Cu Precipitation Dynamics in Fe-Cu Alloy

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Abstract

The precipitation of copper during aging at 600°C in high-purity Fe-Cu alloy was examined by means of transmission electron microscopy. Nano-scale copper-rich clusters with B2-like structure were observed during either solution treatment or aging, which should play important role on precipitation strengthening. In addition, the precipitation process has been analyzed in terms of the evolution of microstructure by Monte Carlo method. An description of the coherent precipitation of copper in iron, based on vacancy diffusion mechanism, thermally activated jump frequencies and cohesive energy was discussed to deal with simultaneous precipitation of metastable and stable phases of Cu-containing steel during aging, which gives an estimation of the precipitation dynamics, as well as the evolution of Cu precipitates in a wide range of temperature.

1. Introduction

Many metallic alloys for structural applications gain their mechanical properties through the small scale precipitation of second phase [1]. Dispersion of second-phase particles within the matrix is very effective for strengthening structural materials because the moving dislocation is pinned by the particles. This is known as the dispersion strengthening or the precipitation strengthening.

Fe–Cu alloys are well known as the steels which exhibit precipitation strengthening through precipitation of fine Cu particles within the ferrite matrix. Copper precipitations are a major contribution to the hardness increase, and many investigations in Fe-Cu alloys and steels have been carried out under various conditions [2, 3].

It is believed that the structure sequence during the aging precipitation should be BCC, 9R and ε-Cu [4]. Precipitations morphologies, sizes, structure and distributions in steel are dominant factors. Therefore, it is very necessary to obtain their size and distribution rules for improve the property of Cu-containing steels.

In order to describe the precipitation process of Fe-Cu alloy, much effort has been devoted to model the precipitation kinetics and the relationship between the precipitate microstructure and the material mechanical properties. Numerical methods based on statistical physics (Monte Carlo) has been bring forward by T.A. Abinandanan, et al [5], which have been successfully used in the description of simple systems. These methods need a space-time description of precipitation and precise knowledge of interaction potentials between the different atomic species. Moreover, they are restricted to the first stages of precipitation since the phase transformation of hardening precipitates from a supersaturated solid solution is often complex.

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It has been revealed that in thermally-aged Fe–Cu alloys and some commercial ferrite steels the copper precipitates experience the stages of nucleation, growth and coarsening.

The formation of Cu clusters, growth and coarsening of the coherent BCC Cu phase in Fe during aging course have been studied in our pervious work [6, 7], which indicated that there were lots of Cu clusters in exist in solid solution, and subsequent phase transformation course involves a sequence of metastable phases, which compensate a higher Gibbs energy by coherent or semi-coherent interfaces with the ferrite matrix.

A important feature of the process is that with increasing aging time the Cu-rich precipitates nucleate and grow from supersaturated solid solution to Cu clusters and are coherent with the ferrite matrix, which have B2-like structure character, and after reach a critical size they lose full coherency, transforming to 9R and 3R transition phase in turn, finally to the fcc \( \varepsilon \)-copper in Fe-Cu alloys.

To give a detailed description of precipitation course, not only on the structure, amount of the Cu particles but also their sizes, morphologies and distributions, the mechanism of their nucleation and growth is important. For this purpose, precipitation model based on the classical nucleation, growth theories and a combination of transmission electron microscopy (TEM) will be adapted in this work.

Existing models of the Cu precipitation assume nucleation of precipitates and migration of Cu atoms via a vacancy mechanism. The observations of the binding energy are consistent with loss of the coherency of the bcc Cu precipitates during their growth [8,9]. Results of this approach are applied to the Fe-Cu system presenting two stages of precipitation (metastable and stable phase).

2. Cu precipitates during thermal ageing

High purity Fe-1.18%Cu alloy was prepared by vacuum melting. The steel was forged and rolled, then treated for solution at 850°C for 2hours to reach a fully solid dissolved state and quenched into salt water. An aging treatment was conducted in a salt-bath furnace for a time range of 10s to 10^4s followed by air-cooling. The microstructure observation was carried out by using a TEM of JEOL JEM-2010 operated at 200KV.

Strength values are taken as an average of three measurements on each sample. Fig.1 shows changes in strength of the specimens during the aging at 600°C as a function of aging time. Typical age strengthening and over-aging softening behavior are observed in all specimens. These behaviors are closely related to the Cu precipitation and growth.

![Fig.1 Changes in strength of Fe-1.18 %Cu alloy during aging at 600°C](image)

The copper solubility in bcc \( \alpha \)-Fe is low, varying from -0.4at% at 823K to a maximum of 1.8at% at 1123K [10]. At lower temperatures, copper is practically insoluble in iron. It is known that Cu precipitates as bcc clusters which are coherent with the Ferrite matrix in the early stages of aging. Beyond a precipitate size of 4.5nm, 9R structure has been directly observed in High Resolution
Transmission Electron Microscopy by Othens et al; later undergo a second transition to a 3R structure, in the over-aging stages, coherency at the interface between the Cu particle and the matrix is almost lost [4], thus, precipitation strengthening in over-aged Cu-bearing steels is influenced only by $\lambda$ and $\theta_c$[11]. Our previous work [6, 7] indicates nano-scale meta stable precipitations with B2-like structure play important role on the property of structural steel, instead of $\varepsilon$-Cu equilibrium phase. In a conclusion, Cu precipitation is highly a rather complicated course.

