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Recombination mechanism of point defect loss to coherent precipitates in alloys under irradiation

A.A. Turkin *, A.S. Bakai

National Science Center 'Kharkov Institute of Physics and Technology', Akademicheskaya St. 1, Kharkov 310108, Ukraine

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Abstract

A new mechanism of defect loss by enhanced recombination inside coherent precipitates in alloys under irradiation is described. The mechanism is examined quantitatively to find the microstructural parameters responsible for resistance to dimensional instability. The proposed model explains why radiation properties of Zr–Nb alloys depend on density of fine-grained precipitates of β_{Nb}-phase. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Complex structural-phase transformations that are observed in materials under irradiation essentially influence their properties. Though the basic mechanisms of these transformations are well established and investigated, the development of radiation-resistant structural materials and long-term forecasting of their behavior appears to be a rather challenging task, since it requires understanding of the interrelationships between various processes of microstructural and microchemical evolution. As a rule, change of mechanical properties, dimensional instability and rearrangement of phase microstructure (which is characterized by type, size and distribution of second phase particles) are observed simultaneously (see for example Refs. [1,2] and the literature cited there). For instance, it is known that in austenitic stainless steels the duration of the incubation period of void swelling correlates with the time of the redistribution of the alloying elements and the formation of the precipitate distribution. Moreover, it is frequently found that the material exhibits enhanced radiation resistance when the precipitates are coherent with the matrix. The swelling resistance of PE16 stainless steel [3] and other nickel rich alloys [4,5] is attributed usually to the population of fine-grained precipitates of γ'-phase homogeneously distributed in the matrix. Other examples are steels stabilized by carbide-producing elements (Ti and Nb) in which, during the initial stage of irradiation, fine-grained particles of Ti- and Nb-carbonitride precipitate [6–9]. Despite a large misfit parameter, the lattice of MX-particles is isomorphic with the matrix lattice. These particles are coherent with the matrix at small sizes ($d < 5$ nm) up to irradiation fluences amounting to tens of displacements per atom. The onset of swelling of the steel is observed simultaneously with the loss of coherency [9].

It should be noted that in this respect steels used in fast reactors have been investigated more than zirconium alloys. It is established experimentally that in Zr–Nb alloys α'-, ω- and β-phases are formed during quenching from the β-phase field. The composition of Zr-alloy and the second phase particles formed after thermal and mechanical treatment affects essentially the behavior of Zr-alloys under irradiation. For example, it was found that Zr–Nb alloys thermally treated by high frequency currents show an enhanced resistance to radiation growth [10]. This effect is more pronounced in Zr–2.5 at.% Nb alloy as compared to Zr–1 at.% Nb alloy. The difference is that in Zr–2.5 at.% Nb the density of β_{Nb}-precipitates is higher than that in Zr–1 at.% Nb. It appears that the second phase precipitates intensify the recombination of point defects (vacancies and interstitials) created by the irradiation.

The experimental papers cited here indicate that the coherent precipitates of second phases reduce the aver-

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* Corresponding author. Tel.: +380-572 356 203; fax: +380-572 353 858; e-mail: anatole.turkin@kipt.kharkov.ua

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age concentrations of point defects (PD), thereby suppressing the processes of swelling and radiation growth. A mechanism of PD absorption by coherent precipitates was considered in Refs. [11,12]. It was supposed that the interface of precipitates contains saturable PD traps which offer recombination sites for vacancies and interstitial atoms. It appears that the maximum strength of such sinks (at a high density of traps) does not exceed the sink strength of incoherent precipitates or voids of the same radius [11,12]. This mechanism is essential in the balance of PD if the total sink strength of coherent precipitates is higher than the strength of dislocations (certainly, provided that temperature is sufficiently high, so that the volume recombination is insignificant).

Among other mechanisms of reduction of PD concentrations a mechanism of 'forced recombination' of PD due to their redistribution in the fields of elastic deformation formed around coherent precipitates was widely discussed in Ref. [4]. The efficiency of this mechanism was questioned in Ref. [13], because in the general case the energy of interaction of PD with stress field is significantly less than the difference between chemical potentials of the matrix and the precipitates. However, the influence of this difference on volume recombination of PD was not specified in Ref. [13].

The objective of the present paper is to consider the effect of second phase precipitates on the average concentrations of PD, with particular reference to Zr–Nb alloys. We describe a new mechanism for the enhancement of point-defect recombination within the internal volume of the coherent precipitates in alloys under irradiation, which was originally proposed in Ref. [14]. As distinct from the incoherent interface, atomic planes are continuous across the coherent interface [15]. This means that the perfect coherent boundary does not contain defect sites or traps, which serve as a sink for PD. For this reason PD easily cross the coherent boundary. Since formation and migration energies of PD inside the precipitate differ from those in the matrix, the rate of mutual annihilation of vacancies and interstitials differs too. Below we show that the coherent precipitate absorbs PD if the formation energy of the Frenkel pair in the matrix is greater than that in the precipitate. At a negative misfit between lattices of the precipitate and the matrix the probability of absorption of Frenkel pairs increases. If the volume fraction of coherent precipitates is sufficiently high, and the recombination rate in precipitates is higher than in the matrix, they can contribute noticeably to the decrease of PD concentrations.

