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ScienceDirect
Journal of Nuclear Materials 366 (2007) 238–247
journal of nuclear materials
www.elsevier.com/locate/jnucmat

A probable scenario of copper precipitate clustering in model FeCu alloys under cascade-damage irradiation

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Received 30 December 2005; accepted 19 January 2007

Abstract

We consider below kinetics of copper precipitate clustering in model FeCu alloys under cascade-damage irradiation. The investigation is carried out for rather high copper content compared with the solubility limit. The nucleation and growth stage preceding the coarsening kinetics is analysed. It is assumed that atomic collision cascades create embryos that are the growing centers during supersaturation decay. The time dependencies of copper precipitates characteristics are obtained as a solution of the Fokker–Planck equation for clusters in the space of their sizes. The results are in a qualitative agreement with some experimental data on copper clustering under neutron irradiation.
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PACS: 61.82.Bg

1. Introduction

For the past decades of nuclear power reactors practical operation had enriched the experience in estimates and forecasts of long-term structural changes and properties degradation in metals and alloys under irradiation. The great amount of accumulated experimental data became a base of contemporary mostly qualitative understanding of the observed complexity and variety in the microstructure evolution nature and origin. The two groups of phenomena are superimposing and closely influencing the final result of irradiation: (i) the primary peculiarities of radiation damage creation and (ii) the diffusion controlled quasi-chemical reaction-like kinetics of micro-processes between matrix, impurities, alloying elements, point and extended defects, nuclides, etc. The group of effects (ii) is very sensitive to temperature conditions. Mechanical loading may introduce additional complicated features to behavior of nuclear materials in irradiation environment. The primary radiation processes (i) are associated with spectral effects resulting in different spatial and instant clustering characteristics of atomic collision cascades for various irradiation sources.

All we said above is equitable with respect to processes in reactor pressure vessel steels (RPVS). The structural compositions of RPVS are complicated and contain different elements. The development

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doi:10.1016/j.jnucmat.2007.01.218

of experimental technique (creation of the tomographic atom probe) gave a possibility to reproduce in the real space a three-dimensional distribution of atoms in an irradiated material. This method of analysis was applied in [1] to investigation of RPVS' specimens (steel CHOOZ) after irradiation at 260 °C to a fluence of 1.6×10^{24} n/m^2 which corresponds to a dose close to 0.2 dpa. According to results of these studies, under neutron irradiation complicated agglomerates containing atoms of Si, Ni, Mn, and Cu in the material are formed. The nature of these clusters (composition, cluster/matrix interface) significantly differs from almost pure copper particles (containing 95% Cu) that form during the aging of model alloys. While irradiation dose is increasing, the size and composition of these clusters do not change but the concentration is increasing. The investigators supposed that the observed clusters might be attributed to vacancies, micro-voids or dislocation loops.

Clusters containing Cu, P, Ni, Mn and Si were detected by the same method in the irradiated steel with high amount of copper (0.24%) to doses 6.6×10^{22} and 3.47×10^{23} n/m^2 [2]. In the steel with low concentration of copper (0.02%) irradiated to dose 1.5×10^{23} n/m^2 only clusters of phosphorus atoms were observed. The average composition of copper clusters and the level of enrichment by individual elements (i.e. the ratio of an element concentration in clusters to a concentration in the matrix) vary with fluence.

It is recognized that copper atoms may have a crucial role in the precipitate cluster formation in a number of RPVS in which the copper content is about or above 0.06%. Consequently, experiments with model FeCu alloys may reproduce and clarify some features of the clustering kinetics in copper rich steels. The peculiarities of structural changes under collision cascade-producing irradiation in the model alloys are of special interest. From this point of view, the comparison of experimental data for electron irradiation and neutron or heavy ion irradiation is very important [3,4].

We give below an analytical consideration, which is modeling the complex processes displaying in the pressure vessel steels interior. In Section 2, we develop a description of structural changes in FeCu alloys under neutron irradiation producing collision cascades. In Section 3, we discuss the results and make a comparison with experimental data. Section 4 includes concluding remarks.

2. A model of precipitate clustering in alloys on the basis of α-Fe under neutron or heavy ion irradiation conditions

Odette and Wirth distinguished the cases of low Cu (<0.1%) and high Cu (>0.1%) contents in steels [5]. As they showed in their analysis, well-formed copper-rich precipitates are the dominant clusters in high Cu steels according to numerous experimental measurements. Therefore, the FeCu alloys may represent basic features of structural transformations in real conditions. The initial phase of such transformations is a supersaturated solid solution of substituted copper atoms in a matrix of α-iron. Let us suppose below that the secondary phase consists of copper clusters. These agglomerates may grow by absorption of migrating surplus copper atoms.

