Nucleation and growth of γ -Fe precipitate in Cu-2%Fe alloy aged under high magnetic field

Xiaowei Zuo¹, Lei Qu¹, Congcong Zhao¹, Bailing An¹, Engang Wang^{1*}, Rongmei Niu², Yan Xin², Jun Lu², Ke Han^{2*}

¹Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education),
Northeastern University, Shenyang 110819, Liaoning, China

²National High Magnetic Field Laboratory, Florida State University, Tallahassee
32310, FL, USA

Corresponding authors at: egwang@mail.neu.edu.cn (E. G. Wang), Tel. & Fax: +86 24
83681739; han@magnet.fsu.edu (K. Han), Tel.: +1 850 6446746, Fax: +1 850
6440867.

Abstract: Cu-2wt%Fe alloy, an inexpensive candidate for a high strength conductor, depends for its conductivity on the precipitation of Fe. We applied an external 12 T high magnetic field (HMF) during ageing treatment of this alloy in order to study the resulting γ -Fe precipitation on the electrical conductivity. When the alloy was aged at 450 °C for up to 16 hrs, coherent γ -Fe precipitates formed within the Cu matrix. Between the γ -Fe precipitates and the Cu matrix, the lattice misfit was $1.4\% \pm 0.7\%$ and the angle between closed packed planes was about 0.3° . These γ -Fe precipitates became semi-coherent with the surrounding Cu matrix in samples aged at 700 °C for over 0.5 h. HMF made insignificant contributions to both the morphology and the volume fraction of γ -Fe at 450 °C. At 700 °C, however, HMF promoted a transformation from coherent to semi-coherent γ -Fe precipitates. Applying HMF during ageing at 700 °C increased electrical conductivity. HMF had little influence on the nucleation of γ -Fe precipitation. We applied the Lifshitz-Slyozov-Wagner (LSW) formula to the coarsening data of the precipitates and determined that HMF increased the diffusion coefficient of Fe in Cu and promoted the growth of γ -Fe precipitation out of the Cu matrix.

Key words: Cu-Fe alloy; ageing; γ -Fe precipitation; high magnetic field; nucleation; coarsening

1. Introduction

Cu-Fe alloy has been studied extensively because it has a potential to be used in next-generation storage, contact bridging, magnet, vacuum device, and high-strength conductor [1]. Because the solidified microstructure in this alloy is coarser than that in high-strength conductors strengthened by component of low melting point and Fe has relatively large solubility in Cu [2], aging is required to promote refined Fe precipitates [3, 4]. Because uniformly distributed, nanoscale Fe precipitates can block movements of dislocations and strengthen Cu matrix [3, 4], the precipitation of Fe and the $\alpha \leftrightarrow \gamma$ martensitic phase transformation within Fe have been studied [4,5].

Calculated Cu-Fe phase diagram, as shown in Fig. 1, using the parameters provided by Ansara et al [6] shows that face-centered-cubic (fcc) γ -Fe phase is stable at temperatures between 912 °C and 1394 °C. When Cu content is high, γ -Fe becomes stable below 912 °C. The γ -Fe becomes more stable as Cu content becomes higher, so metastable γ -Fe can be found in Cu matrix. The lattice parameters of copper, metastable γ -Fe and α -Fe are 0.3607 nm, 0.3562 nm, and 0.2866 nm, respectively [7, 8]. From above parameters, the estimated lattice misfit between Cu matrix and γ -Fe is about 1.25%. This insignificant misfit between fcc γ -Fe and fcc Cu matrix causes γ -Fe to precipitate from the Cu matrix earlier than α -Fe [9]. Metastable spherical fcc γ -Fe precipitate particles are coherent with the Cu matrix and the coarsening kinetics of γ -Fe follows Lifshitz-Slyozov-Wagner (LSW) formula, which says that the average radius of γ -Fe precipitate increases with aging time t as $t^{1/3}$ [10, 11]. Ageing for long

times weakened coherent strains during the growth of particles [9] and the transition from coherency to semi-coherency during ageing affected the coarsening of γ -Fe precipitate [12]. Many researchers [9, 13] have reported that γ -Fe precipitation not only hardens the Cu matrix but also decreases its electrical resistivity. Therefore, it is an interesting topic to increase both the strength and the electrical conductivity of Cu-Fe alloy by controlling the precipitation behavior of γ -Fe.

