrains act as good closely spaced sinks of point defects and serve as sites of microsegregations. Probably, considerable Ni and Cr segregations are present in the disperse structure of Ti-free steels. Analysis by 30 nm microprobe (EDAX-9900) may fail to detect redistribution of alloying elements in such disperse structure and gives only mean concentration.

If the process of dislocation rearrangement is slow (as in 16Cr15N13Mo1Ni steel), relatively large areas (up to 300–400 nm) of a cellular dislocation structure can be formed under irradiation (Fig. 6(c)). These are second-order entities with respect to the initial grain. Wide boundaries of the cells consist (similarly to those formed after cold-deformation) of a great number of dislocations, which are often extended in certain crystallographic directions. They are good sinks of point defects. Due to the inverse Kirkendall effect, these boundaries can be enriched in Ni and depleted of Cr through segregations under irradiation [1]. 'Excess' Cr diffuses from the cell boundaries to the adjacent volume of the cell, which, hence, is enriched in Cr (Fig. 6(c) and (d)). On subsequent irradiation, coarse cell boundaries made up of chaotic dislocations disappear and ultrafine subgrains are formed (Fig. 6(d)). In other words, disperse subcrystals of the third-order infinitesimal appear. Subboundaries of ultrafine subgrains do not change the general pattern of the segregation redistribution of alloying elements: intragrain microscale (200–500 nm) regions (Fig. 6(d)) with composition-oscillations are preserved, but, possibly, are coagulated. Moreover, ordering can take place in certain directions (similarly to order of particles [7]). This is due to the interaction of elastic fields around Cr-enriched regions. Orientation of the segregation regions (mosaic) is determined probably by the initial direction of wide dislocation boundaries of the cells.

What is the reason that mainly Cr (by 5%) rather than Ni (just by 1%) is redistributed in Ti steel? Probably Ti and Ni cannot quickly approach and enrich the sinks, because these elements form the coherent Ni_3Ti γ'-phase in grain (not at dislocations only). As a result, the total Ti and Ni redistribution decreases. Of course, Cr can form carbides $Cr_{23}C_6$ when it moves from the cell boundary to the volume. But Cr carbides are few owing

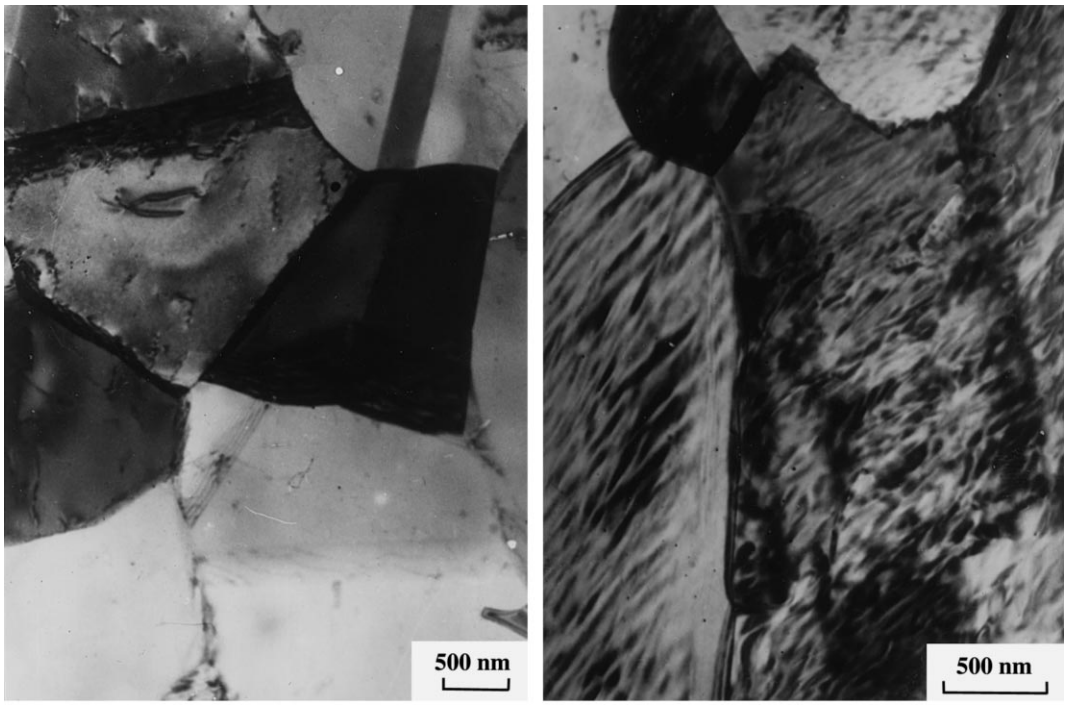

Fig. 7. Initial homogeneous (a) and inhomogeneous (b) austenite formed during $\alpha \rightarrow \gamma$ transformation under slow heating (0.3°C/min) to 550°C.

to a small carbon concentration. High damaging doses and temperatures of 500–650°C are sufficient for diffusion of Cr to a distance of 150–200 nm and creation of large segregations.