We introduce the following notations: $Q_{\mathrm{Cu-Cu}}$ and $Q_{\mathrm{Fe-Fe}}$ are, accordingly, the binding (cohesive) energies per atom of copper or iron in their bcc lattices; N_{Cu} is the initial number of copper atoms in the matrix, containing N atomic places. The final phase consists of N_g spherical clusters that include g copper atoms up to a maximum size G. $Q_{\mathrm{Cu-Fe}}$ is the binding energy of an isolated copper atom in the lattice of α-Fe, σ is the FeCu interface energy, Ω is the atomic volume, $\Omega = a^3/2$, a is the lattice constant. The critical size of a copper cluster is determined by the actual supersaturation and takes the following form (see Appendix A):

$$g_{\mathrm{c}}^{1/3}(t) = \frac{\alpha}{\ln \frac{C(t)}{C_{\mathrm{s}}}}, \quad \alpha \equiv \frac{2\sigma\Omega}{kTa}. \tag{1}$$

Here k is the Boltzmann constant, T is the absolute temperature, $C(t) = N_{\mathrm{Cu}}/N$ is the atomic concentration of copper atoms in the supersaturated solution, C_{s} is the thermodynamic equilibrium concentration of copper atoms at the given temperature.

With these definitions, further consideration may be based on the nucleation theory. The corresponding equation for a distribution function of clusters in their size space [6], $f(g,t)$, takes the form:

$$\frac{\partial f(g,t)}{\partial t} = Kq(g,t) - \frac{\partial}{\partial g}\left[V(g,t) - \frac{\partial}{\partial g}D(g,t)\right] f(g,t). \tag{2}$$

Here the hydrodynamic velocity in the space of sizes, $V(g,t)$, corresponds to the deterministic growth of a new phase cluster, which is consisting of g particles at a moment t. The diffusion coefficient

in the space of sizes, $D(g,t)$, is determined by statistical properties of stochastic process of embryos evolution. The consideration of statistical legitimacies in point defects absorption by a spherical cluster demonstrates, that [7]

$$D(g,t) = D^{s} + D^{c}, \tag{3}$$

where the term D^{s} corresponds to concentration fluctuations of point defects near to a cluster surface, which are caused by random walks processes, while the probabilistic nature of atomic collisions is accounted by the second term

$$D^{c} \equiv \frac{\pi R_v^2 K_v \langle N_{dv}^2 \rangle}{k_v \Omega N_{dv}} + \frac{\pi R_i^2 K_i \langle N_{di}^2 \rangle}{k_i \Omega N_{di}}. \tag{4}$$

The following notations are introduced here: R_j is the capture radius by a sink of point defects of a kind j ($j = v,i$); k_j^2 is the full strength of sinks; K_j is the effective rate of generation for defects of a kind j; N_{dj} is the average number of free point defects which are generated in one collision cascade. It is supposed also, that the mean concentration of surviving freely migrating defects in solution, C_j, is determined by the following equations of balance:

$$\begin{aligned} K_i - D_i C_i k_i^2 &= 0, \\ K_v - D_v C_v k_v^2 &= 0. \end{aligned} \tag{5}$$

D_j is the diffusion coefficient for defects of the kind j with the concentration C_j. This approximation means that the subsystem of freely migrating point defects (the rapid subsystem) is in a quasi-steady state at time scales of structural transformations [7]. We consider below the clustering kinetics of copper atoms as such a transformation. So time dependencies of point defects sinks may be ignored and k_j^2 may be estimated as constant values.

For consequent consideration of processes in structural evolution of model binary alloys Fe–x at.%Cu it is necessary to take into account miscellaneous capabilities for spatial migration of components. We describe diffusion processes in the alloy following the approach [8]. Let us enter such characteristics of diffusion process by vacancy and interstitial mechanisms, which are independent of point defect concentrations, namely the partial diffusion coefficients $d_{Fe,v}$, $d_{Cu,v}$ and $d_{Fe,i}$, $d_{Cu,i}$. Then the diffusion coefficients for the components of the solid solution may be expressed via these terms [8].

The equations of balance presented above do not contain the term corresponding to recombination of vacancies and interstitials. Such approximation may be justified for atomic cascade-producing irradiation [7]: concentrations of freely migrating point defects, which had avoided intracascade processes of recombination and clustering, are noticeably below those calculated according to the NRT standard model [9].

The diffusion coefficient in the space of sizes is defined by the contribution of stochastic fluctuations, which are associated with migrations of atoms, to the nucleation of copper clusters. At the analysis of copper clustering kinetics in model alloys FeCu, the corresponding term takes the form:

$$\begin{aligned} D^{s}(g) &= \frac{3 g^{1/3} D_{Cu} C}{2 r_0^2} \\ &\cong \frac{3 g^{1/3} C K}{2 r_0^2} \left[\frac{(1-\varepsilon_v)}{k_v^2} \frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i^2} \frac{d_{Cu,i}}{d_{Fe,i}} \right]. \end{aligned} \tag{6}$$

We denote $C \equiv C_{Cu}$ and take into account that $C \ll 1$, and accept the following notations:

ε_v, ε_i are the vacancy and interstitial clustering fractions in the cascade volume.
$K_j \equiv (1-\varepsilon_j)K$, K is the effective generation rate of freely migrating point defects.
$K < K_0$, K_0 is the calculated generation rate (NRT standard).
$k_j^2 = Z_j k_d^2 + k_s^2$, k_d^2 is the dislocation sink strength.
k_s^2 corresponds to other possible sinks.
Z_j are the bias factors.
r_0 is determined as $r_0 = \sqrt[3]{\frac{3\Omega}{4\pi}}$.