Fig. 1. (a) Cu-Fe phase diagram in Fe-rich side showing the phase transformation temperatures of Fe, and (b) Cu-Fe phase diagram in Cu-rich side showing the solubility of Fe in Cu between 300 °C and 750 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

External high magnetic field (HMF) is one of the thermodynamic parameters affecting the temperature at which precipitation occurs [14]. Magnetic energy is capable of changing Gibbs free energy of a given system because of the difference in magnetization energy between parent and product [15]. Therefore, HMF can be used to alter the microstructure in various materials, including steels (where the major

phases are either α - or γ -Fe, both can be found in Cu-Fe alloys) [16-19], by influencing phase equilibrium [20], phase transformation [21-23], solid solubility [24], diffusion [25], and precipitation behaviors [26, 27]. In particular, HMF has been found to influence precipitation and particle growth behaviors in Cu-based alloy [24, 28]. The effect of HMF on nucleation and growth in solid-state phase transformation, however, is subject to some debates. For example, Zhang et al [29] held that HMF had little effect on nucleation of precipitation because of an insignificant contribution of magnetization energy by HMF compared to the driving force for nucleation. Other researchers [27, 30-32], however, stated that HMF reduced the nucleation barrier and increased the nucleation rate according to the classical nucleation theory. HMF was also reported to change the growth behavior of phases in solid transformation [27, 29, 30]. Onodera et al [31] thought that HMF changed the growth of FeSiB amorphous alloy. Jia et al [33], however, stated that HMF suppressed the crystallization of Fe_{23}B_6 -type phase from the amorphous matrix, instead of the growth of the amorphous matrix.

The present work was undertaken to study the effect of HMF on the precipitation behavior of γ -Fe in Cu-Fe alloy with a special emphasis on the nucleation and growth of γ -Fe, as well as the electrical conductivity of resulting Cu-Fe alloy.

2. Material and Methods

Cu-2wt%Fe alloy was prepared in a vacuum induction furnace, homogenized at 900 °C for 48 hrs and then solution treated at 960 °C for 24 hrs. The sample sectioned

from the alloy was isothermally aged for 0.5 h -16 hrs at 450 °C and 700 °C under Ar atmosphere. The heat-treatment furnace was installed in a 12-Tesla (T) superconducting high magnet. A static HMF was switched on and off during ageing of the alloy. Foils sectioned from the Cu-2wt%Fe aged sample were jet polished in a solution of 20% nitric acid in water and were examined in a JEOL-2011 Transmission Electron Microscope (TEM) operated at 200 kV. Because most of our TEM foils were with similar thickness, the area fraction taken from TEM images was measured to qualitatively estimate the volume fraction of the precipitates. The electrical resistivity was measured at room temperature by standard four-probe method.

3. Results

3.1 Morphology of γ -Fe

Ageing at 450 °C causes Fe particles to precipitate from Cu-2%Fe alloy whether or not 12 T HMF is applied (Fig. 2). The selected-area electron diffraction pattern (SAED) (Fig. 2 a) and its locally enlarged SAED (Fig. 2 b) show that the precipitates are γ -Fe. The measured lattice misfit is about $1.4\% \pm 0.7\%$. Fe precipitate and Cu matrix have cube-on-cube orientation relationship, but the measured angle between close-packed planes of $(111)_{\text{Cu}}$ and $(111)_{\gamma\text{-Fe}}$ is about 0.3° . Consequently, $(600)_{\text{Cu}}$ and $(422)_{\text{Cu}}$ are not parallel to $(600)_{\gamma\text{-Fe}}$ and $(422)_{\gamma\text{-Fe}}$, as shown in Fig 2a

Fig.2 TEM morphologies and SAED of Cu-2%Fe alloy aged at 450 °C under zero and 12 T external magnetic field (direction is indicated by arrow in the figure): (a) the corresponding SAED from sample aged for 16 hrs under 0 T; (angles between $(600)_{\text{Cu}}$ and $(600)_{\gamma\text{-Fe}}$, and $(422)_{\text{Cu}}$ and $(422)_{\gamma\text{-Fe}}$, are indicated by arrows.) (b) enlarged local SAED from image (a) showing doorbell shaped diffraction spots from $(006)_{\text{Cu}}$ and $(006)_{\gamma\text{-Fe}}$. Bright-field TEM micrographs showing morphology of $\gamma\text{-Fe}$ precipitations in Cu-2%Fe alloy aged at 450 °C under 0 T for (c) 2 hrs, (e) 4 hrs, (g) 16 hrs, and under 12 T for (d) 2 hrs, (f) 4 hrs, and (h) 16 hrs. In TEM images, the light contrast is from the Cu matrix and the dark contrasts are the strain field from $\gamma\text{-Fe}$ precipitates.

Because the misfit between γ -Fe and Cu matrix is barely larger than 1%, and Cu and γ -Fe has the same crystallographic structure, γ -Fe particle precipitates out of the matrix earlier than α -Fe. This result is consistent with previous literature [5,11].