3.5. Stability of radiation-induced intragrain segregations

A sample of the 16Cr15Ni3Mo1Ti steel was exposed to irradiation with 450 keV Fe ions at 550°C up to the damaging dose of 30 dpa. Then the sample was annealed for 7 h at the same temperature (550°C) in the absence of irradiation. Post-radiation annealing induced insignificant changes in the mosaic segregation structure of the steel. This fact attested to relatively high thermal stability of segregations.

The question arises whether this redistribution of alloying elements in Fe–Ni and Fe–Ni–Cr FCC alloys is of the equilibrium one and if it can take place in the high-temperature range (over 500°C) without irradiation, as the researchers [3] conceived (see the thermal dome of redistribution in the Fe–Ni diagram, Fig. 3). To find the answer to the question posed, we examined metastable austenitic steels type 32Ni and 34Ni, where martensite is formed upon cooling to −196°C. Compositions of these alloys are marked with vertical lines in the Fe–Ni diagram, Fig. 3. Thermal treatment of the alloys induced microconcentration inhomogeneities (see [8,9]), which appeared during the $\alpha \rightarrow \gamma$ transformation in accordance with the Fe–Ni equilibrium diagram. Fig. 7 shows the structure of the 32Ni alloy in the initial homogeneous (a) and inhomogeneous (b) austenitic states. The Ni-enriched (up to 40%) thin-plate γ-phase formed after direct martensitic transformation $\gamma \rightarrow \alpha$ during cooling in liquid nitrogen and the reverse $\alpha \rightarrow \gamma$ transformation upon slow heating to 490°C. Concentration-inhomogeneous globular austenite formed in 32Ni steel upon slow heating to 778 and 823 K [9]. This austenite is formed instead of the mixture comprising Ni-enriched γ-crystals and Ni-depleted regions of retained α-martensite. It contains concentration-oscillations (Fig. 7(b)) in the form of a dark–white alternating regions similar to the contrast formed during ionic irradiation. According to Mössbauer measurements, the Ni concentration of the high-Ni component is 36–40%, while that of the low-Ni component is less than 28% [8,9]. The composition oscillations and the dark–white contrast vanish when the alloy undergoes diffusion annealing at 750°C for 1 h.

The concentration-inhomogeneous 32Ni austenite was annealed [10] at temperatures from 520°C to 550°C in the range of the supposed dome of thermal redistribution. If the Fe–Ni equilibrium diagram does not contain the region of equilibrium decomposition (narrow dome, Fig. 3), the concentration inhomogeneity should vanish at these temperatures. To accelerate diffusion processes, concentration-inhomogeneous samples of 32Ni and 34Ni alloys were cold-deformed to 75%.

Mössbauer spectra (Fig. 8) suggest that annealing of the undeformed samples of 32Ni at 570°C during 24 and 168 h decreases, but does not eliminate Ni redistribution (compare the spectra in Fig. 8(a)–(c)). When thedeformed sample of the 32Ni alloy is annealed even at a lower temperature (520°C) for 48 h, it becomes almost fully homogenized (Fig. 8(e)): its NGR spectrum is similar to the spectrum of the homogeneous sample of the 32Ni steel. Annealing of the deformed

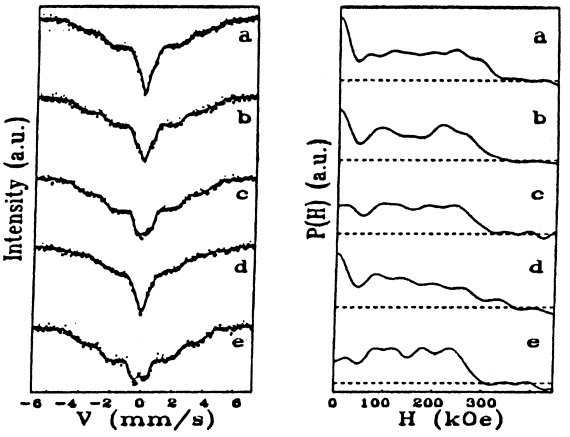

Fig. 8. Mössbauer spectra of the 32Ni alloy (298 K) and the corresponding magnetic field density functions $P(H)$. Treatment: (a) Ni redistribution: quenching from 1050°C + $\gamma \rightarrow \alpha$ transformation, −196°C + $\alpha \rightarrow \gamma$ transformation, 550°C (0.2°C/min); (b) as in 'a' + annealing, 570°C (24 h); (c) as in 'a' + annealing, 570°C (168 h); (d) as in 'a' + deformation ($\psi = 75\%$); (e) as in 'd' + annealing, 520°C (48 h).