The diffusion coefficient in the size space of copper clusters, which describes nucleation of clusters as a result of redistribution of impurity atoms by cascade fluctuations, can be written as

$$\begin{aligned} D^{c}(g) &\cong \frac{3 g^{2/3} N_d}{4 r_0} (k_v d_{Cu,v} C_v + k_i d_{Cu,i} C_i) \\ &= \frac{3 g^{2/3} N_d K}{4 r_0} \left[\frac{(1-\varepsilon_v)}{k_v} \frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i} \frac{d_{Cu,i}}{d_{Fe,i}} \right]. \end{aligned} \tag{7}$$

The hydrodynamic velocity in the size space is given by the known expression [10,11]:

$$\begin{aligned} V(g,t) &= \frac{3 D_{Cu}}{a^2} g^{1/3} [C - C_e(g)] \\ &\approx \frac{3 D_{Cu}}{a^2} g^{1/3} C_s \alpha \left(\frac{1}{g_c^{1/3}(t)} - \frac{1}{g^{1/3}} \right). \end{aligned} \tag{8}$$

Here $C_e(g) = C_s \exp\left(\frac{\alpha}{g^{1/3}}\right)$ is the concentration of monomers near the cluster of size g.

We guess above, that irradiation by fast neutrons creates embryos of copper clusters in the cascade volumes. To take into account this circumstance, the source of embryos generated in collision cascades is entered into Eq. (2): the value $Kq(g,t)\Delta V\Delta t/\Omega$ is equal numerically to a quantity of embryos of clusters with g copper atoms, created by collision cascade in a volume ΔV at a time Δt. According to this definition, the quantity

$$\int_{g_{\min}}^{G_m} gq(g,t)\mathrm{d}g \equiv \varepsilon(C), \tag{9}$$

where $g_{\min}$ is the least number of atoms in an embryo and G_m is the maximum number of atoms in a primary cluster, is equal to a mean fraction of number of copper atoms in embryos relatively to one displacement.

Thus, the generation rate of embryos, K_{cl}, for irradiation with a generation rate of defects K, can be presented as

$$K\varepsilon(C) \equiv K_{cl}. \tag{10}$$

Let us use the following parameters: V_{casc} is the mean volume of cascade event; then $K\Omega/V_{casc}$ is the average rate of cascades generation; let m be an average number of embryos of copper clusters in calculation per one cascade; then $mK\Omega/V_{casc}$ is the average rate of embryos generation for copper clusters; if C is the atomic concentration of copper in the solution, CV_{casc}/Ω is the number of copper atoms in a cascade volume; let us designate as η *a* fraction of a total number of copper atoms in the cascade volume, which have formed embryos with an average size g_0 during a relaxation of a cascade. Then

$$m = \frac{\eta C V_{casc}}{g_0 \Omega}. \tag{11}$$

Here the parameters m and η are some functions of the concentration of copper atoms in the solution. Consequently, one may write that the rate of embryo generation is

$$K_{cl}(t) = \left(\eta\frac{C(t)}{g_0}\right)K = \left(\frac{m(C)\Omega}{V_{casc}}\right)K. \tag{12}$$

Let us take into account, that the value

$$\int_{g_{\min}}^{G_m} f(g,t)\mathrm{d}g = N(t) \tag{13}$$

is the atomic concentration of clusters. We take the norm of the distribution function in a form that accounts for the boundary condition of embryos generation under cascade-producing irradiation. As it follows from the presented above equation, such relation must take place:

$$\lim_{t\to 0+}\frac{\mathrm{d}N(t)}{\mathrm{d}t} = \lim_{t\to 0+} K\int_{g_{\min}}^{G_m} q(g,t)\mathrm{d}g. \tag{14}$$

Let us suppose that the embryos of the mean size g_0 will be created in a cascade of atomic collisions. The rate of embryos generation may be written as

$$Kq_0(g,t) = \frac{K_{cl}(t)}{g_0}\delta(g-g_0). \tag{15}$$

Then the boundary condition on rate of clusters generation becomes

$$\lim_{t\to 0}\frac{\mathrm{d}N(t)}{\mathrm{d}t} = \frac{\eta C(t=0)K}{g_0^2}. \tag{16}$$

Here $C(t=0)$ is the initial concentration of copper atoms. Let us enter the dimensionless time

$$\tau \equiv \frac{K_{cl}}{\lambda g_0}t, \tag{17}$$

where

$$\lambda \equiv \frac{4K_{cl}r_0}{3KN_d g_0}\left[\frac{(1-\varepsilon_v)}{k_v}\frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i}\frac{d_{Cu,i}}{d_{Fe,i}}\right]^{-1}, \tag{18}$$

and the dimensionless flux i in the space of sizes as

$$i \equiv I\cdot\frac{4}{3}\cdot\frac{r_0}{KN_d}\cdot\left[\frac{(1-\varepsilon_v)}{k_v}\frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i}\frac{d_{Cu,i}}{d_{Fe,i}}\right]^{-1}. \tag{19}$$