Plastic deformation is needed for the $\gamma \rightarrow \alpha$ phase transformation to occur. In our work, no plastic deformation was imposed. Consequently, Fe precipitates were γ -Fe. At 450 °C, extremely small sized γ -Fe precipitates were coherent with the Cu matrix, which is consistent with previous reports [10,11]. Increase in ageing time (Figs. 2 c, e&g) caused no change in the size and shape of γ -Fe precipitates. The application of HMF applied during the ageing treatment at 450 °C (Figs. 2 d, f&h) had no detectable effect on the size, shape or volume fraction of γ -Fe precipitates.

At 700 °C for 0.5 h (Figs.3 a&b), γ -Fe precipitates were still coherent with the Cu matrix, but the size was larger than at 450 °C (Fig. 2). With increasing ageing time (Fig. 3c), precipitates gradually became larger, and lattice misfit dislocations aggregated along Cu/Fe interfaces. Coherency between Cu and γ -Fe gradually diminished, and semi-coherent precipitates began to appear. As ageing time increased further, more and more precipitates became semi-coherent with the Cu matrix (Figs. 3 d, e&f). By comparison with samples aged without HMF (Figs.3 a, c&e), those aged with HMF at 700 °C (Figs. 3 b, d&f) showed increases in both volume fraction and size of γ -Fe precipitates, indicating that HMF promotes semi-coherent precipitation (Cf. Fig. 3d and Fig. 3e). Our results indicate that HMF accelerates the transition from coherency to semi-coherency of γ -Fe precipitates, beyond the point that can be

achieved using high aging temperature alone. Both the volume fraction and the size of γ -Fe might be increased in the presence of HMF during high temperature ageing of Cu-2%Fe alloy.

Fig. 3 Bright field TEM micrographs showing morphology of Fe precipitations in Cu-2%Fe alloy aged at 700 °C under 0 T for (a) 0.5 h, (c) 1 h, (e) 4 hrs, and under 12 T for (b) 0.5 h, (d) 1 h, (f) 4 hrs. Dislocation occurs around the γ -Fe precipitates.

3.2 Transition from coherency to semi-coherency in γ -Fe

The transition from coherency to semi-coherency in Cu-Fe alloy occurs when γ -Fe precipitates reach a critical diameter. In order to clarify the change brought about by HMF, we estimated an experimental value of this critical diameter using equation

(1) [9]

$$d_c = \frac{d_{\max}^{\text{Coherent}} + d_{\min}^{\text{Semi-coherent}}}{2} \quad (1)$$

where $d_{\max}^{\text{Coherent}}$ and $d_{\min}^{\text{Semi-coherent}}$ are the maximum diameter of coherent particles and the minimum diameter of semi-coherent ones, respectively. In order to arrive at the diameter of coherent γ -Fe precipitates, we analyzed TEM images of aged samples, taking a diagonal measurement of the light space shown between the two darker strain fields in each particle. In the case of semi-coherent precipitates, measurement was made somewhat more uncertain by the presence of dislocation lines near the particles. By tilting TEM foils, we dimmed these lines enough to allow direct measurement of particle size [9]. The critical diameters for coherent loss of γ -Fe under 0 T and 12 T were shown to be 45.7 nm and 46.9 nm, respectively (Table 1). T-test indicated that the difference of between these diameters was insignificant (at level 0.05). The similarity between these two numbers indicates that HMF did not measurably influence the critical diameter for transition from coherent to semi-coherency.

Table 1 Experimental diameter of coherent and semi-coherent γ -Fe precipitates

	$d_{\max}^{\text{Coherent}}/\text{nm}$	$d_{\min}^{\text{Semi-coherent}}/\text{nm}$	d_c/nm
0 T	37.5 ± 4.2	53.1 ± 5.7	45.7 ± 7.1
12 T	40.3 ± 4.7	54.6 ± 4.4	46.9 ± 6.5

3.3 Electrical conductivity

The electrical conductivity of aged Cu-2wt%Fe alloy increases with increasing ageing time, regardless of temperature (Fig. 4). At an ageing temperature of 450 °C, HMF makes no detectable contribution to electrical conductivity. At 700 °C, however,

electrical conductivity in samples subjected to 12-T HMF is higher than without HMF treatment, possibly because HMF reduces the supersaturated Fe dissolved in Cu matrix. The precipitation of alloying elements in Cu can reduce the impurity-scattering resistivity and increase the electrical conductivity [34-37]. Because a combination of high ageing temperature and HMF promotes γ -Fe precipitation, it decreases the concentration of the supersaturated Fe Cu matrix, thus increasing the electrical conductivity of the alloy.

