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Reallocation of impurity atoms in a supersaturated solid solution by thermodiffusion in collision cascades

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Abstract

We consider a weak supersaturated binary solid solution under continuous irradiation. Irradiation produces collision cascades in the media. Local energy deposition within a cascade zone, as is known, causes relaxation of the excess temperature to an ambient level. A simple model, that is taking into account the effect of temperature relaxation to a clustering formation of alloying atoms, is presented. The model is based on general principles of irreversible non-equilibrium thermodynamics. It is shown that the relaxation and thermodiffusion processes in supersaturated alloys may result in spatial redistribution of solute atoms in the media.

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1. Introduction

According to contemporary point of view, many principal features of a long-term behavior of nuclear materials under irradiation should be attributed to specific details of primary radiation damage (PRD). The PRD fine structure depends on characteristics of atomic collision cascades. The most comprehensive information about PRD, if it is possible, may be available as a result of computer modeling of collision cascades and their relaxation in a crystal lattice (see, for example [1]). Such characteristics of PRD as an effective volume of cascades, survival fractions of point defects per cascade, primary interstitial and vacancy clustering in a cascade zone are regarded as input parameters in an analysis of radiation damage kinetics in metals and alloys.

Non-equilibrium freely migrating interstitials and vacancies remarkably enhance diffusion processes in irradiated media. Irradiation producing atomic collision cascades brings additional complications to a spatial redistribution of components in alloys. For example, electron irradiation stimulates the process of aging of reactor pressure vessel steels (RPVS) regarded to quasi-thermodynamic decay of solid solution without irradiation [2]. Correspondingly, neutron irradiation causes more significant formation of copper precipitates in RPVS compared to electron irradiation [3]. The latter fact attracts ones attention to an importance of understanding of precipitate clustering in irradiation induced collision cascades.

The presented below paper gives our consideration of the cascade relaxation and its influence on redistribution of impurity atoms in a binary alloy. In Section 2 we formulate some general approach to the analysis of irreversible heat and mass transport processes in a binary system after the energy release in the cascade volume. In Section 3 we apply this formulation to demonstrate spatial reallocation of solute component in supersaturated solid solution under cascade producing irradiation conditions. Section 4 contains conclusions.

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2. Description of thermodiffusion processes in a non-equilibrium binary solution

Let us consider what is going on in a media during atomic collision cascade relaxation. An average cascade takes place within some mean volume V_c. At the collisional phase, some energy Q is transferred to atoms in this volume. A part of this energy, Q_1, is lossed to creation of Frenkel Pairs (elastic interactions of primary particles with target atoms), a remaining part, $Q_2 = Q - Q_1$, results in heating of a lattice (energy loss of primary particles to the electronic subsystem).

This energy release descends during short period, resulting to local heating of the lattice from temperature T_0 up to some temperature T_1, superior, for enough developed stage, the melting point of a matrix. As a result, the mean supersaturation of a solution of impurity atoms in the cascade volume at the stage of the cascade relaxation can appear less, than in the ambient lattice. This difference may play a role of a driving force for spatial redistribution of impurity atoms. Such reallocation may occur both by interior transformation of the impurity subsystem in the cascade volume and as a result of diffusion from the external volume to the cascade zone. Accordingly, it is possible to expect ascending of the probability for impurity atoms clustering in the bulk of cascade.

We demonstrate such possibility by the following considerations.

According to the theory of non-equilibrium processes in a binary solution [4,5], it is possible to use the following expressions for average values of diffusion, $\vec{J}_\mathrm{d}$, and heat transfer, $\vec{J}_\mathrm{q}$, flows

$$\begin{aligned} \vec{J}_\mathrm{d} &= -\frac{L_1}{T^2}\vec{\nabla}T - L_{11}\vec{\nabla}\left(\frac{\mu}{T}\right), \\ \vec{J}_\mathrm{q} &= -\frac{L_0}{T^2}\vec{\nabla}T - L_1\vec{\nabla}\left(\frac{\mu}{T}\right). \end{aligned} \tag{1}$$

Here L_0, L_1, L_{11} are the kinetic coefficients of Onsager; μ is the chemical potential of impurity atom. We use in this section, for sake of simplicity, units with the Boltzmann constant, k, equal to unity.

For atoms in a solution, we write the following relation:

$$\frac{\mu}{T} = \ln\left(\frac{C}{C_\mathrm{s}(T)}\right), \quad C_\mathrm{s}(T) = C_1 \exp\left(-\frac{Q_0}{T}\right). \tag{2}$$

We suppose above, that it is possible to describe relation of a solubility limit of impurity atoms to temperature, $C_\mathrm{s}(T)$, entering energy of dissolution Q_0. It should be noticed that such a presentation might be not exact in a sufficiently wide temperature range (see for example experimental results [6]). However, we shall apply it below for at least a quantitative approach to the problem.