2. Point defect fluxes to second phase precipitates

Consider an alloy containing spherical precipitates of a second phase. The precipitate boundary will be assumed to be either perfectly coherent or completely disordered (incoherent). For the sake of simplicity we shall not take into account the influence of heterogeneity in distribution of the alloying elements around precipitates on PD diffusion. This means that we shall use diffusion equations for a single component material.

2.1. Incoherent precipitate

The disordered boundary of the incoherent precipitate is a sink for PD. In the diffusion-controlled case the equilibrium values of PD concentrations are maintained at the incoherent boundary. Therefore, in the approximation of a quasi steady state, with the accuracy proportional to the volume fraction of structural defects, the fluxes of vacancies and interstitial atoms to the precipitate is given by expressions similar to expressions for a void of the same radius

$$J_{\mathrm{i}}^{\mathrm{inc}} = 4\pi R D_{\mathrm{i}} \overline{C_{\mathrm{i}}} Y_{\mathrm{i}}, \tag{1}$$

$$J_{\mathrm{v}}^{\mathrm{inc}} = 4\pi R D_{\mathrm{v}} \left(\overline{C_{\mathrm{v}}} - C_{\mathrm{v}}^{\mathrm{em}}\right) Y_{\mathrm{v}}, \tag{2}$$

where R is the radius of the precipitate; $D_{\mathrm{i,v}}$ are the diffusion coefficients of interstitials and vacancies, $\overline{C}_{\mathrm{i,v}}$ are the average concentrations of interstitials and vacancies far from the precipitate, $C_{\mathrm{v}}^{\mathrm{em}}$ is the equilibrium concentration of vacancies in the matrix. The factors $Y_{\mathrm{i,v}}$ are about unity.

In the case of a thin platelet, its incoherent edge absorbs PD similarly to a dislocation loop. Therefore, the expressions for PD fluxes is given by

$$I_{\mathrm{i}}^{\mathrm{p}} = 2\pi r_{\mathrm{p}} Z_{\mathrm{i}}^{\mathrm{p}} D_{\mathrm{i}} \overline{C_{\mathrm{i}}}, \tag{3}$$

$$I_{\mathrm{v}}^{\mathrm{p}} = 2\pi r_{\mathrm{p}} Z_{\mathrm{v}}^{\mathrm{p}} D_{\mathrm{v}} \left(\overline{C_{\mathrm{v}}} - C_{\mathrm{v}}^{\mathrm{em}}\right), \tag{4}$$

where r_{p} is the precipitate radius; $Z_{\mathrm{i,v}}^{\mathrm{p}}$ are the sink strength [16].

2.2. Coherent precipitate

When the precipitate is coherent with the matrix, atomic planes keep continuity across the interface. For this reason the coherent boundary does not block the exchange of PD between the matrix and the precipitate. Indeed, from the topological viewpoint the lattices of the matrix and the coherent precipitate are the same. In other words the coherent precipitate–matrix interface is transparent for migrating PD. Due to thermally activated random walks of PD a balance (or a kinetic equilibrium) is established in the PD population on a local scale in each point of the system, including the coherent interface. The time scale of this process is about of time of a few defect jumps to the neighboring lattice sites. In a formalism offered by the linear theory of non-equilibrium thermodynamics this means that one can define locally the chemical potentials.

The chemical potentials of vacancies and interstitial atoms are given by the conventional expressions

$$\mu_n(r) = \begin{cases} \mu_n^{\mathrm{p}} = kT\ln\left(C_n^{\mathrm{p}}/C_n^{\mathrm{ep}}\right), & r \,\epsilon\, \text{precipitates} \\ \mu_n^{\mathrm{m}} = kT\ln\left(C_n^{\mathrm{m}}/C_n^{\mathrm{em}}\right), & r \,\epsilon\, \text{matrix},\ n = \mathrm{i}, \mathrm{v}, \end{cases} \tag{5}$$

where k is the Boltzmann constant; T is the temperature; $C_n^{\mathrm{p,m}}$ are the concentrations of PD (vacancies, $n = \mathrm{v}$, and interstitial atoms, $n = \mathrm{i}$) in the precipitate and in the matrix, respectively; C_n^{ep} and C_n^{em} are the thermodynamic equilibrium concentrations of PD in the precipitate and in the matrix

$$C_n^{\mathrm{ep}} = \exp\left(-E_{n\mathrm{f}}^{\mathrm{p}}/kT\right), \quad C_n^{\mathrm{em}} = \exp\left(-E_{n\mathrm{f}}^{\mathrm{m}}/kT\right), \tag{6}$$

where $E_{n\mathrm{f}}^{\mathrm{p}}$ and $E_{n\mathrm{f}}^{\mathrm{m}}$ are the Gibbs free energies for point defect formation. In the general case $E_{n\mathrm{f}}^{\mathrm{p}}$ and $E_{n\mathrm{f}}^{\mathrm{m}}$ differ, because of difference in chemical compositions of the coherent precipitate and the matrix.

The local PD balance at the coherent precipitate–matrix interface is expressed in terms of the chemical potential

$$\lim_{r\to S-0}\mu_n(r) = \lim_{r\to S+0}\mu_n(r), \tag{7}$$

where $r \to S \pm 0$ implies that the point r is taken close to the interface S either in the matrix or in the precipitate, respectively.

From Eqs. (5) and (7) we find the relation between steady state and equilibrium PD concentrations on each side of the coherent precipitate–matrix interface

$$\frac{C_n^{\mathrm{p}}}{C_n^{\mathrm{ep}}} = \frac{C_n^{\mathrm{m}}}{C_n^{\mathrm{em}}}, \quad n = \mathrm{i}, \mathrm{v}. \tag{8}$$

To show important consequences of this relation, at first we shall consider the limiting case when the properties of the precipitate and the matrix differ only a little.