Fig. 4 Electrical conductivity of Cu-2%Fe alloy aged at 450 °C and 700 °C under 0 T and 12 T HMF, where IACS=the International Annealed Copper Standard, and 100%IACS=1.7241 $\mu\Omega\cdot\text{cm}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Discussion

4.1 Effect of HMF on the transition from coherent to semi-coherent γ -Fe

The theoretical critical diameter relating to the transition from coherency to

semi-coherency within γ -Fe can be expressed by [9, 38]

$$d_c^{\text{Theo}} = \frac{2a_{\gamma\text{-Fe}}a_{\text{Cu}}}{a_{\text{Cu}} - a_{\gamma\text{-Fe}}} \quad (2)$$

where $a_{\gamma\text{-Fe}}$ and a_{Cu} are lattice parameters of γ -Fe (0.3562 nm [7]) and Cu (0.3607 nm [8]), respectively. This equation is based on two assumptions: 1) that dislocation nucleates at the interface, and 2) that dislocation results from purely geometrical considerations of lattice misfit between two phases. The d_c^{Theo} is estimated to be 57 nm. This value is significantly larger than the precipitate sizes measured in all the samples aged at 450 °C (Fig. 5). Therefore, no precipitate lost its coherency in these samples. d_c^{Theo} is also larger than d_c estimated from the precipitates in samples aged at 700 °C, indicating chemical misfit may also play a role for losing coherency of the precipitates.

Equation (2) can also be rearranged to:

$$d_c^{\text{Theo}} = \frac{2a_{\gamma\text{-Fe}}}{1 - a_{\gamma\text{-Fe}}/a_{\text{Cu}}} \quad (3)$$

Our measured $a_{\gamma\text{-Fe}}/a_{\text{Cu}}$ is 0.986 ± 0.007 . If we let $d_c^{\text{Theo}} = d_c$, $a_{\gamma\text{-Fe}}$ is estimated to be 0.31 nm, smaller than reported from the literature. This indicates that above two assumptions are not completely valid and other factors, such as chemical misfit, may also play a role in determination of the critical diameter. Even the assumptions are incomplete; we can qualitatively conclude that HMF is incapable of changing the critical diameter for the transition from coherency to semi-coherency within γ -Fe.

4.2 Effect of HMF on nucleation of γ -Fe

Generally, the paramagnetic Gibbs free energy change contributed by a magnetic

field is given as [32]

$$\Delta G_M^{Para} = -\frac{1}{2}\mu_0\chi H^2 \quad (4)$$

where μ_0 is the magnetic permeability of free space [$4\pi \times 10^{-7} \text{ N} \cdot \text{A}^{-2}$], H is magnetic field intensity [A m^{-1}], and χ is the magnetic susceptibility of γ -Fe, dependent on temperature [39], which can be calculated by Curie-Weiss law [32, 39]

$$\chi = \frac{7.31}{T+3370} \quad (5)$$

Classical nucleation theory [40] shows that the nucleation rate is formulated as

$$N = N_0 \exp\left(-\frac{\Delta G_m}{RT}\right) \exp\left(-\frac{16\pi\delta^3}{3RT\Delta G_V^2}\right) \quad (6)$$

where N_0 is a constant, ΔG_m is the activation energy [J m^{-3}], R is the gas constant [$\text{J mol}^{-1} \text{ K}^{-1}$], T is the temperature [K], δ is the interfacial energy, and ΔG_V is free energy per unit of volume [J m^{-3}], which is the driving force for precipitation (normally negative). Free energy can be expressed as [41]

$$\Delta G_V = \frac{RT(1-X_{\gamma\text{-Fe}})\ln\left(\frac{X_0}{X_{\gamma\text{-Fe}}}\right)}{V_{\gamma\text{-Fe}}} \quad (7)$$

where $V_{\gamma\text{-Fe}}$ is the molar volume of the Fe phase ($7.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$), $X_{\gamma\text{-Fe}}$ is coherent solubility of γ -Fe in the Cu phase (0.47% at 700 °C and 0.031% at 450 °C from our calculated phase diagram, as shown in Fig. 1b), and X_0 is the initial atomic fraction of Fe solute in Cu (2.27 at % or 2 wt%).

When a magnetic field is applied during the ageing of Cu-Fe alloy, the driving force for precipitation should be calculated as $(\Delta G_V + \Delta G_M^\gamma)$. According to Eqs. (4) and Eqs. (5), the ΔG_M^γ is about $-1.02 \times 10^5 \text{ J m}^{-3}$ and $-9.64 \times 10^4 \text{ J m}^{-3}$ for 450 °C and 700 °C, respectively. These values are consistent with the order of magnitude in