The following relations are useful:

$$D = \frac{L_{11}}{T}\left(\frac{\partial\mu}{\partial C}\right)_{p,T} = \frac{L_{11}}{C} \tag{3}$$

is the diffusion coefficient of a dissolved component;

$$\begin{aligned} K_\mathrm{T}D &= \frac{L_1}{T} + L_{11}T\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_{C,p} \\ &= \frac{L_1}{T} - DC\frac{Q_0}{T} \equiv \left(K_\mathrm{T}^0 - C\frac{Q_0}{T}\right)D \end{aligned} \tag{4}$$

is the thermal diffusion coefficient;

$$\lambda = \left(\frac{L_0}{T^2} - \frac{L_1^2}{L_{11}T^2}\right) \tag{5}$$

is the thermal conductivity of a binary mixture.

Then the expressions for flows become

$$\begin{aligned} \vec{J}_\mathrm{d} &= -D\left(\vec{\nabla}C + \frac{K_\mathrm{T}^0}{T}\vec{\nabla}T - \frac{Q_0 C}{T^2}\vec{\nabla}T\right), \\ \vec{J}_\mathrm{q} &= -\lambda\vec{\nabla}T + \frac{L_1}{L_{11}}\vec{J}_\mathrm{d} = -\lambda\vec{\nabla}T + \left(\frac{K_\mathrm{T}^0 T}{C}\right)\vec{J}_\mathrm{d}. \end{aligned} \tag{6}$$

Accordingly, the basic equations may be presented in the form

$$\begin{aligned} C_p\frac{\partial T}{\partial t} + \mathrm{div}\vec{J}_\mathrm{q} &= Q_2(\vec{r}, t), \\ \frac{\partial C}{\partial t} + \mathrm{div}\vec{J}_\mathrm{d} &= 0. \end{aligned} \tag{7}$$

Here C_p is the thermal capacity of the solid solution.

Let us take into account further that the thermal conductivity depends on concentration of an impurity [4,5]

$$K_\mathrm{T}^0 \equiv \beta C(1 - C) \cong \beta C. \tag{8}$$

It follows that

$$\mathrm{div}\vec{J}_\mathrm{q} = -\vec{\nabla}(\lambda\vec{\nabla}T) + \beta\vec{J}_\mathrm{d}(\vec{\nabla}T) + \beta T\,\mathrm{div}\vec{J}_\mathrm{d}. \tag{9}$$

Then Eq. (7) of heat transfer and diffusion in the solution become

$$\begin{aligned} C_p\frac{\partial T}{\partial t} - \beta T\frac{\partial C}{\partial t} &= \vec{\nabla}(\lambda\vec{\nabla}T) + \beta D\left[\vec{\nabla}C + \frac{C}{T}\vec{\nabla}T\left(\beta - \frac{Q_0}{T}\right)\right]\vec{\nabla}T \\ &\quad + Q_2(\vec{r}, t), \\ \frac{\partial C}{\partial t} &= \vec{\nabla}\left\{D\left[\vec{\nabla}C + \frac{C}{T}\vec{\nabla}T\left(\beta - \frac{Q_0}{T}\right)\right]\right\}. \end{aligned} \tag{10}$$

The last equation describes change of a concentration as due to customary diffusion with a diffusion coefficient, dependent on space coordinates, and as a result of thermodiffusion (the Soiret effect). Presented above expressions demonstrate, that the contribution to thermodiffusion is given by two mechanisms. First one, corresponding to the term K_{T}^{0}, will be realized in quasi-equilibrium solution of impurity atoms, when the role of a supersaturation is small. Thus a flow of impurity atoms implements against a gradient of temperature.

The second mechanism is possible in conditions of small dissolubility of impurity atoms and large initial supersaturations and acts in a direction of temperature gradient.

We guess further, that $|\vec{\nabla}C| \ll C \cdot |\vec{\nabla}T|/T$ and $\beta \ll 1$. Let us take into account also, that in case of small dissolubility, one has really $Q_0/T \gg 1$. Then, as a first approximation, equations can be written as follows:

$$\begin{aligned} C_p\frac{\partial T}{\partial t} &= \vec{\nabla}(\vec{\nabla}T) + Q_2(\vec{r},t), \\ \frac{\partial C}{\partial t} &= -\mathrm{div}\{\vec{V}C\}, \quad \vec{V}(\vec{r},t) \equiv D\frac{Q_0}{T^2}\vec{\nabla}T. \end{aligned} \tag{11}$$

It should be outlined that the physical meaning of the second equation above is quite clear: it looks like a simple equation of continuity for impurity atoms concentration in absence of sources but with the temperature and its gradient dependent macroscopic velocity $\vec{V}(\vec{r},t)$.

According to this equation, during a relaxation of the cascade there is an offset of impurity atoms into area of heat release. Propulsion of such reallocating of impurity atoms is the difference in a relative supersaturation of solution outside of and inside a cascade volume. We consider herein consequences of Eqs. (11).