Let us suppose further for estimates, that $k_v \approx k_i \approx k_0$. We designate also

$$\mu \equiv \frac{4D_{Cu}C_s\alpha}{r_0KN_d}\left[\frac{(1-\varepsilon_v)}{k_v}\frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i}\frac{d_{Cu,i}}{d_{Fe,i}}\right]^{-1} \cong \frac{4C_s\alpha}{(k_0r_0)N_d}. \tag{20}$$

Accordingly, the kinetic equation becomes

$$\frac{\partial f(g,\tau)}{\partial\tau} = -\frac{\partial}{\partial g}\left\{\mu g^{1/3}\left(\frac{1}{g_c^{1/3}} - \frac{1}{g^{1/3}}\right)f(g,\tau) - \frac{\partial}{\partial g}[g^{2/3}f(g,\tau)]\right\} \equiv -\frac{\partial}{\partial g}i. \tag{21}$$

This equation should be solved in view of fulfillment of an equation of balance for the number of copper atoms in solution and clusters:

$$C(0) = C(t) + \int_{g_0}^{\infty} f(g,t) g \, \mathrm{d}g \equiv C(t) + N(t)\bar{g}(t). \quad (22)$$

Here $\bar{g}$ is the mean size of copper clusters.

We shall follow the approach of the paper [12] to a solution of the kinetic equation in the space of cluster sizes.

Static solution, $f_0(g)$, corresponding to the zero value of the flux in the space of sizes, $i = 0$, can be given as

$$f_0(g) = \frac{A}{g^{2/3}} \exp\left\{\frac{3}{2}\mu\left(\frac{g^{2/3}}{g_c^{1/3}} - 2g^{1/3}\right)\right\}, \quad (23)$$

A is a constant of integrating.

By consideration of evolution in the ensemble of clusters it is natural to assume, that the distribution function responds to the locally equilibrium solution, restricted by position of the distribution frontier at a considered instant. The formal locally equilibrium distribution function $f_i(g)$, for a pseudo-steady flux i in the space of sizes, can be given as

$$f_i(g) = \frac{\mathrm{i}}{g^{2/3}} \exp\left\{\frac{3}{2}\mu\left(\frac{g^{2/3}}{g_c^{1/3}} - 2g^{1/3}\right)\right\} \times \int_g^{\infty} \exp\left\{-\frac{3}{2}\mu\left(\frac{x^{2/3}}{g_c^{1/3}} - 2x^{1/3}\right)\right\} \mathrm{d}x. \quad (24)$$

The estimate of parameters demonstrates, that under conditions, representing practical concern, $\lambda \ll \mu \ll 1$. With allowance for it, we make out the approximated solution:

$$f_i(g) = \frac{\mathrm{i}}{g^{2/3}} \cdot \begin{cases} \left(\frac{5}{2} g_{\mathrm{eff}} - g\right), & g \leqslant g_{\mathrm{eff}} \equiv g_c^{1/2}\left(\frac{2}{3\mu}\right)^{3/2}, \\ \frac{3}{2} g_{\mathrm{eff}}^{2/3} g^{1/3}, & g \geqslant g_{\mathrm{eff}} \gg g_0. \end{cases} \quad (25)$$

We search a non-steady distribution of clusters as it follows:

$$f(g,\tau) = f_i(g)\Psi(g,\tau), \quad (26)$$

where the function $\Psi(g,\tau)$, according to its sense, describes motion of a distribution frontier in the space of sizes. Large enough clusters introduce the main contribution to the process of evolution in the ensemble of clusters; it is possible to write a following approximate equation for the function $\Psi(g,\tau)$:

$$\frac{\partial \Psi(g,\tau)}{\partial \tau} + \left[\frac{4g^{2/3}}{5g_{\mathrm{eff}} - 2g} - \frac{2g^{1/3}}{3g_{\mathrm{eff}}^{2/3}}\right] \cdot \frac{\partial \Psi(g,\tau)}{\partial g} = 0, \quad g < g_{\mathrm{eff}},$$
$$\frac{\partial \Psi(g,\tau)}{\partial \tau} + \frac{2g^{1/3}}{3g_{\mathrm{eff}}^{2/3}} \cdot \frac{\partial \Psi(g,\tau)}{\partial g} = 0, \quad g > g_{\mathrm{eff}}. \quad (27)$$

The corresponding solution may be written as

$$\Psi(g,\tau) \cong \Theta(G(\tau) - g) = \Theta(\tau - T(g)), \quad \Theta(x) = \begin{cases} 1, & x \geqslant 0; \\ 0, & x < 0. \end{cases} \quad (28)$$

Thus, at an instant moment τ, the equilibrium distribution is established locally for the left-side positions below the distribution frontier $G(\tau)$. The point set $(g_0, G(\tau))$ is filled, the point set $(G(\tau), \infty)$ is empty.