previous literature [42]. The values of ΔG_V , however, are about $1.79 \times 10^9 \text{ J m}^{-3}$ at 700°C and $3.63 \times 10^9 \text{ J m}^{-3}$ at 450°C . In other words, ΔG_M^γ is significantly smaller than ΔG_V and the contribution of HMF to the nucleation energy of γ -Fe is negligible, so we can conclude that HMF has little influence on the nucleation of paramagnetic γ -Fe precipitation. Many previous studies have indicated that applying a magnetic field during heat treatment increases the nucleation rate of ferromagnetic crystal because the contribution of HMF to the nucleation energy is significant in that case [30, 31, 43-45]. Other researchers [29, 46] reported, however, that applying a magnetic field during high-temperature tempering effectively prevented the lamellar growth of cementite, but showed insignificant influence on the nucleation sites of cementite. Takeda et al [28] stated that HMF had a primary influence on the precipitation growth kinetics of Cu-Co aged alloy, but not on precipitate nucleation or transformation. Because of the low magnetization energy of paramagnetic γ -Fe precipitates, our result is consistent with the experimental results from Zhang et al [29] and Takeda et al [28].

4.3 Effect of HMF on growth and coarsening of γ -Fe

The kinetics of particle coarsening is described by the Lifshitz-Slyozov-Wagner (LSW) formula [47-49]

$$r^3 - r_0^3 = Kt \quad (8)$$

where r is the average particle radius at time t , r_0 is the radius of γ -Fe precipitates at the beginning of coarsening and K is a variable given by

$$K = \frac{8D\delta C_e V_{\gamma\text{-Fe}}^2}{9RT} \quad (9)$$

where D is the diffusion coefficient of Fe in Cu matrix, δ is the interfacial energy between γ -Fe and Cu (0.3 J m^{-2} [47]), C_e is the equilibrium solubility of γ -Fe in Cu matrix (44 mol m^{-3} at 450°C , and 663 mol m^{-3} at 700°C converted from our calculated phase diagram, as shown in Fig. 1b), and $V_{\gamma\text{-Fe}}$ is the molar volume of the γ -Fe precipitate ($7.09 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ [50]).

The r_0 can be measured using images shown in Figs. 2&3. The measured r_0 at 450°C was $6.2 \pm 1.5 \text{ nm}$, the same for both samples aged with or without HMF (Figs. 2f and 2e). The measured radii (r_0) at 700°C differed only slightly between the two samples ($21.9 \pm 1.9 \text{ nm}$ and $21.6 \pm 2.2 \text{ nm}$, Fig. 3b and Fig. 3c). Thus, we concluded that HMF had no appreciable effect on the initial radius (r_0) of γ -Fe in any of the samples at either temperatures.

The curves of r^3 against t demonstrate that both the size and growth rate of γ -Fe precipitates aged at 450°C are smaller than at 700°C (Fig. 5). The difference between two temperatures is most likely attributable to a change in the diffusion rates of Fe ($4.08 \times 10^{-18} \text{ m}^2/\text{s}$ at 450°C compared to $3.69 \times 10^{-16} \text{ m}^2/\text{s}$ at 700°C based on exponential fitting [47]).

In Cu-2wt%Fe aged at 450°C , precipitate size and growth rate were too small to show any obvious difference between samples aged with and without HMF (Fig. 5 and Table 2). The two parameters indicated by K and D in the LSW equation, however, did show an increase of about 7%.

At 700 °C, γ -Fe precipitates were larger in samples aged under 12 T than those without HMF. Given that HMF has no influence on the nucleation of γ -Fe precipitation (section 4.2), the size difference must be attributable to the impact of HMF on growth rate described by K . The estimated values of K are 9% higher in samples aged at 12 T than those aged without HMF. The value for K is primarily dependent on both the equilibrium solubility of γ -Fe and the diffusion coefficient of Fe in Cu matrix. The equilibrium solubility of γ -Fe remains unchanged by HMF, so any change in the estimated K value must be due to diffusion coefficient. Aging under HMF increases the diffusion of Fe by 9%, thus stimulating the growth of Fe precipitation (see Table 2). We concluded that HMF raises the diffusion coefficient of Fe in Cu matrix for Cu-2wt%Fe alloy aged at 700 °C. Our conclusion is supported by similar results reported by Takeda et al [28] for Cu-Co alloy aged at 0.9 T magnetic field.

The accelerated growth rate of precipitates by an increased diffusion leads to coarsening, which in turn decreases the density of precipitates (Figs. 3e and 3d). The decrease of both the density and solubility of the γ -Fe precipitates by HMF increases the conductivity of Cu-2wt%Fe alloy.