Precipitate for larger sizes could be obtained from the TEM micrographs. The exact form of the distribution, however, cannot be obtained since the part of the distribution for small size is not available. The strengthening mechanism of Cu precipitates is proved to be dependent on their size and distance. The size of precipitates could quantitatively measure by several TEM micrographs.

Fig.2 shows TEM microstructure, as well as the diffraction pattern and index of the Cu clusters of the Fe-Cu alloy in solid solution. Cu particles are finely dispersed in the ferrite matrix and the average size of Cu ordering domain is about 20nm. Some super lattice faint diffraction spots were observed regularly around center incidence spots in Figure2 (b), which indicates the appearance of (001) $\alpha$ and (002) $\alpha$ planes diffraction spots, that should highly likely result from the segregation of Cu atoms nearby the (001)$\alpha$ plane. Similar to the research by Osamura et al [12], the observation reveals that, the particles should also have the BCC structure with higher copper content.

Fig.2 Transmission electron micrograph (a) and (b) electron diffraction index in Fe-1.18%Cu alloy, aged at 600$^\circ$C for 100S

Fig.3 Transmission electron micrograph (a) and (b) electron diffraction index in Fe-1.18%Cu alloy, aged at 600$^\circ$C for 1000S
Fig.3 shows TEM observations and diffraction pattern of the Cu precipitation at aged hardness peak. As shown in Figure 3(a), the particle size is roughly 15nm and the interval of precipitates seems to smaller than that in Fig.2. Energy spectrum analysis shows that the Cu copper content in Cu precipitates is much higher than the matrix, which indicates that the particle belongs to high copper phase. The analysis of the diffraction pattern obtained from the matrix and the particles demonstrate a (110)* reciprocal plane, some faint spots can also be observed regularly besides that of matrix, the previous work [6, 7, 13] indicated the little spots come from nano-scale meta met stable precipitations phase with B2-like structure.

Compare to the diffraction pattern of solution state and aging hardness peak, the diffraction spot become more evident and in focus in Fig.3 (b). The differences lead to an assumption that the Cu atoms move several atom space and reach the exact (001) position by way of thermally activated jump with increasing aging time, that make the ordering array of Cu atoms on the (001) crystal plane greater in number, consequently, the diffraction spots become more clearly. The aging hardness curve change can be perfectly explained under this assumption, too. Furthermore, diffraction spot distributing regularly when electron beams indent from [110], direction, that also indicate the Cu atoms segregate on some crystal planes, but the physics nature of these spots need a in-depth study.

3. Precipitation dynamic analysis
The aim of the precipitates and dynamic study was to investigate the precipitation kinetics in the Fe-Cu alloy, namely: provides interesting information on precipitate microstructure evolution and growth mechanisms which are useful for experimental data analysis [14].

We assumed that Copper atoms diffuse homogeneously via the vacancy mechanism, i.e. an initially distribution of Copper atoms in solid solution within the ferrite matrix is homogeneous. Copper atoms nucleate and grow from supersaturated solid solution to bcc with increasing aging time, then to B2-like structure Cu clusters, and after reach a critical size ,transforming to 9R and 3R transition phase in turn, finally to the fcc ε-copper in Fe-Cu alloys. The binding energy of a copper atom with precipitate varies with the size of the precipitate during the process. Give an example, when the precipitates start to lose coherency at the precipitate size corresponding to the body center cubic to 9R transformation, the binding energy should have a step increase [15], while the binding energy of bigger precipitates with the bcc structure and coherent with the iron matrix, should depend more weakly on the precipitate size.

Atomistic computer simulations of the formation of precipitates can contribute to a deeper understanding of the mechanical behaviors of Cu-containing alloyed steels. A model is presented which is able to simulate the diffusion of atoms by vacancy jumps [16], which performed a series of Monte Carlo simulations, with a unique atomic copper concentration and with a constant vacancy concentration.

