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On possible mechanism of copper precipitate clustering in model *Fe*Cu alloys under cascade-damage irradiation

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Abstract

We consider below kinetics of copper precipitate clustering in model *Fe*Cu 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 centres 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.

1. Introduction

The structural compositions of reactor pressure vessel steels (RPVS) are complicated and contain different elements. The development 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 after irradiation at 260°C to dose 16×10^{19} n/cm^2. According to results of these studies, under neutron irradiation there are friable "clouds" containing atoms of Si, Ni, Mn, and Cu in the material. 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 enlarging. 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 to doses 6.6×10^{22} and 3.47×10^{23} n/m^2 steel with high amount of copper (0.24%) [2]. In the steel with low concentration of copper (0.02%) irradiated to dose 1.5×10^{23} n/cm^2 only clusters of phosphorus atoms were observed. The average composition of copper clusters and the level of enrichment by separate 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 have crucial role in the precipitate cluster formation in a number of RPVS with high enough copper content. Consequently, experiments with model *Fe*Cu 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].

Here, in Section 2 we give a description of structural changes in *Fe*Cu alloys under neutron irradiation producing collision cascades [5]. In Section 3 we discuss the results and give a comparison with experimental data. Section 4 includes concluding remarks.

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

As it was outlined in [6], well-formed copper-rich precipitates are the dominant clusters in steels containing more than about 0.1% Cu according to numerous experimental measurements analyzed in that paper. Therefore, the *Fe*Cu 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: 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, σ is the *Fe*Cu interface energy, Ω is the atomic volume, $\Omega=a^3/2$, a is the lattice constant. The critical size of copper clusters is determined by the actual supersaturation and takes the following form:

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

Here k is the Boltzmann constant, T is the absolute temperature, $C(t)=N_{Cu}/N$ 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 homogeneous nucleation theory. The corresponding equation for a distribution function of clusters in their size space [7], $f(g,t)$, takes the form [5]:

$$\frac{\partial f(g,t)}{\partial t}=\frac{K_{cl}(t)}{g_0}\delta(g-g_0)- -\frac{\partial}{\partial g}\left[V(g,t)-\frac{\partial}{\partial g}D(g,t)\right]f(g,t). \qquad (2)$$

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 [8,5]

$$D(g,t) = D^s + D^c, \qquad (3)$$

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. K_{cl} is the generation rate of embryos [5] of size g_0.

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 [9], namely, the following partial diffusion coefficients $d_{Fe,v}$, $d_{Cu,v}$ and $d_{Fe,i}$, $d_{Cu,}$ are introduced.

The hydrodynamic velocity in the size space is given by the known expression [10, 11, 5].

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 equation (2) [5].

Let us enter the dimensionless time

$$\tau \equiv \frac{K_{cl}}{\lambda g_0} t, \qquad (4)$$

where

$$\lambda \equiv \frac{4K_{cl}r_0}{3KN_d g_0} \times \times \left[\frac{(1-\varepsilon_v)}{k_v} \frac{d_{Cu,v}}{d_{Fe,v}} + \frac{(1-\varepsilon_i)}{k_i} \frac{d_{Cu,i}}{d_{Fe,i}} \right]^{-1} \qquad (5)$$

The following notations are introduced here: for point defects of a kind j ($j = v,i$) k_j^2 is the full strength of sinks; K is the effective rate of generation of freely migrating point defects; ε_v, ε_i are the vacancy and interstitial clustering fractions in the cascade volume; r_0 is determined as $r_0 = \sqrt[3]{\frac{3\Omega}{4\pi}}$; N_d is the average number of free point defects which are generated in one collision cascade. Let us suppose further for estimates, that $k_v \approx k_i \approx k_0$;

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

$$C(0) = C(t) + \\ + \int_{g_0}^{\infty} f(g,t) g dg \equiv C(t) + N(t)\bar{g}(t). \qquad (6)$$

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

At the solution of a kinetic equation, we use physical submissions about a motion of the frontier of a new phase in the space of cluster sizes during the decay of initial supersaturation [12].

The time dependence of concentration for copper clusters looks like:

$$N(t) = \begin{cases} N_{eff}\left(\frac{t}{t_{eff}}\right) = \frac{K_{cl} t}{g_0}, \\ \quad t \le t_{eff} \equiv \frac{15 g_{eff}^{4/3}}{4} \lambda g_0; \\ \\ \quad \frac{1}{2} N_{eff}\left(1 + \frac{t}{t_{eff}}\right), \qquad t \ge t_{eff}. \end{cases}$$

$$N_{eff} \equiv \lambda \frac{15}{4} g_{eff}^{4/3} K_{cl}. \qquad (7)$$

Here $g_{eff} \equiv g_c^{1/2}\left(\frac{2}{3\mu}\right)^{3/2}$, $\mu \equiv \frac{4 C_s \alpha}{(k_0 r_0) N_d}$.