Fig. 5 Coarsening plots of γ -Fe precipitates in Cu-2%Fe alloy aged at 450 °C and 700 °C under 0 T and 12 T, where r is the average particle radius at time t , and the slope is K in Equation (8). r^3 is roughly linear to the ageing time, t . The dashed line indicates d_c^{Theo} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2 Calculated K and diffusion coefficient D by Equation (9)

	0 T-450 °C	12 T-450 °C	0 T-700 °C	12 T-700 °C
K (nm ³ /s)	$(1.20 \pm 0.11) \times 10^{-3}$	$(1.28 \pm 0.12) \times 10^{-3}$	0.79 ± 0.02	0.86 ± 0.02
D (10^{-16} m ² /s)	$(1.22 \pm 0.30) \times 10^{-2}$	$(1.30 \pm 0.35) \times 10^{-2}$	7.19 ± 0.06	7.83 ± 0.06

5. Conclusions

1) Applying a HMF during ageing treatment of Cu-2%Fe alloy has much greater impact on the morphology and volume fraction of γ -Fe precipitates at 700 °C than at 450 °C has marginal effects. Thus, the application of a HMF during ageing at 700 °C increases both the volume fraction and the size of γ -Fe in Cu-2%Fe alloy, leading to a decrease in both the Fe dissolved in the Cu matrix and the density of γ -Fe within the

matrix, and consequently an increase in the electrical conductivity of the alloy.

2) Ageing at 450 °C, both with and without HMF, results in formation of coherent γ -Fe precipitates in the Cu matrix. The measured lattice misfit between Cu and Fe is about $1.4\% \pm 0.7\%$. Fe precipitates and Cu matrix have a cube-on-cube orientation relationship, but the angle between $(111)_{\text{Cu}}$ and $(111)_{\gamma\text{-Fe}}$ is about 0.3° . Ageing at 700 °C for over 0.5 h, on the other hand, results in semi-coherent precipitates, regardless of whether HMF is applied. Applying a HMF introduces no changes in the critical diameter for the transition from coherency to semi-coherency in γ -Fe.

3) Applying a HMF at 700 °C increases the diffusion coefficient of Fe in Cu matrix, but has no impact on either the nucleation or the initial radius of γ -Fe precipitates.

Acknowledgements

The authors would like to gratefully acknowledge the support of the National Natural Science Foundation of China (Nos. 51474066 and 51004038), the Research Fund for the Doctoral Program of Higher Education (No. 2012004211008), the 111 Project of China (No. B07015), the US-NSF Cooperative Agreement (DMR-1157490), the State of Florida and the US Department of Energy. We thank Dr. Y.F. Su for assistance in TEM work and Dr. M. Tyler for editing the manuscript.

References

[1] N. Wada, K. Takamatsu, M. Takeda, M. Takeguchi, M.G. Blanchin, The

- microstructure and magnetic properties of nano-scale Fe magnetic particles precipitated in a Cu-Fe alloy, *Int. J. Mater. Res.*, 101 (2010) 361-365.
- [2] K. Han, R.M. Niu, C.C. Zhao, Selected In-Situ Copper Matrix Composite, in: *Proceedings of the 1st International Symposium on Nonferrous Alloys and Special Casting Technologies*, Shanghai, 2014, pp. 56-59.
- [3] J.M. Denney, Precipitate kinetics and structure in a Cu-2.4% Fe alloy, *Acta Metall. Mater.*, 4 (1956) 586-592.
- [4] G. Shi, X. Chen, H. Jiang, Z. Wang, H. Tang, Y. Fan, Strengthening mechanisms of Fe nanoparticles for single crystal Cu-Fe alloy, *Mat. Sci. Eng. A*, 636 (2015) 43-47.
- [5] M. Kato, R. Monzen, T. Mori, Stress-induced martensitic-transformation of spherical iron particles in a Cu-Fe alloy, *Acta Metall. Mater.*, 26 (1978) 605-613.
- [6] I. Ansara, A. Jansson, Trita-Mac 533, Assessment of the copper-iron system, Materials Research Center, Royal Institute of Technology, Stockholm, 1993.
- [7] Z.S. Basinski, W. Hume-Rothery, A.L. Sutton, The Lattice Expansion of Iron, *Proc. R. Soc. London A*, 229 (1955) 459-467.
- [8] D.B. Williams, C.B. Carter, *Transmission electron microscopy a textbook for materials science*, Second ed., Springer, New York and London, 2008.
- [9] A.M. Wusatowska-Sarnek, H. Miura, T. Sakai, Coherency strains influence on martensitic transformation of γ -Fe particles in compressed Cu-Fe alloy single crystals, *J. Mater. Sci.*, 34 (1999) 5477-5487.
- [10] R. Monzen, K. Kita, Ostwald ripening of spherical Fe particles in Cu-Fe alloys,

Phil. Mag. Lett., 82 (2002) 373-382.

[11] K.E. Easterling, H.M. Miettinen-Oja, The martensitic transformation of iron

precipitates in a copper matrix, Acta Metall. Mater., 15 (1967) 1133-1141.