2.2.1. Precipitate with properties close to matrix properties

Let PD diffusion coefficients and recombination rate constants in the matrix and in the precipitate are identical, but the energies of PD formation differ. The distributions of vacancies and interstitials inside the coherent precipitate and outside it satisfy equations

$$K - \alpha D_{\mathrm{i}} C_{\mathrm{i}} C_{\mathrm{v}} - \operatorname{div} j_n = 0, \quad j_n = -D_n \nabla C_n,\ n = \mathrm{i}, \mathrm{v}, \tag{9}$$

where K is the rate of generation of freely-migrating PD, α is the recombination rate constant.

Since there are no traps for PD at the coherent interface, vacancy and interstitial fluxes are continuous at the precipitate interface,

$$j_n^{\mathrm{p}} = j_n^{\mathrm{m}}, \quad n = \mathrm{i}, \mathrm{v}. \tag{10}$$

If the difference between equilibrium concentrations of defects in the precipitate and in the matrix is small ($\gamma_n = C_n^{\mathrm{ep}}/C_n^{\mathrm{em}} \sim 1$), the precipitate produces small disturbances to the PD distribution. In the case of a strong recombination (the recombination length is less than the average distance between sinks), in the zero-order approximation, PD inside and outside the coherent precipitate are distributed homogeneously. The equations for deviations of PD concentrations from the average values, $s_n = C_n - \overline{C_n}$, are given by

$$\Delta D_n s_n - \alpha D_{\mathrm{i}}\left(\overline{C_{\mathrm{i}}} s_{\mathrm{v}} + \overline{C_{\mathrm{v}}} s_{\mathrm{i}}\right) = 0, \quad n = \mathrm{i}, \mathrm{v}. \tag{11}$$

Solving these equations together with conditions (8) and (10), we can show that the total fluxes of vacancies and interstitials to the precipitate equal

$$\begin{aligned} J_{\mathrm{v}}^{\mathrm{coh}} &= J_{\mathrm{i}}^{\mathrm{coh}} \\ &= 4\pi R\frac{1+\beta R}{\beta R}\mathrm{e}^{-\beta R}(\beta R\,\mathrm{ch}\beta R - \mathrm{sh}\beta R)(\gamma_{\mathrm{i}} + \gamma_{\mathrm{v}} - 2) \\ &\quad \frac{D_{\mathrm{i}}\overline{C_{\mathrm{i}}}D_{\mathrm{v}}\overline{C_{\mathrm{v}}}}{D_{\mathrm{i}}\overline{C_{\mathrm{i}}} + D_{\mathrm{v}}\overline{C_{\mathrm{v}}}}, \end{aligned} \tag{12}$$

where β is the inverse recombination length,

$$\beta^2 = \frac{\alpha}{D_{\mathrm{v}}}\left(D_{\mathrm{i}}\overline{C_{\mathrm{i}}} + D_{\mathrm{v}}\overline{C_{\mathrm{v}}}\right). \tag{13}$$

The physical meaning of Eq. (12) is apparent in limiting cases $\beta R \ll 1$ and $\beta R \gg 1$,

$$\begin{aligned} J_{\mathrm{v}}^{\mathrm{coh}} &= J_{\mathrm{i}}^{\mathrm{coh}} = \Delta\alpha D_{\mathrm{i}}\overline{C_{\mathrm{i}}}\,\overline{C_{\mathrm{v}}}\begin{cases} \frac{4\pi}{3}R^3, & \beta R \ll 1 \\ 2\pi R^2\beta^{-1}, & \beta R \gg 1 \end{cases} \\ \Delta\alpha &= \alpha(\gamma_{\mathrm{i}} + \gamma_{\mathrm{v}} - 2) = \alpha\frac{E_{\mathrm{F}}^{\mathrm{m}} - E_{\mathrm{F}}^{\mathrm{p}} - U}{kT} \end{aligned} \tag{14}$$

where $E_{\mathrm{F}}^{\mathrm{m,p}} = E_{\mathrm{vf}}^{\mathrm{m,p}} + E_{\mathrm{if}}^{\mathrm{m,p}}$ are the energies of formation of the Frenkel pair in the matrix and the precipitate, respectively; U is the energy of interaction of the Frenkel pair with the field of elastic stresses inside the coherent precipitate, which, in the isotropic model, is given in Ref. [17]

$$U = \frac{3K_{\mathrm{p}}\delta}{1 + 3K_{\mathrm{p}}/4\mu_{\mathrm{m}}}(\Omega_{\mathrm{i}} + \Omega_{\mathrm{v}}) \tag{15}$$

here K_{p} is the Young modulus of the precipitate; μ_{m} is the matrix shear modulus; $\delta = (a_{\mathrm{p}} - a_{\mathrm{m}})/a_{\mathrm{m}}$ is the parameter of dimensional misfit between lattices of the precipitate and the matrix; Ω_{i} and Ω_{v} are the dilatation volumes of an interstitial atom and a vacancy.