The kinetics in a Fe-Cu alloy was described on a rigid bcc lattice, by the following model [17]: Firstly, diffusion proceeds via vacancy jumps towards nearest neighbor atoms; secondly, the vacancy jump is a thermally activated process and its frequency $\Gamma_N$ is given by:

$$\Gamma_{Fe,V} = v_{Fe} \exp\left(-\frac{\Delta E_{Fe,V}}{kT}\right)$$

$$\Gamma_{Cu,V} = v_{Cu} \exp\left(-\frac{\Delta E_{Cu,V}}{kT}\right)$$

Here the $v$ represents attempt frequencies independent of the atom configuration, and the activation energy $\Delta E$ is the energy increase on moving an atom, nearest-neighbor of the vacancy $V$, from its stable site to the saddle point position; the migration energy is estimated assuming that the cohesive energy of the alloy is a sum of pair interactions.
For the sake of simplicity, assume that an Cu atom in saddle point position contributes $E_{Cu}$ to the energy of the system, the energy is

$$E = N_{FeFe} \varepsilon_{FeFe} + N_{CuCu} \varepsilon_{CuCu} + N_{FeCu} \varepsilon_{FeCu} + N_{FeV} \varepsilon_{FeV} + N_{CuV} \varepsilon_{CuV}$$

where $N$ are the number of nearest-neighbor atoms pairs, moreover, interaction energies between vacancies and atoms ($\varepsilon_{FeV}$ and $\varepsilon_{CuV}$) have been introduced.

The above kinetic model can be handled by direct Monte Carlo simulations, which is appropriate to our case, where fluctuations play a major role. We consider a rigid body center cubic lattice with $N = 2 \times L^3$ lattice sites, periodic boundary conditions and $L$ is 64. The lattice sites are occupied by $N_{Fe}$ iron atoms, $N_{Cu}$ copper atoms and $N_{V}$ vacancies, for the total number of lattice sites the following equation holds: $N = N_{Fe} + N_{Cu} + N_{V}$.

S. Schmauder and coworkers [18] considered a Monte Carlo method and a binary system with components A and B based on above description. In the model, the formation and growth of precipitates is simulated at a constant temperature of 600°C starting from a fully disordered initial configuration. At longer simulation times a significant decrease of the number of small precipitates and an increase of the averaged precipitate radius is found.

In order to simulate the system Fe-Cu, material data are required. The kinetic parameters were adjusted to diffusion data. A study is presented which demonstrates how the precipitates form and grow. The used base centered cubic lattice with periodic boundary conditions have a side length of $L=64$ lattice constants which means a side length of $64 \times 0.287 = 18.4$ nm in Ferrite matrix. At the beginning, the Cu atoms are randomly distributed on the crystal lattice, and at the end of the simulation [18], spherical precipitates can be observed. The picture is in agreement with Pareige and Auger’s investigation [19], and more recently proved by our research during thermal ageing and TEM direct observations. Lots of Cu atom clusters with BCC structure keep coherency with the bcc supersaturated ferrite matrix, the effect come from the Cu clusters increases with the growth in size and increase in number with the aging time. Subsequently, Cu-rich B2-like Fe-Cu metastable phase precipitate at the aging hardness peak, and finally transform to fcc $\varepsilon$-Cu precipitates and lose coherency with the bcc matrix, when exceed a critical radius.

Fig.4 show a comparison of precipitate size evolution as predicted from the present model with the experimental data of our present research. The curve indicate the increase of the average precipitates radius during ageing at 600°C for 1-1000s. The precipitate sizes was obtained from theory simulation and actual annealing condition by measuring the dispersions size directly from the TEM image of Fe-1.18%Cu alloy, respectively.

As simulation times and sizes remain limited, it is of great interest to determine if a dynamical scaling behavior exists. Many experimental measurements, on various systems [20], support the fact that during phase separation processes the average domain size $R$ grows with time according to a power law $R(t) \sim t^\alpha$, where $\alpha$ is the growth exponent. The coarsening of widely spaced precipitates in the matrix occurs by the condensation of the smaller precipitates due to the growth of the larger ones, the rate of these two processes being limited by the rate at which diffusion from a precipitate to another one occurs.

The influence of the size distribution of ageing precipitation particles, and the blocking effect of the precipitates on dislocation slips in high purity Fe-Cu alloys were investigated in previous work [21]. It is found that the precipitation particles belong to a meta stable Cu-Fe phase containing certain iron instead of pure Copper, which leads to a high ductility combined with high yield strength. On the other hand, the precipitation particles containing higher iron will enhance the volume fraction of precipitates. The blocking effect on dislocation as well as the corresponding yield strength will be intensity with increasing copper content of the precipitation particles during ageing process.

As a result, the values of the parameters as a function of time show a good agreement on the experimental. In addition, most experimental values are greater than simulated ones. Taking this into account, we conclude that the model provides a reasonable fit to the experimental measurements of...
copper precipitation in Fe–Cu alloys and, therefore, appropriate validation of the model. The exact form of the distribution, however, cannot be obtained since the part of the distribution for too small size is not available, a detailed treatment with respect to particle radii and distance will be future work.

![Graph](image_url)

Fig.4 Experimental data from compared with calculated results for the size distribution function of copper precipitates, aged at 600°C

4. Conclusion
A Monte Carlo simulation technique was introduced to study TEM observation of copper precipitation base on diffusion phase transformations. As a result, the values of the precipitates size parameters as function of time show good agreement on the experimental, moreover, experimental values are little greater than that of simulated ones, which owing to the enhance of the volume fraction of Fe-Cu metastable containing higher iron.

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