We find the rate-fixing constant i from the boundary condition:

$$\left.\frac{\mathrm{d}N}{\mathrm{d}t}\right|_{t=0} = \lim_{t\to 0} \int_{g_0}^{\infty} \frac{\partial f(g,t)}{\partial t} \mathrm{d}g \cong f_i(g_0) \left.\frac{\mathrm{d}G(t)}{\mathrm{d}t}\right|_{t=0}. \quad (29)$$

The substitution of the solution suggested above gives the following value:

$$i = \frac{1}{2}\lambda. \quad (30)$$

The function $G(\tau)$ looks like

$$G(\tau) = \begin{cases} \left(g_0^{1/3} + g_{\mathrm{eff}}^{1/3}\frac{\tau}{\tau_{\mathrm{eff}}}\right)^3, & \tau \leqslant \tau_{\mathrm{eff}}, \\ g_{\mathrm{eff}}\left(\frac{5\tau}{3\tau_{\mathrm{eff}}} - \frac{2}{3}\right)^{3/2}, & \tau \geqslant \tau_{\mathrm{eff}}, \end{cases} \quad \tau_{\mathrm{eff}} \equiv \frac{15}{4} g_{\mathrm{eff}}^{4/3}. \quad (31)$$

The time dependence of concentration for copper clusters looks like

$$N(t) = \begin{cases} N_{\mathrm{eff}}\left(\frac{t}{t_{\mathrm{eff}}}\right) = \frac{K_{\mathrm{cl}} t}{g_0}, & t \leqslant t_{\mathrm{eff}} \equiv \frac{15 g_{\mathrm{eff}}^{4/3}}{4}\frac{\lambda g_0}{K_{\mathrm{cl}}}, \\ \frac{1}{2} N_{\mathrm{eff}}\left(1 + \frac{t}{t_{\mathrm{eff}}}\right), & t \geqslant t_{\mathrm{eff}}, \end{cases} \quad N_{\mathrm{eff}} \equiv \lambda \frac{15}{4} g_{\mathrm{eff}}^{4/3}. \quad (32)$$

It may be useful to point out that, according to the presented model, a measurement of concentration for copper clusters at times, which are not superior the effective time, allows to estimate the generation rate of embryos in cascades.

In the explicit form

$$t_{\text{eff}} \cong \frac{5}{36} g_c^{2/3} \frac{N_d (k_0 r_0)^3}{K (C_s \alpha)^2 \left[(1-\varepsilon_v) \frac{d_{\text{Cu},v}}{d_{\text{Fe},v}} + (1-\varepsilon_i) \frac{d_{\text{Cu},i}}{d_{\text{Fe},i}} \right]}. \tag{33}$$

The mean number of copper atoms in clusters is described by the expression:

$$\bar{g}(t) = \left(\frac{g_{\text{eff}}}{2}\right) \cdot \begin{cases} \frac{1}{2}\left(\frac{t}{t_{\text{eff}}}\right)^3, & t \leqslant t_{\text{eff}}, \\ \left[\frac{13}{25} + \frac{12}{25}\left(\frac{5t}{3t_{\text{eff}}} - \frac{2}{3}\right)^{5/2}\right] \Big/ \left(1 + \frac{t}{t_{\text{eff}}}\right), & t \geqslant t_{\text{eff}}. \end{cases} \tag{34}$$

The consideration conducted above assumes fulfillment of a condition

$$\gamma \equiv \frac{D^c}{D^s} \cong \frac{g_0^{1/3} N_d k_0 r_0}{2C} \gg 1. \tag{35}$$

Selected values of parameters are listed in Table 1.

It may be seen that this condition is valid for real cascade-irradiation conditions. In the consideration presented above the most indefinite parameter is the quantity m that determines the amount of copper embryos in the cascade volume. In the following section some reasonable estimates are given.

3. Discussion

Results of calculations within the model developed above, for copper contents in experiments with different steels [13,2,14,15], are presented in Figs. 1–3. The corresponding data sets are given in the legends to Figs. 1 and 2. First, the curve for copper concentration in the solution was fitted to the last available experimental point. The basic parameter that plays a role of a fitting value is the sink strength k_0^2 that is not cited in the data [13,2,14,15]. The curves are very sensitive to k_0^2. The curve for the number density of clusters was simultaneously varied by value of the parameter m