Expression (14) shows that the PD flux to the precipitate arises due to enhanced PD recombination inside the precipitate. The PD flux is directed to the precipitate, if $\Delta\alpha > 0$, that is, when the energy of formation of the Frenkel pair in the precipitate is less than that in the matrix. In both limiting cases the value of the flux is proportional to the rate of mutual recombination. However at a small recombination length ($\beta R \gg 1$) the PD flux is proportional not to the whole volume of the precipitate, but to the volume of a spherical layer with the thickness equal to the PD recombination length.

The results are qualitatively illustrated in Fig. 1 depicting the profiles of the PD concentration (for example, the vacancy concentration) inside and outside the coherent precipitate of radius R. The dotted line corresponds to the equilibrium concentration without irradiation. The dashed line shows the concentration profile under irradiation, but when the recombination of PD is not allowed. If we allow PD to recombine, the concentration of vacancies decreases (see the solid line), the decrease being greater in the precipitate than in the matrix. This leads to fluxes of PD to the coherent precipitate. PD penetrate into the precipitate and recombine there.

2.2.2. *Precipitate with properties strongly different from matrix properties*

We shall consider the coherent precipitate, in which equilibrium concentrations, PD diffusion coefficients and the recombination rate constant strongly differ from those in the matrix (just this case will interest us in the following). We shall find a solution to the diffusion problem in the matrix and the precipitate, and then, taking advantage of Eqs. (8) and (10), we shall find PD fluxes to the precipitate.

In the approximation of a small volume fraction of structural defects and a large recombination length in the matrix ($\beta R \ll 1$), the PD fluxes from the matrix to the precipitate of radius R is given by

$$J_n^{\mathrm{coh}} = 4\pi R D_n\left(\overline{C_n} - C_n^{\mathrm{m}}\right), \quad n = \mathrm{i}, \mathrm{v}. \tag{16}$$

The sign of the flux depends on the PD concentration at the precipitate boundary, C_n^{m}, that, in turn, depends on properties of the precipitate.

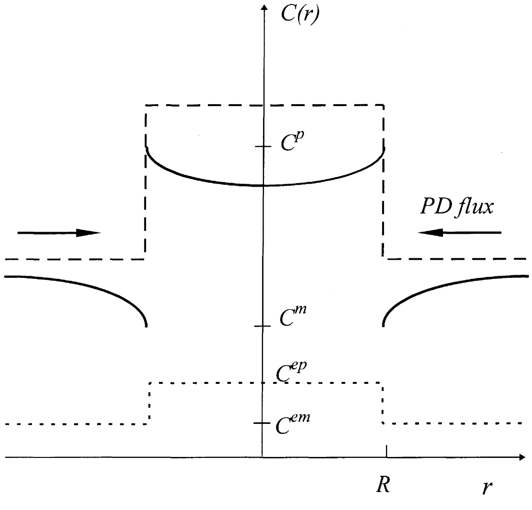

Fig. 1. Concentration profiles of PD in a neighborhood of the coherent precipitate. The PD concentrations inside and outside the precipitate are connected by Eq. (8).

Point defect concentrations inside the precipitate satisfy the equations similar to Eq. (9). To obtain simple analytical expressions, we expand the recombination term in series of the deviation of PD concentrations from values at the precipitate boundary ($s_n = C_n^{\mathrm{p}} - C_n$, $n = \mathrm{i}, \mathrm{v}$). The equation for deviations

$$\Delta D_n^{\mathrm{p}} s_n - \alpha_{\mathrm{p}} D_{\mathrm{i}}^{\mathrm{p}}\left(C_{\mathrm{i}}^{\mathrm{p}} s_{\mathrm{v}} + C_{\mathrm{v}}^{\mathrm{p}} s_{\mathrm{i}}\right) = \alpha D_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{v}}^{\mathrm{p}} - K, \quad n = \mathrm{i}, \mathrm{v} \tag{17}$$

yields

$$D_{\mathrm{v}}^{\mathrm{p}} s_{\mathrm{v}} = D_{\mathrm{i}}^{\mathrm{p}} s_{\mathrm{i}} = \frac{\alpha_{\mathrm{p}} D_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{v}}^{\mathrm{p}} - K}{\beta_{\mathrm{p}}^2}\left(\beta_{\mathrm{p}} R \frac{\mathrm{ch}\beta_{\mathrm{p}} R}{\mathrm{sh}\beta_{\mathrm{p}} R} - 1\right), \tag{18}$$

where $\beta_{\mathrm{p}}^2 = \alpha_{\mathrm{p}}/D_{\mathrm{v}}^{\mathrm{p}}(D_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{i}}^{\mathrm{p}} + D_{\mathrm{v}}^{\mathrm{p}} C_{\mathrm{v}}^{\mathrm{p}})$ is the inverse recombination length in the precipitate; α_{p} is the PD recombination constant in the precipitate.

Requiring equality of PD fluxes defined by Eqs. (16) and (18), and using the condition of the local equilibrium (Eq. (8)), we find the concentration of vacancies $C_{\mathrm{v}}^{\mathrm{m}}$ at the boundary of the precipitate

$$\begin{gathered} C_{\mathrm{v}}^{\mathrm{m}} = \sqrt{A^2 + \tfrac{K}{D_{\mathrm{v}}\mu} + \tfrac{3a}{\mu R^2}\overline{C_{\mathrm{v}}}} - A, \\ A = \tfrac{3a}{2\mu R^2} + \tfrac{D_{\mathrm{i}}\overline{C_{\mathrm{i}}} - D_{\mathrm{v}}\overline{C_{\mathrm{v}}}}{2D_{\mathrm{v}}}, \; a = \begin{cases} 1, & \beta_{\mathrm{p}} R \ll 1 \\ \beta_{\mathrm{p}} R/3, & \beta_{\mathrm{p}} R \geqslant 1, \end{cases} \end{gathered} \tag{19}$$

where $\mu = \alpha_{\mathrm{p}}(D_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{i}}^{\mathrm{ep}} C_{\mathrm{v}}^{\mathrm{ep}})/(D_{\mathrm{i}} C_{\mathrm{i}}^{\mathrm{em}} C_{\mathrm{v}}^{\mathrm{em}})$ is the effective recombination rate constant in the precipitate.