Notice that $K_{cl}(t) = \left(\frac{m(C)\Omega}{V_{casc}}\right) K$, m is an average number of embryos of copper clusters in calculation per one cascade, V_{casc} is the mean volume of cascade event

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

$$t_{eff} \cong \frac{5}{36} g_c^{2/3} \times \\ \times \frac{N_d (k_0 r_0)^3}{K (C_s \alpha)^2 \left[(1-\varepsilon_v) \frac{d_{Cu,v}}{d_{Fe,v}} + (1-\varepsilon_i) \frac{d_{Cu,i}}{d_{Fe,i}} \right]}. \qquad (8)$$

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

$$\bar{g}(t) = \left(\frac{g_{eff}}{2}\right) \cdot \begin{cases} \frac{1}{2}\left(\frac{t}{t_{eff}}\right)^3, \quad t \le t_{eff}; \\ \\ \frac{\left[\frac{13}{25} + \frac{12}{25}\left(\frac{5t}{3t_{eff}} - \frac{2}{3}\right)^{5/2}\right]}{\left(1 + \frac{t}{t_{eff}}\right)}, \\ t \ge t_{eff}. \end{cases} \qquad (9)$$

The conducted above consideration guesses fulfillment of a condition

$$\gamma \equiv \frac{D^c}{D^s} \cong \frac{g_0^{1/3} N_d k_0 r_0}{2C} >> 1. \qquad (10)$$

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

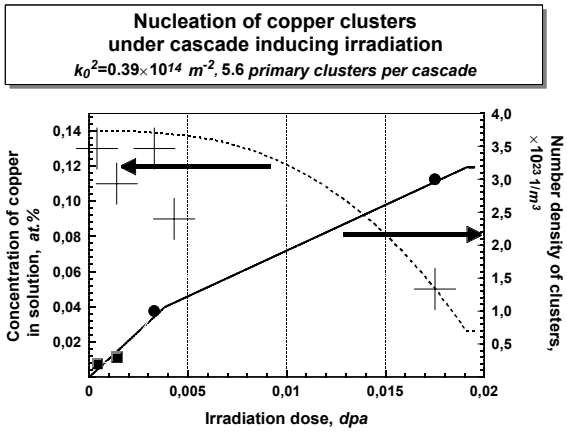

Fig. 1. Estimates for given below experimental data with approximation 1 dpa=2×10^{25} n/m^2

3. Discussion of results

Results of calculations within the developed above model, for copper contents in experiments with different steels [13,14], are presented in Fig 1. 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 [13,14]. The curves are very sensitive to k_0^2. Experimental points in Figs are given by translation of neutron dose data to NRT *dpa* with relation 1 *dpa* ≅ 2×10^{25} *n/m*^{2}. The resulting values for the sink strength that give the last experimental point for $C(t)$ at the dose 0.0175 *dpa* for C_0=0.14 *at.%* are shown in the legend. The parameter *m* at some value, given in Fig 1, then supplies with the proper experimental meaning of the number density at this point.

Steel	**Fluence** (n/m^2)	**Matrix Cu**, at.%	**Density**, 10^{23} 1/m^3
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
WELD	3.5×10^{23}	0.05±0.01	3.0

Material parameters are listed in [5] from data of [15,16,17,6,18]

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 of calculated within the proposed model results and the experimental data points looks as 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.

For less pronounced cascades, as may be seen according to the presented above results of analytical consideration, the process of copper clustering develops weaker. Finally, for irradiation by electrons or slow neutrons one has $N_d \cong 1$, and the inequality (10) may be no valid for an initial copper content above the solubility limit. As a result, that follows also from the experimental data [3], the kinetics of copper clustering under irradiation by electrons or aging conditions have quite different the quasi-thermodynamic nature.

The given above approach does not consider the processes of asymptotic evolution of distribution function of clusters. The further coarsening of over-critical clusters in expenses of subcritical ones [19,20] is beyond the present consideration.

4. Conclusions

- The initiated by collision cascades quasi-homogeneous decay of supersaturated solid solution of copper in alloys on the basis of α-Fe is considered, that corresponds to a situation of irradiation by fast neutrons or heavy ions. On the basis of the carried out model calculations, the temporary time-scale, the dose dependencies for number density and average dimensions of copper clusters as functions of irradiation conditions and cascade characteristics are defined.

- The numerical estimates of these data were compared with experimental results for the process at the RPVS operating temperature 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 clusters formation has the irradiation-stimulated nature with the crucial role of collision cascades in nucleation of clusters.

The presented above model approach is not completely self-consistent because the number of copper embryos per cascade, m, is treated as a free parameter. Moreover, the homogeneous nucleation kinetics may be applied as a qualitative rather then quantitative consideration of the complicated processes. Results of MD modeling of the cascade events in *Fe*Cu alloys do not yet show noticeable copper clustering [21,18]. However, there are some additional physical considerations [22] that demonstrate some possibility for copper atoms redistribution, towards the center of

the thermal spike, following the cascade relaxation as a result of temporal difference in the actual supersaturations of copper atoms *in* and *out* the cascade volume. The corresponding investigation demands some material parameters on thermodiffusion that are not yet well defined.

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