Table 1
Material parameters used in calculations

Parameter	Value	Units
Partial diffusion coefficient of copper atoms via vacancies, $d_{\text{Cu},v}$	$0.5 \times 10^{-5} \exp(-0.61\ \text{eV}/kT)$[a]	m^2/s
Partial diffusion coefficient of copper atoms via interstitials, $d_{\text{Cu},i}$	Neglected for a diluted alloy of Cu in Fe[b]	
Partial diffusion coefficient of iron atoms via vacancies, $d_{\text{Fe},v}$	$10^{-6} \exp(-0.68\ \text{eV}/kT)$[c]	m^2/s
Partial diffusion coefficient of iron atoms via interstitials, $d_{\text{Fe},i}$	$10^{-5} \exp(-0.30\ \text{eV}/kT)$[d]	m^2/s
Binding energy, $Q_{\text{Cu–Cu}}$	3.43 [e]	eV/atom
Binding energy, $Q_{\text{Fe–Fe}}$	4.28[e]	eV/atom
Binding energy, $Q_{\text{Cu–Fe}}$	3.83	eV/atom
Surface tension energy, σ	0.3[e]	J/m^2
Binding energy of two copper atoms, $E_{2\text{Cu}}$[b]	0.129[e]	eV
Atomic volume, Ω	10.00	$10^{-30}\ m^3$
Intracascade interstitial clustering fraction, ε_i	0.4 [f]	
Intracascade vacancy clustering fraction, ε_v	0.3[f]	
Minimum size of copper cluster, g_0	2	
Average number of point defects per cascade, N_d	45[f]	
Volume of the cascade molten zone, V_{casc}	$10\,000\Omega$	m^3
Irradiation temperature, T	563	K
Equilibrium copper concentration, C_s	0.00026 [g]	
Defect production rate, K_0	10^{-9}, 1.5×10^{-10}[h]	NRT dpa/s
Effective defect production rate, K	$0.2K_0$	dpa/s

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[c] R.A. Johnson, Phys. Rev. 134 (1964) A1329–A1336.
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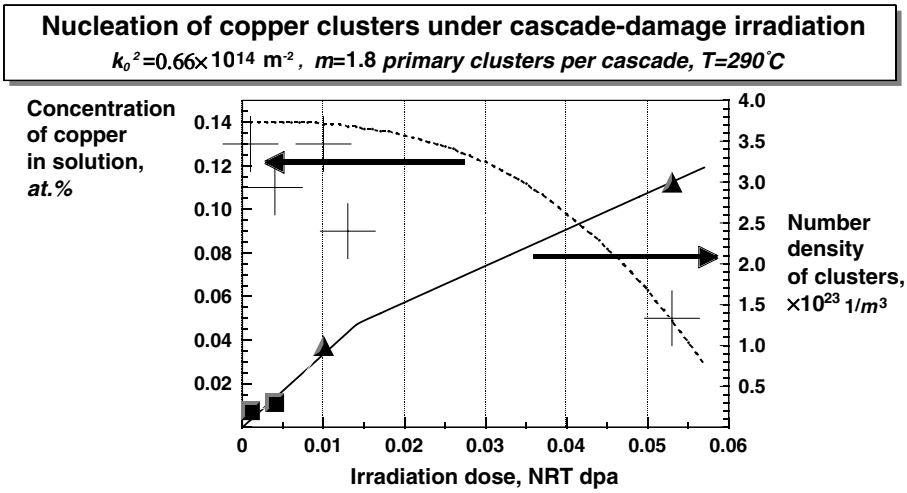
[g] See Appendix A. This value is close to the data of Jackson et al. (see discussion in Ref. [3]).
[h] For Fe–0.14 at.%Cu and Fe–0.08 at.%Cu alloys correspondingly (see the text).



Steel	Fluence (n/m^2)	Matrix Cu, at.%	Data marker	Density, 10^{23} 1/m^3	Data marker
KRB-A	8.4×10^{21}	0.13	+	0.2	■
KRB-A	2.7×10^{22}	0.11±0.01	+	0.3	■
WELD	6.6×10^{22}	0.13±0.04	+	1.0	▲
KRB-A	8.5×10^{22}	0.09±0.01	+	-	
WELD	3.5×10^{23}	0.05±0.01	+	3.0	▲

Fig. 1. Estimates for experimental data at initial copper content 0.14 at.%. References are given in the text.

to approach the experimental meaning at the same dose. This value of m gives an estimate for the average number of embryos of copper clusters in a cascade volume.

Experimental points in Figs are given by translation of fast neutron dose data to NRT dpa with relation 10^{25} n/m$^2 \cong 1.5$ dpa [3,16]. The resulting values for the sink strength that give the last experimental point for $C(t)$ at the dose of 0.053 dpa for $C_0 = 0.14$ at.% and the dose of 0.18 dpa for $C_0 = 0.08$ at.%, as well as the corresponding values of m are shown in the legends.

The experimental data are better defined for the higher value of copper, i.e. $C_0 = 0.14$ at.%. For $C_0 = 0.08$ at.%, errors in actual values of concentration at measured doses are larger. No error limits were cited for the measured cluster density values. With such uncertainties, the agreement between calculated results within the proposed model and the experimental data points look quite reasonable and outlines the crucial role of cluster embryos formation in cascade relaxation volume and their subsequent growth by copper atoms migration mechanisms via surviving point defects.[1]

[1] The important role of freely migrating defects in copper clustering measured by electrical resistivity during electron and ion irradiations in FeCu alloys was outlined in the paper [4].