Eq. (19) together with Eq. (16) determines the PD flux to the coherent precipitate. The analysis shows that for the PD flux one can use a more simple expression, which follows from Eqs. (19) and (16) under assumption $D_{\mathrm{i}}\overline{C_{\mathrm{i}}} \approx D_{\mathrm{v}}\overline{C_{\mathrm{v}}}$. [1]

$$\begin{aligned} J_{\mathrm{i,v}}^{\mathrm{coh}} &= V\mu D_{\mathrm{i}}\overline{C_{\mathrm{i}}}\,\overline{C_{\mathrm{v}}} \begin{cases} 1, & \beta_{\mathrm{p}} R \ll 1 \\ 3/\beta_{\mathrm{p}} R, & \beta_{\mathrm{p}} R \geqslant 1 \end{cases} \\ &\approx V\mu D_{\mathrm{i}}\overline{C_{\mathrm{i}}}\,\overline{C_{\mathrm{v}}}\left(1 + \tfrac{\beta_{\mathrm{p}} R}{3}\right)^{-1} \\ \beta_{\mathrm{p}}^2 &= \tfrac{\alpha_{\mathrm{p}}}{D_{\mathrm{v}}^{\mathrm{p}}}\left(\tfrac{D_{\mathrm{i}}^{\mathrm{p}} C_{\mathrm{i}}^{\mathrm{ep}}}{D_{\mathrm{i}} C_{\mathrm{i}}^{\mathrm{em}}} + \tfrac{D_{\mathrm{v}}^{\mathrm{p}} C_{\mathrm{v}}^{\mathrm{ep}}}{D_{\mathrm{v}} C_{\mathrm{v}}^{\mathrm{em}}}\right) D_{\mathrm{v}}\overline{C_{\mathrm{v}}}, \end{aligned} \tag{20}$$

where V is the precipitate volume.

When deriving Eq. (20) we assumed that the recombination length is greater than or comparable with the average size of precipitates. At $\mu \gg \alpha$ (at low temperatures) the recombination length in the precipitate can be considerably less than the precipitate size. In this case Eq. (20) overestimates the value of the PD flux (the PD flux to the coherent precipitate cannot exceed the PD flux to a perfect sink). Obviously, in this case PD recombine inside the precipitate in a thin subsurface layer.

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[1] $D_{\mathrm{i}}\overline{C_{\mathrm{i}}}$ and $D_{\mathrm{v}}\overline{C_{\mathrm{v}}}$ differ due to presence of sinks biased to one of the types of PD. However, here this is insignificant, because the bias factors influence essentially the difference between the vacancy and interstitial fluxes rather than the value of fluxes.

In other words the precipitate absorbs PD as an incoherent sink of the same radius

$$J^{\mathrm{coh}}_{\mathrm{i,v}} = 4\pi R D_{\mathrm{v}} C_{\mathrm{v}}. \tag{21}$$

The interpolation formula combining both limiting cases is given by

$$J^{\mathrm{coh}}_{\mathrm{i,v}} = V\mu D_{\mathrm{i}}\overline{C}_{\mathrm{i}}\overline{C}_{\mathrm{v}}\left(1+\frac{V\mu\overline{C}_{\mathrm{v}}}{4\pi R}\right)^{-1}. \tag{22}$$

3. Rate equations for average concentrations of point defects

Taking into account the absorption of vacancies and interstitials by the second phase precipitates the rate equations is given by (see Eqs. (1)–(4) and (22))

$$K - \alpha^{*} D_{\mathrm{i}}\overline{C}_{\mathrm{i}}\,\overline{C}_{\mathrm{v}} - k_{\mathrm{i}}^{2} D_{\mathrm{i}}\overline{C}_{\mathrm{i}} = 0, \tag{23}$$

$$K - \alpha^{*} D_{\mathrm{i}}\overline{C}_{\mathrm{i}}\overline{C}_{\mathrm{v}} - k_{\mathrm{v}}^{2} D_{\mathrm{v}}\left(\overline{C}_{\mathrm{v}} - C^{\mathrm{e}}_{\mathrm{v}}\right) = 0, \tag{24}$$

where $k_n^2 = k_{nV}^2 + k_{n,\mathrm{inc}}^2 + k_{n\mathrm{d}}^2$ is the total strength of all sinks (voids, incoherent precipitates and dislocations, respectively), $n = \mathrm{i,v}$; α^{*} is the effective recombination rate constant

$$\begin{aligned} \alpha^{*} &= \alpha\left(1 - Q_{\mathrm{p}}\right) + Q_{\mathrm{p}}\mu\left(1+\tfrac{V\mu\overline{C}_{\mathrm{v}}}{4\pi R}\right)^{-1}, \\ \mu &= \alpha_{\mathrm{p}}\frac{D^{\mathrm{p}}_{\mathrm{i}} C^{\mathrm{ep}}_{\mathrm{i}} C^{\mathrm{ep}}_{\mathrm{v}}}{D_{\mathrm{i}} C^{\mathrm{em}}_{\mathrm{i}} C^{\mathrm{em}}_{\mathrm{v}}} \end{aligned} \tag{25}$$

where $Q_{\mathrm{p}} = (4\pi/3)R^3 N$ is the volume fraction of coherent precipitates of radius R, and N is the density of coherent precipitates.