3. Collision cascade as a reason of spatial redistribution of components

The solution of the first equation in (11) may be written as follows:

$$\begin{aligned} T(\vec{r},t) &= T_0 + \frac{1}{(4\pi\chi t)^{3/2}}\int \exp\left(-|\vec{r}-\vec{r}'|^2/4\chi t\right) \\ &\quad \cdot \Delta T(\vec{r}',0)\,\mathrm{d}\vec{r}', \\ \chi &\equiv \frac{\lambda}{C_p}. \end{aligned}$$

For a point-like model of energy release in the cascade event with an instant increase of temperature in a spherical volume $V_{\mathrm{c}} \equiv \frac{4\pi}{3}R^3$ in the form

$$\Delta T(\vec{r},0) = \Delta T \cdot V_{\mathrm{c}}\delta(\vec{r}), \tag{13}$$

one has

$$T(\vec{r},t) = T_0 + \Delta T \cdot \frac{4\pi}{3} \cdot \frac{R^3}{(4\pi\chi t)^{3/2}} \cdot \exp\left(-\frac{r^2}{4\chi t}\right). \tag{14}$$

Accordingly,

$$\frac{\partial C}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2 D(t,r)C\frac{Q_0}{(T)^2}\frac{\partial}{\partial r}T\right\}. \tag{15}$$

By averaging of this expression over the cascade volume, one has the following: by definition

$$\overline{C} \equiv \frac{3}{4\pi R^3}\int_{V_{\mathrm{c}}} C(\vec{r},t)\,\mathrm{d}\vec{r},$$

consequently, expression (15) may be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{C} = -\frac{3}{R^3}\left\{r^2 D(r,t)C(r,t)\frac{Q_0}{(T)^2}\frac{\partial}{\partial r}T\right\}_{r=0}^{r=R}. \tag{16}$$

As a result, after integrating with respect to the time

$$\overline{C} \cong C(0)\left\{1 - \frac{3}{R}\int_0^t \mathrm{d}t D\frac{Q_0}{T^2}\frac{\partial T}{\partial R}\right\}. \tag{17}$$

Taking into account that

$$\begin{aligned} \frac{\partial T}{\partial R} &= -\frac{8\pi\Delta T}{3\pi^{3/2}(\chi t)^{1/2}}\left(\frac{R^2}{4\chi t}\right)^2 \exp\left(-\frac{R^2}{4\chi t}\right) \\ &= -\frac{3\Delta T}{\pi^{1/2}}\frac{\sqrt{6}}{Rx^{5/2}}\exp\left(-\frac{3}{2x}\right) = -\frac{3}{Rx}[T - T_0] \end{aligned} \tag{18}$$

and

$$T(R) - T_0 = \Delta T \cdot \left(\frac{6}{\pi x^3}\right)^{1/2} \exp\left(-\frac{3}{2x}\right), \tag{19}$$

where we denote by $x \equiv 6\chi t/R^2$, we may write down the estimate of impurity atom concentration in the cascade zone

$$\overline{C} \cong C(0)\left\{1 + \frac{3Q_0}{2\chi}\int_0^\infty \mathrm{d}x\,\frac{D}{T^2}\frac{[T - T_0]}{x}\right\} > C(0). \tag{20}$$

It is important to outline here once again that the mechanism considered for $\beta \ll Q_0/T$ leads to the increase of the number of impurities in the cascade volume. This situation may enhance the nucleation of embryos for solute atoms in the alloy.

In the opposite case when $\beta \gg Q_0/T$ thermal conductivity spreads the spatial distribution of solute atoms beyond the cascade volume. As a consequence, one may easily see that the average concentration of impurity atoms in the cascade region is reduced

$$\overline{C} \cong C(0)\left\{1 - \frac{3\beta}{2\chi}\int_0^\infty \mathrm{d}x\,\frac{D}{T}\frac{[T - T_0]}{x}\right\} < C(0). \tag{21}$$

4. Conclusions

The presented above consideration demonstrates, at least qualitatively, the role of temperature relaxation in a volume of atomic collision cascade. The thermodiffusion process may act as a driving force for spatial redistribution of solute atoms (see also [7]).

In the case of low solubility, the final concentration of such atoms becomes higher than in the surrounding media.

In the contrary case of high thermal conductivity, the decrease of impurity concentration in the cascade volume takes place.

Quantitative estimates depend on a number of material parameters. Some of them are purely defined. The problem of parameters was discussed, for example, in [8,9]. Possible estimates depend on a set of data used. It is considered that the cooling half time is of the order of 10^{-11} s [10–12]. For a reasonable value of the thermal conductivity, estimates show that a noticeable number of jumps of atoms may occur during this time [8,9] at least via interstitials. This circumstance may be regarded as being rather sufficient for applicability of the continuous approach. The molecular dynamic calculations [1,13] did not demonstrate influence of displacement cascades on solute atoms redistribution. Note that in [13], as the authors outlined it, the role of interstitials was not analyzed comprehensively. So the question of correct quantitative estimates in modeling of cascade relaxation is still open.

From the qualitative point of view, the presented above consideration clearly shows that a tendency for spatial redistribution of solute atoms must be enhanced in conditions of cascade generating irradiation. Consequences of the temperature relaxation at cascades for nucleation kinetics of cluster formation demand additional consideration. Results of a corresponding analysis will be published elsewhere.

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