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Letter to the Editors

On the validity of the cluster model to describe the evolution of Cu precipitates in Fe–Cu alloys

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Abstract

Recently M.H. Mathon et al. [J. Nucl. Mater. 245 (1997) 224] applied the so called 'cluster model' for the description of Cu precipitates evolution in Fe–Cu model alloys both during aging and irradiation. It was concluded that the model does not work in both cases. The main purpose of this letter is to show that the model can be successfully applied for the case of aging and to discuss the reasons why the cluster evolution is different in the case of irradiation. © 2000 Elsevier Science B.V. All rights reserved.

It is well known that the formation of copper precipitates plays an important role in embrittlement of pressure vessel steels. This is the reason why several theoretical models have been applied to describe the evolution of Cu precipitates in Fe–Cu alloys both during aging and under irradiation. In a recent paper Mathon et al. [1] applied the so-called 'cluster dynamics type model' which is based on less restrictive hypothesis than the earlier models [2,3]. Nevertheless, a common feature of all these models is that none of them is able to reproduce the current coarsening rate, which remains too low to have the possibility to fit both the nucleation-growth and coarsening regimes with the same parameters. Moreover, in papers [1,3] the respective models were applied with the same parameters to describe the evolution of two different kinds of precipitates, namely the ones obtained under irradiation and the ones obtained during aging. The main purpose of this letter is to prove the validity of the cluster model for aging and to discuss the reasons why different sets of parameters and additional mechanisms for atomic transport have to be considered in the case of irradiation. Finally, an explanation is given as to why the calculations failed in the attempts made in [1,3].

The cluster model was introduced by Golubov et al. [4] for the description of the Cu precipitates evolution. The same model has been used in [1] since Eq. (8) in [1] is just the combination of Eqs. (1) and (2) in [4]. The model treats the evolution of Cu precipitates in terms of homogeneous nucleation and Ostwald ripening mechanism. The most important input for the model is the binding energy of Cu atoms with the precipitates, which is a function of the precipitate size. It follows that if the chemical composition of Cu precipitates created under irradiation is different from that created during aging [5,6], then the binding energy should be different in these two cases. It is worth emphasizing that the cluster model as formulated in [4] can well describe aging (where only the vacancy mechanism operates) as long as the correct binding energy function is used. In the irradiation case, in addition to the correct binding energy function, the atomic transport via irradiation-induced interstitials needs to be considered.

Let us first consider the evolution of Cu precipitates during aging. As shown in [4], the binding energy function has to be a much more complex function than that given by the capillary model used in [1,3]. The main reason for this is the fact that the crystal lattice of copper precipitates changes from bcc at small sizes to fcc

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at large ones. The binding energy function proposed in [4] was fitted to reproduce the evolution of the size distribution function found experimentally by Buswell et al. [7] in a Fe–1.1 at.% Cu alloy aged at 550°C. It is important to note that these data were obtained using two different techniques, namely, transmision electron microscopy (TEM) and small angle neutron scattering (SANS). The size distribution function thus obtained has two peaks, showing coexistence of bcc and fcc precipitates for the aging time used [4]. Later on, the binding energy function of this type [8] (see Fig. 1) was then used to calculate the evolution of Cu clusters in the following alloys: (a) Fe–0.70 at.% Cu aged at 500°C; (b) Fe–0.85 at.% Cu aged at temperatures in the range from 420°C to 660°C. The diffusion coefficient for Cu atoms used was $D_{\mathrm{Cu}} = 7.08 \times 10^{-4} \exp(-2.53\ \mathrm{eV}/k_{\mathrm{B}}T)\ \mathrm{m}^2/\mathrm{s}$, where the pre-exponential factor and activation energy are described in [8,9]. The results calculated were compared with the experimental data obtained in [5,10]. It was found [8] that in both cases the calculated results are in a quantitative agreement with the experiment. Nevertheless, this model could not reproduce the experimental results reported in [1,3]. Like in the calculations produced in [1,3] the rate of coarsening was found to be much lower than that observed experimentally. This lack of agreement led Mathon et al. [1] to question the validity of the cluster model [4]. However, as described above, the model is able to describe the experimental data obtained in [5,7,10]. This raises the question as to why the experimental data given in [1,3] cannot be explained in terms of the cluster model? In order to answer this question, the treatment reported in [1] is re-analysed.

Contrary to the results presented in [7], experimental data in [1,3] were obtained using only SANS. The data were analyzed with the assumption that the size distribution function of precipitates is described by a gaussian-like function. This approximation is consistent with the capillary model for the binding energy used in the calculations in [1,3]. It is obvious that if the real form of the size distribution function is not gaussian-like, then the treatment of the SANS data cannot give the correct result. The experimental results reported in [7] show that the size distribution function of Cu precipitates is more complex, i.e. has two peaks. The result of our calculations using the cluster model for the alloy described in [1,3] also yielded size distributions with one and two peaks (see Fig. 2). These size distributions are similar to those found in [7]: in both the cases it has one peak at small aging times and two peaks at large ones. For comparison, two gaussian functions corresponding to the aging times 142 and 312 h given in [1] are also plotted in Fig. 2 (dotted lines).