The distinction of Eqs. (23) and (24) from those for a pure metal is that the effective recombination coefficient depends exponentially on temperature

$$\alpha^{*} = \alpha(1 - Q_{\mathrm{p}}) + Q_{\mathrm{p}}\frac{D^{\mathrm{p}}_{\mathrm{i}_0}}{D_{\mathrm{i}_0}}\exp\left(\frac{W}{kT}\right)\left(1+\frac{V\mu\overline{C}_{\mathrm{v}}}{4\pi R}\right)^{-1}, \tag{26}$$

where $D^{\mathrm{p}}_{\mathrm{i}_0}/D_{\mathrm{i}_0}$ is the ratio of pre-exponential factors of interstitial diffusion coefficients in the precipitate and in the matrix; $W = E^{\mathrm{m}}_{\mathrm{F}} - E^{\mathrm{p}}_{\mathrm{F}} - U - E^{\mathrm{p}}_{\mathrm{im}} + E^{\mathrm{m}}_{\mathrm{im}}$; $E^{\mathrm{p,m}}_{\mathrm{im}}$ are the activation energies of interstitial diffusion in the precipitate and in the matrix.

Let us estimate the parameter W. The formation energy of the Frenkel pair equals several electronvolts, therefore the difference $E^{\mathrm{m}}_{\mathrm{F}} - E^{\mathrm{p}}_{\mathrm{F}}$ can achieve values of the same order. The sum of energies of interaction of a vacancy and an interstitial atom with the field of elastic stresses inside the coherent precipitate, U, does not exceed several tenths of electronvolt. The activation energies $E^{\mathrm{p,m}}_{\mathrm{im}}$ usually equal several tenths of electronvolt. Thus, because of a strong difference of properties of the precipitate and the matrix, W can be rather large. At the value of W about of an electronvolt this means that at typical irradiation temperatures the effective recombination coefficient can exceed the recombination coefficient in the matrix despite a small volume fraction of coherent precipitates. For this reason the PD concentrations in the alloy containing coherent precipitates can be much lower than that in alloys without precipitates. Therefore, one can expect that processes of radiation growth, nucleation and growth of voids, which are controlled by PD fluxes, will be suppressed. The effect should be observed at $E^{\mathrm{p}}_{\mathrm{F}} < E^{\mathrm{m}}_{\mathrm{F}}$. The negative dimensional misfit increases the effect.

4. Calculations of point defect concentrations

To demonstrate the influence of coherent precipitates on the growth of voids we shall find the ratio $(\dot{R}_{\mathrm{V}})_{\mathrm{act}}/(\dot{R}_{\mathrm{V}})_{\mathrm{ref}}$, where $(\dot{R}_{\mathrm{V}})_{\mathrm{act}}$ is the actual rate of void growth in the alloy with the precipitates absorbing PD, and $(\dot{R}_{\mathrm{V}})_{\mathrm{ref}}$ the void growth rate in the same alloy without precipitates (in the reference state). Assuming that the only preferential sinks leading to partition of fluxes of vacancies and interstitials are dislocations with the sink strength $k^2_{n\mathrm{d}} = Z_n\rho$ (Z_n is the sink efficiency, ρ is the density of dislocations), the growth rate of a large void is given by

$$\begin{aligned} \frac{\mathrm{d}R_{\mathrm{V}}}{\mathrm{d}t} &= \frac{1}{R_{\mathrm{V}}}\left[D_{\mathrm{v}}\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right) - D_{\mathrm{i}}\overline{C_{\mathrm{i}}}\right] \\ &= \frac{(Z_{\mathrm{i}} - Z_{\mathrm{v}})\rho}{R_{\mathrm{v}}k^2_{\mathrm{i}}} D_{\mathrm{v}}\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right), \end{aligned} \tag{27}$$

where the concentration of vacancies, in view of the relation $D_{\mathrm{i}}\overline{C_{\mathrm{i}}} \approx D_{\mathrm{v}}\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right)$, satisfies the equation

$$\begin{aligned} &K - \left[\alpha\left(1 - Q_{\mathrm{p}}\right) + Q_{\mathrm{p}}\mu\left(1+\frac{V\mu\overline{C}_{\mathrm{v}}}{4\pi R}\right)^{-1}\right] D_{\mathrm{v}}\overline{C_{\mathrm{v}}}\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right) \\ &\quad - k^2_{\mathrm{v}} D_{\mathrm{v}}\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right) = 0. \end{aligned} \tag{28}$$

According to Eq. (27) the relative void growth rate is the ratio of vacancy supersaturations in two states of the alloy

$$v_{\mathrm{rel}} = \frac{(\dot{R}_{\mathrm{V}})_{\mathrm{act}}}{(\dot{R}_{\mathrm{V}})_{\mathrm{ref}}} = \frac{\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right)_{\mathrm{act}}}{\left(\overline{C_{\mathrm{v}}} - C^{\mathrm{e}}_{\mathrm{v}}\right)_{\mathrm{ref}}}. \tag{29}$$

Note that Eq. (29) can be used for the evaluation of suppression of other processes of dimensional instability, because rates of these processes depend on PD concentrations too.