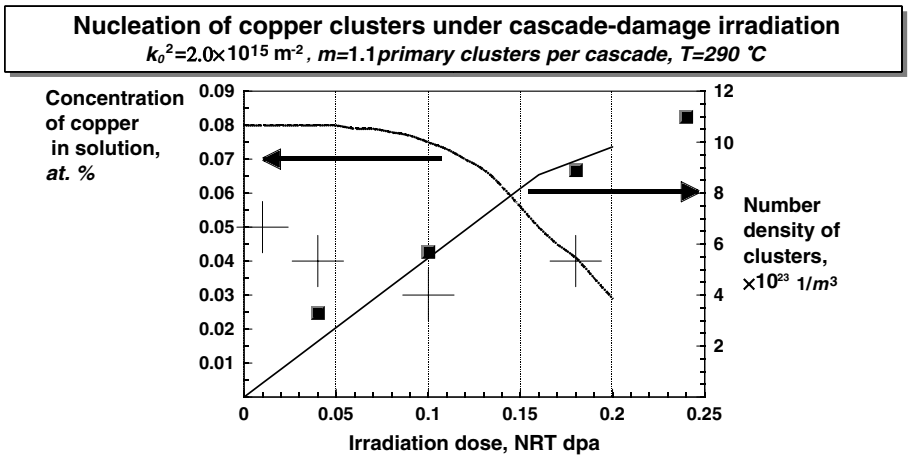
For less pronounced cascades, as may be seen according to the results presented above, the process of copper clustering develops weaker. Finally, for irradiation by electrons or slow neutrons one has $N_d \cong 1$, and the inequality (35) may be no longer valid for an initial copper content above the solubility limit.

The kinetics of copper clustering under irradiation by electrons have quite different quasi-thermodynamic nature from those under aging conditions [17] (see also the experimental data [3]).

The approach given above does not consider the processes of asymptotic evolution of distribution function of clusters. Further coarsening of overcritical clusters in expenses of subcritical ones [18,19] is beyond the present consideration.

4. Conclusions

(1) The quasi-homogeneous decay of supersaturated solid solution of copper in FeCu alloys initiated by collision cascades is considered. The condition corresponds to a situation of irradiation by fast neutrons or heavy ions. On the basis of the model calculations, the temporary time-scale, the dose dependencies for number density and average dimensions of copper clusters as functions of irradiation



Steel	Fluence (n/m^2)	Matrix Cu, at.%	Data marker	Density, 10^{23} 1/m^3	Data marker
CHOOZ	4.7×10^{22}	0.05±0.01	+	-	
CHOOZ	2.5×10^{23}	0.04±0.01	+	3.3	■
CHOOZ	6.6×10^{23}	0.03±0.04	+	5.7	■
CHOOZ	1.2×10^{24}	0.04±0.01	+	8.9	■
CHOOZ	1.6×10^{24}	-		11	■

Fig. 2. Estimates for experimental data at initial copper content 0.08 at.%. References are given in the text.

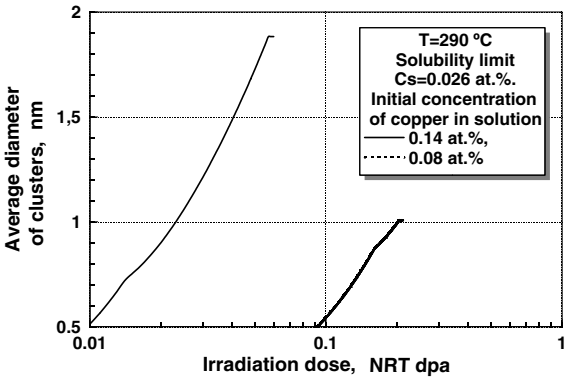


Fig. 3. Estimates for the average diameter dose dependency for cited experimental data.

conditions and cascade characteristics are defined. The considered structural transformations precede the stage of coarsening kinetics for copper clusters.

(2) The numerical estimates of these data were compared with experimental results for the process at the RPVS at operating temperature of 290 °C. The indicated theoretical outcomes agree with available experimental data and confirm the point of view that at temperatures of pressure vessel exploitation the process of copper cluster formation has the irradiation-stimulated nature with the crucial role of collision cascades in nucleation of clusters.

(3) Under cascade-damage irradiation the time dependence of concentration for copper clusters has the quasi-linear dependence (as given by Eq. (32)) with the kink point N_{eff} that is determined by characteristics of the kinetics in cascade volumes. The quasi-linear trend of cluster concentration with irradiation dose agrees with experimental observations.

(4) The time-dependence of average dimensions of copper clusters given by Eq. (34), as it is predicted by the considered model, is more complicated and may vary from about t^3 to $\sim t^{3/2}$ if the initial supersaturation is large enough.

(5) The model approach presented above is not completely self-consistent because the number of copper embryos per cascade, m, is treated as a free parameter. From general point of view, the homogeneous nucleation kinetics may be applied as a qualitative rather than quantitative consideration of the complicated processes. Results of MD modeling of the cascade events in FeCu alloys do not yet show noticeable copper clustering [20,21]. However, there are some additional physical considerations [22,23] that demonstrate some possibility for copper atoms redistribution in α-Fe.