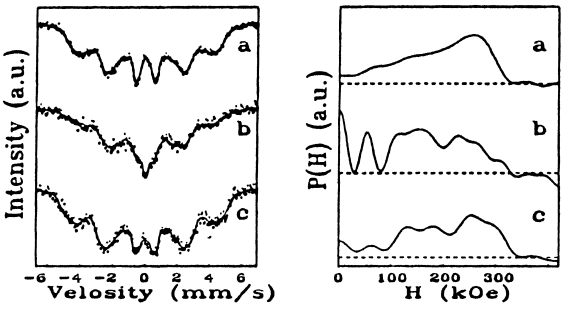

Fig. 9. Mössbauer spectra of the 34Ni alloy (25°C) and the corresponding magnetic field density functions $P(H)$. Treatment: (a) initial homogeneous austenite; (b) Ni redistribution: quenching from 1050°C + $\gamma \rightarrow \alpha$ transformation under deformation, −196°C + $\alpha \rightarrow \gamma$ transformation, 430°C (0.3°C/min)- + 600°C, 10 min + cold-deformation ($\psi = 75\%$, 25°C); (c) as in 'b' + annealing, 520°C (48 h).

inhomogeneous sample of the 34Ni alloy at 520°C brings up the same result: the sample is almost fully homogenized in 48 h (Fig. 9(a)–(c)). The paramagnetic central component of the spectrum having the zero magnetic field disappears too (Fig. 9(c)). The magnetic field distribution $P(H)$ in the samples, which were annealed under the said conditions, is identical to the spectra of homogeneous 32Ni and 34Ni steels. This fact suggests that such narrow region of high-temperature thermal-induced decomposition of austenite does not exist on equilibrium phase diagram Fe–Ni [3]. Some change in concentration, which are observed [11,12] by the low-angle neutron scattering method in Fe–34Ni alloy at 625°C (annealing 230 days), are probably due to precipitation of disperse particles (intermetallics and carbides).

Thus, the intragrain radiation-induced redistribution of alloying elements in austenitic steels at 520–650°C (at least in Fe–Ni FCC alloys) is not in equilibrium. It is eliminated by post-radiation annealing at these temperatures.

4. Conclusions

1. High-dose (up to 10–200 dpa) irradiation of the 16Cr15Ni3Mo1Ti austenitic steel with 1.5 MeV Kr ions at 500–650°C leads to appearance of relatively large (up to 200–400 nm) intragrain regions with a high-Cr content. These regions form a mosaic dark–white diffraction contrast in TEM images. The competing process of formation of an ultrafine subgrain structure (10–50 nm) takes place in Ti-free steel (16Cr15Ni3Mo), where dislocations are not pinned by Ti particles and, therefore, can move. This process impedes formation of large intragrain segregations. Probably, only small regions of Ni and Cr microsegregations are present in this ultrafine titaniumless structure.
2. Appearance of intragrain 'segregations' is not connected with alloying of irradiated foils by Kr. These segregations are also formed in steels exposed to irradiation with Fe ions having the energy of 450 keV.
3. Radiation-induced formation of alternating regions of intragrain redistribution of alloying elements is attributed to the sequence of structural and concentration changes in irradiated steel, such as: accumulation of dislocation loops; transformation of loops into dislocations and appearance of a coarse cellular structure with wide dislocation boundaries; radiation-induced segregation redistribution of alloying elements at the cell boundaries due to the inverse Kirkendall effect and, in particular, removal of Cr to the cell volume; rearrangement of coarse cellular dislocation boundaries to more equilibrium boundaries of ultrafine subgrains (in this case the existing 'large-scale' segregation in the form of the mosaic dark–white diffraction contrast is preserved).
4. Thermal stability of intragrain composition-oscillation regions was determined for metastable 32Ni and 34Ni FCC alloys. It was shown that intragrain Ni redistribution in steels is eliminated by annealing at 793 K, i.e. in the range of the supposed [3] equilibrium thermal decomposition of austenite. This fact suggests that such regions of thermal precipitation do not exist. High-temperature segregations are formed, at least in irradiated Fe–Ni austenitic alloys, through a radiation-induced nonequilibrium process, which always involves radiation-induced vacancies.

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