The microstructural parameters used in numerical calculations are shown in Table 1. The values were taken to be close to experimentally observed in Zr-alloys. The parameter μ was chosen in the form $\mu = \alpha\exp(W/kT)$.

Table 1
Material parameters of Zr–Nb alloy used in calculations

Parameter	Value	Refs.
Displacement rate, K (dpa/s)	10^{-9}–10^{-3}	
Atomic volume of Zr (m^3)	2.32×10^{-29}	
Recombination rate constant, α (m^{-2})	3×10^{20}	
Sink strength of dislocations, k^2 (m^{-2})	5×10^{14}	
Density of coherent precipitates, N (m^{-3})	10^{21}–10^{23}	
Volume fraction of coherent precipitates, Q_p	0.025 (2.5%)	
Diffusion coefficient of vacancies in Zr, D_v (m^2/s)	$10^{-6}\exp(-1\ \mathrm{eV}/kT)$	[18]
Formation energy of vacancies in Zr, E^{m}_{vf} (eV)	1.8	[18]
W (eV)	0.2–0.6	

Fig. 2 shows the temperature dependence of the relative vacancy supersaturation at the displacement rate 10^{-7} dpa/s typical for a thermal nuclear reactor. It is seen that coherent precipitates absorb PD ($v_{rel} < 1$) in a certain temperature range which position depends on migration energy of vacancies (this region shifts to high temperatures with increasing the migration energy of vacancies). The efficiency of the recombination mechanism depends on density of coherent precipitates (Fig. 3). Note that the minimum values of the relative vacancy supersaturation are reached in a neighborhood of operation temperatures of thermal nuclear reactors (500–600 K). The essential reduction of the relative vacancy supersaturation is observed at energies $W \geqslant 0.4$ eV (Fig. 4). Fig. 5 shows the dependence of the relative vacancy supersaturation on displacement rate. It is seen, that at high displacement rates the coherent precipitates do not influence the concentration of vacancies because the volume recombination in the matrix dominates in the PD balance (i.e., the PD recombination length is smaller than the precipitate size).

5. Discussion

In this paper we considered only the indirect influence of second phase precipitates on dimensional stability of a material (by means of decreasing of the average PD concentrations.) The discussion of other mechanisms can be found in Refs. [19–21]. The efficiency of the recombination mechanism of PD absorption by coherent precipitates is determined by the density of precipitates and the value of W that depends on PD formation and migration energies in the matrix and precipitates. The model calculations show that the enhancement of the recombination by coherent precipitates is observed if the sink strength of coherent precipitates is greater than the sink strength of dislocations and at $W \geqslant 0.4$ eV. At a fixed volume fraction of precipitates their efficiency as a sink for PD increases with size decreasing. This result agrees with experimental data indicating that the alloy exhibits high dimensional stability, when second phase particles precipitating from the solid solution are fine-grained.

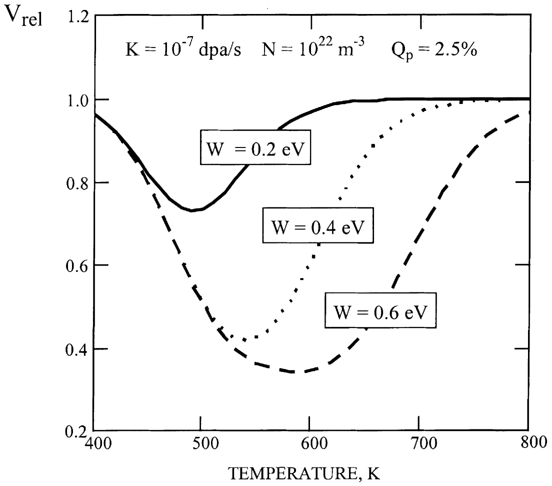

Fig. 2. The temperature dependence of the relative vacancy supersaturation at a fixed volume fraction and density of coherent precipitates.

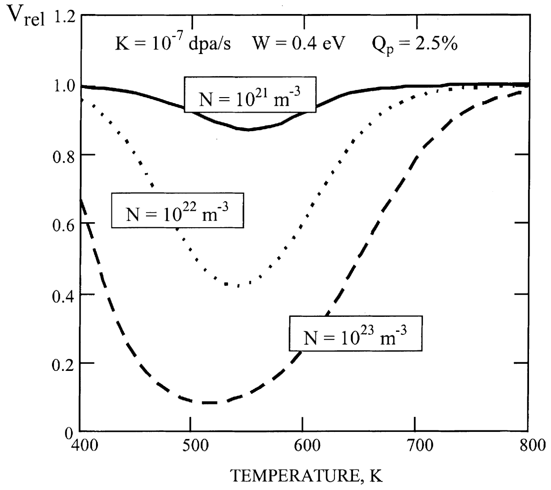

Fig. 3. The dependence of the relative vacancy supersaturation on temperature as a function of density of coherent precipitates.