It was shown in Ref. [22] that copper atoms may migrate towards the center of the thermal spike.

Such redistribution displays itself during the cascade relaxation. The process takes place as a result of temporal difference in the actual supersaturations of copper atoms in the locally overheated cascade volume and the ambient space. The corresponding investigation, which combines both approaches, is not yet finished.

In Ref. [23] the vacancy–Cu clusters in α-Fe were studied. The MD and MC calculations demonstrate that the clusters may consist of a central vacancy cluster decorated, or coated by Cu atoms. The formation energy of such combined clusters is a function of the number of vacancies and Cu atoms.

These examples show that the problem of cluster nucleation remains to be the key issue for modeling of the clustering kinetics. A number of intrinsic parameters, which are describing details of interactions for species involved in the transformations, should be well defined.

Appendix A

Before formation of a solid solution the thermodynamic potential (free energy) of the system of n copper atoms and $(N-n)$ atoms of iron takes the form [24,25]:

$$\Phi_0 = (N-n)\mu_0 + n\mu_0'. \tag{A.1}$$

Here μ_0 is the chemical potential for atoms of iron and μ_0' is the chemical potential of copper atoms before formation of a solution. In a diluted solid solution the thermodynamic potential may be written as

$$\Phi_1 = N\{(1-C)\mu_0 + C\psi_1 + kTC[\ln C - 1]\} \tag{A.2}$$

and, correspondingly,

$$\mu_1 = \psi_1 - \mu_0 + kT\ln C. \tag{A.3}$$

Here C is the atomic concentration of n copper atoms in the matrix, containing N atomic sites, k is the Boltzmann constant, T is the absolute temperature, ψ_1 is an energy change caused by inserting of one copper atom into the lattice. In the thermodynamic equilibrium the solid solution is saturated. The corresponding condition, at a given temperature and a pressure, takes the form:

$$\left(\frac{\partial\Phi_0}{\partial n}\right)_{p,T} = \left(\frac{\partial\Phi_1}{\partial n}\right)_{p,T}, \tag{A.4}$$

the consequence of which means that

$$\mu_0' = \psi_1 + kT\ln C_s. \tag{A.5}$$

The last expression is the definition of solubility [26], i.e. of the saturation concentration C_s for copper atoms in the solid solution at a given temperature. With this notation expression for Φ_1 may be rewritten as

$$\Phi_1 = \Phi_0 + NCkT\left(\ln\frac{C}{C_s} - 1\right). \tag{A.6}$$

The chemical potential of copper atoms in the solution takes the form:

$$\mu_1 = \mu_0' + kT\ln\frac{C}{C_s} \tag{A.7}$$

Let us suppose below that the secondary phase consists of spherical copper clusters. The latter may grow due to absorption of migrating surplus copper atoms.

The final phase consists of N_g spherical clusters that include g copper atoms up to a maximum size G. The change of thermodynamic potential of the secondary phase takes the form [25]:

$$\Phi_2 = \Phi_1' + \sum_{g=2}^{G}\left[\psi_2 g + 3\frac{\sigma\Omega}{a}g^{2/3}\right]N_g, \tag{A.8}$$

where Φ_1' is the thermodynamic potential with concentration

$$C' = \frac{n'}{N} = C - \frac{\sum_{g=2}^{G} gN_g}{N}. \tag{A.9}$$

Here σ is the Fe–Cu interface energy in the lattice of α-Fe, Ω is the atomic volume, $\Omega = a^3/2 \equiv 4\pi r_0^3/3$, a is the lattice constant, ψ_2 is the energy per atom in the secondary phase.

Finally, the critical size of copper clusters takes the following form:

$$g_c^{1/3}(t) = \frac{\alpha}{\ln\frac{C(t)}{C_s}}, \quad \alpha \equiv \frac{2\sigma\Omega}{kTa}. \tag{A.10}$$

According to the definition of solubility, Eq. (A.5), and assuming that energies per copper atom are, correspondingly, $\psi_1 = Q_{\mathrm{CuFe}}$ and $\mu_0' = Q_{\mathrm{CuCu}}$, the following expression takes place:

$$C_s = \exp\left(-\frac{Q_{\mathrm{CuFe}} - Q_{\mathrm{CuCu}}}{kT}\right). \tag{A.11}$$

Values of binding (cohesive) energies per atom of copper or iron in their bcc lattices Q_{CuCu} and Q_{FeFe} are presented in [5]. The value Q_{CuFe} may be estimated as being equal to $(Q_{\mathrm{CuCu}}\cdot Q_{\mathrm{FeFe}})^{1/2}$. Such estimate agrees well with a general conclusion, which corresponds to the necessary condition of

clustering for substitute atoms in a binary system, namely, with the inequality: $2Q_{CuFe} < Q_{CuCu} + Q_{FeFe}$ [19,27].

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