[12] D.Z. Watanabe, C. Watanabe, R. Monzen, Effect of coherency on coarsening of second-phase precipitates in Cu-base alloys, J. Mater. Sci., 43 (2008) 3946-3953.

[13] J.D. Verhoeven, S.C. Chueh, E.D. Gibson, Strength and conductivity of in situ Cu-Fe alloys, J. Mater. Sci., 24 (1989) 1748-1752.

[14] M. Enomoto, Enhanced phenomena in metals with electric and magnetic fields: II Magnetic fields, Mater. Trans., 46 (2005) 1088-1092.

[15] M. Yamaguchi, Y. Tanimoto, Magneto science: Magnetic field effects on materials, fundamentals and applications, Springer Berlin Heidelberg, 2006.

[16] M. Shimotomai, Influence of magnetic-field gradients on the pearlitic transformation in steels, Mater. Trans., 44 (2003) 2524-2528.

[17] X.J. Hao, H. Ohtsuka, H. Wada, Structural elongation and alignment in an Fe-0.4C alloy by isothermal ferrite transformation in high magnetic fields, Mater. Trans., 44 (2003) 2532-2536.

[18] Y.D. Zhang, C. Esling, M.L. Gong, G. Vincent, X. Zhao, L. Zuo, Microstructural features induced by a high magnetic field in a hypereutectoid steel during austenitic decomposition, Scripta Mater., 54 (2006) 1897-1900.

[19] K.M. Liu, D.P. Lu, H.T. Zhou, Z.B. Chen, A. Atrens, L. Lu, Influence of a high magnetic field on the microstructure and properties of a Cu-Fe-Ag in situ composite,

Mat. Sci. Eng. A, 584 (2013) 114-120.

[20] Y.D. Zhang, C. Esling, M. Calcagnotto, M.L. Gong, X. Zhao, L. Zuo, Shift of the eutectoid point in the Fe-C binary system by a high magnetic field, J. Phys. D Appl. Phys., 40 (2007) 6501-6506.

[21] J. Liu, N. Scheerbaum, D. Hinz, O. Gutfleisch, Martensitic transformation and magnetic properties in Ni-Fe-Ga-Co magnetic shape memory alloys, Acta Mater., 56 (2008) 3177-3186.

[22] K. Kindo, K. Hazumi, T. Kakeshita, K. Shimizu, H. Hori, M. Date, High magnetic field effect in martensitic transformation, Physica B, 155 (1989) 207-210.

[23] Y.D. Zhang, C.S. He, X. Zhao, L. Zuo, C. Esling, Thermodynamic and kinetic characteristics of the austenite-to-ferrite transformation under high magnetic field in medium carbon steel, J. Magn. Magn. Mater., 294 (2005) 267-272.

[24] C. Kanno, T. Fujii, H. Ohtsuka, S. Onaka, M. Kato, Effects of magnetic field on solid solubility of Fe and Co in a Cu matrix, in: 6th International Conference of Electromagnetic Processing of Materials, Dresden, Germany, 2009, pp. 777-779.

[25] W.V. Youdelis, D.R. Colton, J. Cahoon, On the theory of diffusion in a magnetic field, Can. J. Phys., 42 (1964) 2217-2237

[26] T.P. Hou, Y. Li, Y.D. Zhang, K.M. Wu, Magnetic field-induced precipitation behaviors of alloy carbides M_2C , M_3C , and M_6C in a molybdenum-containing steel, Metall. Mater. Trans. A-Phys. Metall. Mater. Sci., 45A (2014) 2553-2561.

[27] Z.N. Zhou, K.M. Wu, Molybdenum carbide precipitation in an Fe-C-Mo alloy

under a high magnetic field, *Scripta Mater.*, 61 (2009) 670-673.

[28] M. Takeda, N. Wada, Z. Hiroi, J. Kadono, M. Perez, S. Rivoirard, Influence of a magnetic field on the precipitation behaviour of nano-scale cobalt particles in a copper matrix, *Mater. Lett.*, 98 (2013) 201-204.

[29] Y.D. Zhang, N. Gey, C.S. He, X. Zhao, L. Zuo, C. Esling, High temperature tempering behaviors in a structural steel under high magnetic field, *Acta Mater.*, 52 (2004) 3467-3474.

[30] M. Miglierini, V. Prochazka, R. Ruffer, R. Zboril, In situ crystallization of metallic glasses during magnetic field annealing, *Acta Mater.*, 91 (2015) 50-56.

[31] R. Onodera, S. Kimura, K. Watanabe, Y. Yokoyama, A. Makino, K. Koyama, Nucleation control for fine nano crystallization of Fe-based amorphous alloy by high-magnetic-field annealing, *J. Alloy. Compd.*, 637 (2015) 213-218.