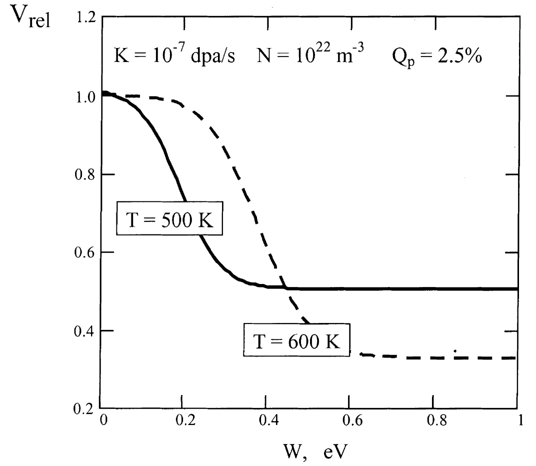

Fig. 4. The dependence of the relative vacancy supersaturation on parameter *W* at temperatures typical for the thermal reactor.

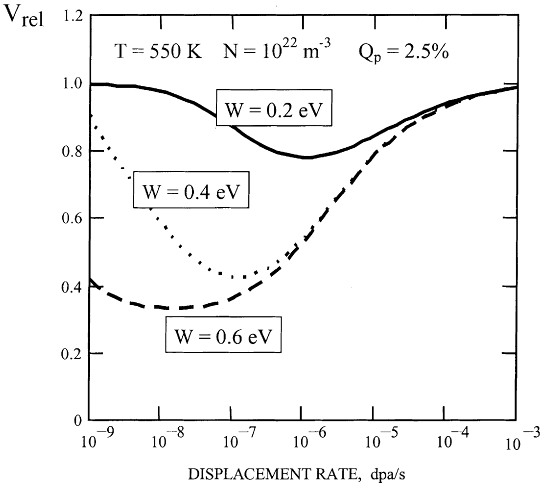

Fig. 5. The dependence of relative vacancy supersaturation on displacement rate at various values of the parameter *W*.

In this paper the stability of precipitates and mechanisms of phase stability loss were not considered. The discussion of these problems can be found in Refs. [22–28]. In Ref. [28] the influence of the radiation-induced segregation and the cascade mixing on the growth of coherent and incoherent precipitates was considered. It was shown, that in the approximation of a weak recombination the segregation does not influence the condition of stability of coherent precipitates because there are no PD fluxes directed to coherent precipitates [28]. The boundary of the incoherent precipitate is a sink for PD. Due to coupling between the atomic fluxes and PD fluxes, the alloying elements segregate to the incoherent precipitate (the inverse Kirkendall effect [29]). Therefore, the criterion for stability of the incoherent precipitate changes [28]. As shown in the present study, in the general case there are directed fluxes of PD to the coherent precipitate (or from it, see Eq. (14)) because of the difference of recombination rates in the precipitate and in the matrix. It means that under irradiation in a neighborhood of the coherent precipitate there are segregation fluxes of alloying elements too. However, as distinct from incoherent precipitates, the direction of these fluxes depends on direction of PD fluxes, which are determined by the relation between properties of the matrix and the precipitate (see Eq. (14)). In a sense, this effect – the separation of alloying elements caused by a spatial heterogeneity of recombination – is similar to the spinodal instability of a homogeneous solid solution with respect to the volume recombination of vacancies and interstitials [30].

The segregation fluxes of alloying elements caused by PD recombination can lead to stabilization of coherent precipitates of non-equilibrium phases. Probably this was observed experimentally [31] in AISI316 steel [31], where the radiation-induced precipitates of γ'-phase dissolved without irradiation. In addition, the recombination-driven segregation may result in a modification of the chemical composition of precipitates because of infiltration of elements which were not present in its structure. This effect was observed experimentally [6,32]. The infiltration, in turn, can stimulate a phase transformation inside the precipitate with the modification of the stoichiometry, lattice type and the morphology. This mechanism is similar to the mechanism of infiltration due to segregation of alloying elements to the semicoherent boundary [32].

Even under the most favorable conditions, with the course of time the coherent precipitates cease to work as PD sinks because the precipitates grow and their density decreases. This process is possible to arrest by selecting a material, doping elements and working conditions under irradiation, so that large precipitates are destroyed by displacement cascades, and, in exchange, small coherent precipitates nucleate. Experimental data [27,33] and theoretical evaluations [28] show that in iron–nickel alloys the cascade destruction starts to play a role at temperatures below $T \sim 700$ K. Since the migration energy of vacancies in zirconium alloys is less than that in iron–nickel alloys, one can expect that in zirconium alloys the temperature threshold for the cascade destruction is located at lower temperatures (500–600 K). The competition between processes of cascade destruction, nucleation and growth of precipitates can lead to the formation of the distribution of fine-grained precipitates with slowly varying parameters.

The analysis shows that by controlling the processes of formation and evolution of the precipitate ensemble one can stabilize the microstructure of the alloy and, eventually, its properties in the radiation environment.

The proposed model explains why radiation properties of Zr–Nb alloys depend on density of fine-grained precipitates of β_{Nb}-phase.

6. Summary

- Coherent precipitates trap point defects if the formation energy of the Frenkel pair in the matrix is greater than that in precipitates. At a negative misfit of the precipitate and matrix lattices the probability of absorption of Frenkel pairs increases.
- The efficiency of the recombination mechanism of point defect absorption by coherent precipitates at a fixed volume fraction of precipitates increases with decreasing the average size of precipitates.
- The segregation fluxes of alloying elements originating because of inequality of recombination rates in precipitates and in the matrix can lead to the stabilization of thermally unstable coherent precipitates or to modification of their composition followed by phase transformation.

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