The remarkable difference in the shape of the size distribution function provides the key for understanding the discrepancy between experimental data and the results of our calculations. It was found that there is agreement in the results related to aging times where the calculated function has one peak and remarkable disagreement when the calculated function has two peaks. This suggests that the treatment of SANS data would be closer to the calculated results if they would be analyzed

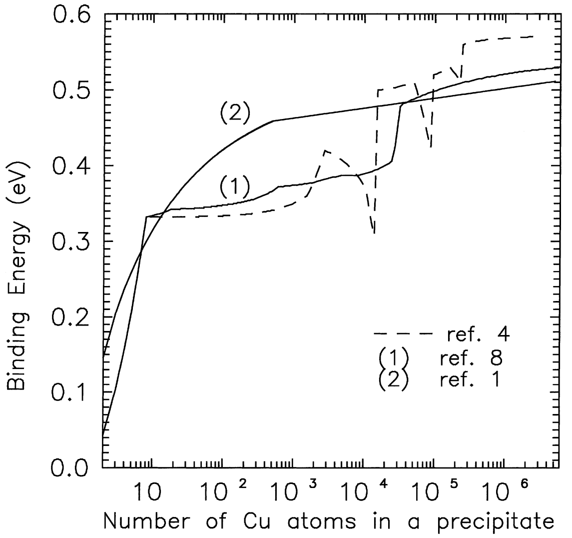

Fig. 1. Binding energy of a copper precipitate in the Fe–Cu alloy as a function of the number of Cu atoms in the cluster. The broken line and curve (1) refer to the calculations made in [4,8], respectively. Curve (2) refers to a capillary approach used in [1] for 500°C and $\Omega/k = 9020$.

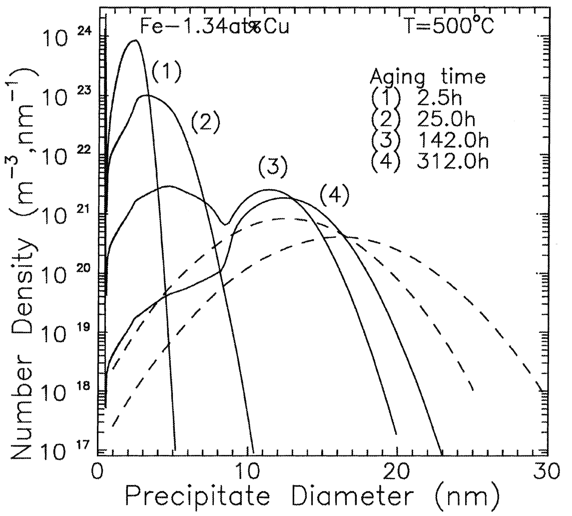

Fig. 2. Size distribution functions of Cu precipitates at different aging times calculated with the cluster model [8]. The dotted lines correspond to the gaussian functions at 142 and 312 h used for the treatment of SANS data in [1].

using a double size distribution function as illustrated by [7]. It could be that even in these experiments [1,3] there exists such an overlapping double size distribution but not resolved clearly by the SANS technique in [1,3]. Note that this could be checked by using the set of functions presented in Fig. 2 in the treatment of the SANS data. Complementary experiments for the alloys used in [1,3] using TEM may help to solve this problem.

The modelling of Cu cluster evolution under irradiation is a more complex problem. The main reason is that the chemical composition of the precipitates produced under irradiation is different from that of the precipitates produced during aging. The experimental evidence is presented in paper [6] where the chemical composition of clusters was investigated by atom probe analysis showing that the concentration of Cu atoms in the cluster can decrease up to 60% and 20% under electron and neutron irradiation, respectively. The measurement of the volume fraction of precipitates was consistent with these observations [6]. Our treatment of these experiments [11] with $D_{\mathrm{Cu}}^{\mathrm{irr}} = D_{\mathrm{Cu}}(C_{\mathrm{v}}^{\mathrm{irr}}/C_{\mathrm{v}}^{\mathrm{eq}})$, where $C_{\mathrm{v}}^{\mathrm{irr}}, C_{\mathrm{v}}^{\mathrm{eq}}$ are vacancy concentrations under irradiation and thermal equilibrium, respectively, resulted in a binding energy smaller than the one obtained under aging conditions [9] showing a lower stability of Cu precipitates. Such a decrease of binding energy can be related to lower Cu content in the precipitates formed under irradiation.

The reason for the change in chemical composition of Cu precipitates under irradiation is not yet understood. However, the fact that less stable precipitates could form means that their evolution is controlled by specific kinetic processes. We attribute this to the generation of highly mobile self-interstitial atoms (SIA) and SIA clusters and their interaction with Cu precipitates. Actually the existence of interstitial defects is the main distinguishing feature of the irradiation conditions. Due to the so-called size effect we should expect that, in the Fe–Cu system, Cu atoms diffuse mainly via vacancy mechanism whereas diffusion of interstitials is associated mainly with Fe atoms. It was shown in [12] that there is a positive binding energy between interstitials and Cu precipitates. Therefore, the attraction of interstitials by Cu precipitates can be a possible mechanism for the decrease in Cu content. In the framework of this mechanism the difference between Cu precipitates formed under electron and neutron irradiation [1,5,6] could be understood. It is well established that under cascade damage conditions (neutron irradiation) atomic transport occurs not only via three-dimensional diffusion of point defects (like under electron irradiation), but via one-dimensional diffusion of interstitial clusters as well (see Production Bias Model [13]). Thus, the difference in transport mechanisms of Fe atoms could be responsible for the difference in precipitation kinetics in Fe–Cu alloys. Other specific processes taking place under cascade damage conditions, e.g. direct dissolution of precipitates by cascades, can also be responsible for this difference.

Nevertheless, the above discussed features of evolution of Cu clusters under irradiation do not mean that the cluster model cannot be used. Indeed, an important feature of the model, namely the homogeneous nucleation of precipitates, is even more applicable for the case of irradiation since the usual irradiation temperatures are essentially lower than the aging ones. However, it is obvious that a correct description of the evolution of Cu clusters under irradiation can be achieved only by incorporating additional mechanisms into the cluster model, i.e. via generalisation of the main master equation describing cluster evolution. This means a normal outgrowth of the cluster model; this work is in progress.

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