[32] H.D. Joo, J.K. Choi, S.U. Kim, N.S. Shin, Y.M. Koo, An effect of a strong magnetic field on the phase transformation in plain carbon steels, *Metall. Mater. Trans. A*, 35A (2004) 1663-1668.

[33] P. Jia, J.M. Liu, E.G. Wang, K. Han, The effects of high magnetic field on crystallization of $\text{Fe}_{71}(\text{Nb}_{0.8}\text{Zr}_{0.2})_{29}\text{B}_{23}$ bulk metallic glass, *J. Alloy. Compd.*, 581 (2013) 373-377.

[34] L. Qu, E.G. Wang, K. Han, X.W. Zuo, L. Zhang, P. Jia, J.C. He, Studies of electrical resistivity of an annealed Cu-Fe composite, *J. Appl. Phys.*, 113 (2013) 173708.

- [35] X.W. Zuo, C.C. Zhao, R.M. Niu, E.G. Wang, K. Han, Microstructural dependence of magnetoresistance in CuAg alloy solidified with high magnetic field, *J. Mater. Process. Technol.*, 224 (2015) 208-212.
- [36] X.W. Zuo, K. Han, C.C. Zhao, R.M. Niu, E.G. Wang, Precipitation and dissolution of Ag in ageing hypoeutectic alloys, *J. Alloy. Compd.*, 622 (2015) 69-72.
- [37] X.W. Zuo, K. Han, C.C. Zhao, R.M. Niu, E.G. Wang, Microstructure and properties of nanostructured Cu28 wt%Ag microcomposite deformed after solidifying under a high magnetic field, *Mat. Sci. Eng. A*, 619 (2014) 319-327.
- [38] S.S. Quek, Y. Xiang, D.J. Srolovitz, Loss of interface coherency around a misfitting spherical inclusion, *Acta Mater.*, 59 (2011) 5398-5410.
- [39] S. Arajs, D.S. Miller, Paramagnetic Susceptibilities of Fe and Fe-Si Alloys, *J. Appl. Phys.*, 31 (1960) 986-991.
- [40] D.A. Porter, K.E. Easterling, Phase transformations in metals and alloys, Second ed., Chapman & Hall, London, 1992.
- [41] A. Chbihi, X. Sauvage, D. Blavette, Atomic scale investigation of Cr precipitation in copper, *Acta Mater.*, 60 (2012) 4575-4585.
- [42] M. Yamaguchi, Y. Tanimoto, *Magneto-science: magnetic field effects on materials: fundamentals and applications*, Kodansha and Springer, Tokyo, 2006.
- [43] B.Z. Cui, C.T. Yu, K. Han, J.P. Liu, H. Garmestani, M.J. Pechan, H.J. Schneider-Muntau, Magnetization reversal and nanostructure refinement in magnetically annealed Nd₂Fe₁₄B/ α -Fe-type nanocomposites, *J. Appl. Phys.*, 97 (2005).

- [44] B.Z. Cui, K. Han, H. Garmestani, J.H. Su, H.J. Schneider-Muntau, J.P. Liu, Enhancement of exchange coupling and hard magnetic properties in nanocomposites by magnetic annealing, *Acta Mater.*, 53 (2005) 4155-4161.
- [45] B.Z. Cui, K. Han, Y. Zhang, J.P. Liu, H. Garmestani, S. Liu, H.J. Schneider-Muntau, Crystallization, morphology and magnetic properties of melt-spun $(\text{Nd, Pr, Dy})_2(\text{Fe, Co, Mo})_{14}\text{B}/\alpha\text{-Fe}$ nanocomposites, *IEEE Trans. Magn.*, 40 (2004) 2867-2870.
- [46] X.L. Zhou, K. Han, Z.M. Ren, Z. Li, Magnetic field-induced granular pearlite at early stages of phase transformation, *Adv. Mater. Res.*, 650 (2013) 178-184.
- [47] K. Matsuura, M. Kitamura, K. Watanabe, The growth kinetics and interfacial energy of coherent $\gamma\text{-Fe}$ particles in Cu-Fe alloys, *J. Jpn. Inst. Met.*, 41 (1977) 1285-1289.
- [48] J. Boisse, N. Lecoq, R. Patte, H. Zapolsky, Phase-field simulation of coarsening of γ precipitates in an ordered γ matrix, *Acta Mater.*, 55 (2007) 6151-6158.
- [49] R. Monzen, T. Tada, K. Kita, Effect of Sb on coarsening of Fe particles in a Cu-Fe alloy, *Philos. Mag. Lett.*, 83 (2003) 433-440.
- [50] Y. Watanabe, M. Kato, A. Sato, Growth-kinetics and martensitic-transformation of large Fe particles in a Cu-1.5 mass% Fe alloy, *J. Mater. Sci.*, 26 (1991) 4307-4312.