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Low-temperature phase transition of nanoscale copper precipitates in Fe-Cu alloys

Milan J. Konstantinović* and Boris Minov
Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucléaire (SCK·CEN), Boeretang 200, 2400 Mol, Belgium

Zdravko Kutnjak
Jozef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia

Marko Jagodić
Institute of Mathematics, Physics, and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia

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The low-temperature internal friction spectra and specific-heat measurements of Fe-1%Cu alloys show the existence of a discontinuity at 122 K which is assigned to the structural phase transition of nanosize-Cu precipitates. The change in the internal friction coefficient across the phase transition, and the enthalpy change are found to be proportional to the precipitate average radius R, showing a linear dependence in the case of internal friction and a R^3 dependence in the case of specific-heat anomalies in a very good agreement with theoretical model.

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The formation and stability of solute nanoclusters in a variety of alloys, used either as electronic or structural materials, is a key issue relevant for technological application of embedded atomic-scale structures.[1] Nanoclusters can be regarded as the bridging form between molecules and crystals, so the main issue is to reveal their structures, interactions at the interface, and thermal stability. In iron-based alloys, which are among the most widely used structural materials, typical working conditions, such as elevated temperatures, application of the stress, neutron irradiation, etc., trigger the formation of small clusters also known as precipitates, affecting the phase stability of the alloy. Consequently, the effects such as strength and embrittlement increase may occur, leading to severe macroscopic structural failures. These effects are especially enhanced in copper-rich iron alloys which are used as reactor-pressure vessel steels,[2,3] pointing to the importance of understanding the physical properties of copper nanoclusters in these materials.

In that respect, the binary Fe-Cu is a typical unmixing system with low mutual solubility of Fe and Cu, which can be used to analyze the structural properties and transformation kinetics of Cu nanoclusters.[4–7] In supersaturated Fe-Cu solid solution, the copper clusters with a face centered cubic (fcc) structure of bulk Cu are formed after cluster reach certain critical size, as a result of bulk instability prevailing the influence of the cluster interface. Interestingly, at early stages of precipitation growth, the additional Cu-cluster structure defined as 9R is observed.[5] This phase is argued to be an intermediate structure between the body centered cubic (bcc) structure, fully coherent with the iron lattice and the noncoherent fcc cluster structure. The origin of the bcc-9R phase transition is still not resolved and it is a matter of some debate in the literature. The main question concerns the origin of relatively large structural disorder[5] and the role of vacancies. According to molecular-dynamics calculation, the bcc-9R transition occurs only in precipitates with increased vacancy concentrations.[8] The resulting structure, with twin boundaries and close packed planes, seems to be in agreement with high-resolution electron microscopy and electron-diffraction experiments which indicated the existence of 9R structural imperfections. On the other hand, the bcc-9R transition in Fe-Cu alloys can be also explained on the basis of (110) bcc plane-slipping effect[9] in a similar way as in other binary alloys such as Cu-Al, with 9R structural imperfections probably appearing as a consequence of complex cluster boundary conditions.

The presence of structural disorder in Cu nanoclusters affects their thermal stability. In this paper, we report the study of low-temperature properties of Cu precipitates, on the basis of internal friction (IF) and specific-heat measurements. In both experiments we observe the existence of characteristic discontinuities at 122 K which can be attributed to the structural phase transition. The discontinuities are found to depend on the average Cu-cluster radius, R, and can be described with the classical precipitation kinetics model, so we assign this transition to the structural phase transition of copper precipitates.

The material used in this study is a polycrystalline Fe-1 wt. %Cu alloy with less than 200 ppm of additional impurities. The details of sample preparation were published elsewhere.[10] The various stages of copper precipitation, related to different Cu-cluster sizes, are achieved by thermal aging for different times at 773 K in argon atmosphere, and subsequent fast quenching into water. The characteristic stages of precipitation hardening and softening are confirmed by Vickers hardness measurements. The internal friction measurements are performed in an inverted torsion pendulum[10] operating in free vibration at about 1.8 Hz (with a typical sample size of $1.3 \times 1.3 \times 30$ mm^3), in the temperature range between 100 and 600 K. From the free decay signal, the resonance frequency (modulus), ω, and the internal friction coefficient (damping), Q^{-1}, are determined. Q^{-1} is proportional to the ratio of the energy dissipated during one cycle to the maximum elastic energy stored in the sample. The measurements have been performed at a strain amplitude of about 10^{-4}, in a He atmosphere with a heating rate of about 1.5 K/min, and no magnetic field is applied.

The specific-heat measurements are performed with a PPMS calorimeter in the temperature range from 4–150 K in a He atmosphere. Platelets of Fe-1%Cu alloys with a typical

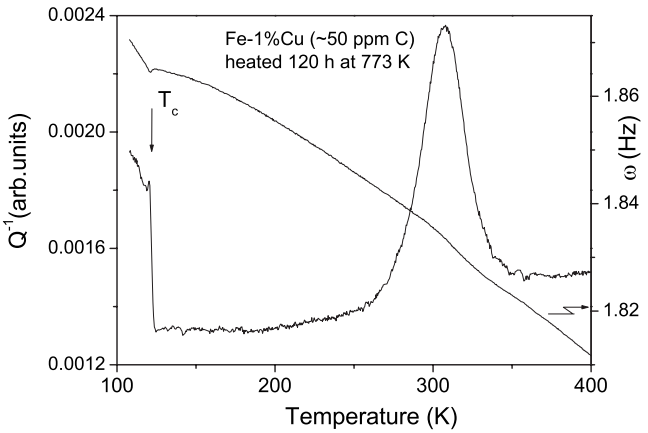

FIG. 1. Internal friction coefficient and resonant frequency as a function of temperature in Fe1%Cu alloy thermally treated at 773 K for 120 h.

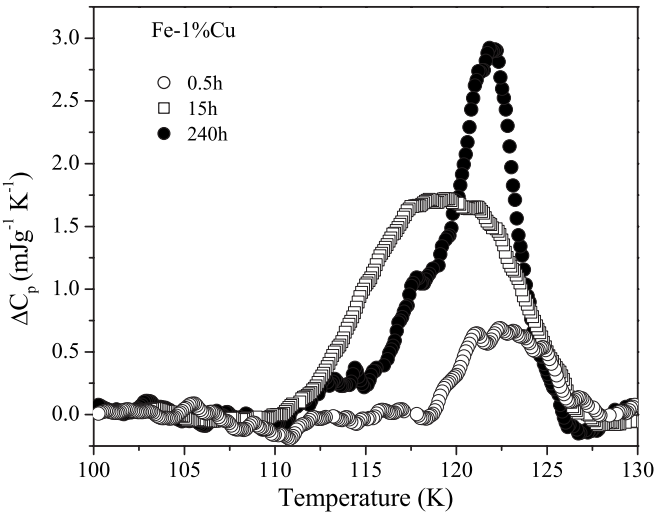

FIG. 2. Excess specific heat as a function of temperature in Fe-1%Cu alloy, thermally treated at 773 K for 0.5, 15, and 240 h.

sample mass of 36 mg are used. A relaxation technique is employed with temperature ramps lower than 0.5 K. The temperature scanning rates of 0.005 K/min were kept low enough to ensure maximum resolution for all samples.

The temperature-dependent internal friction coefficient (Q^{-1}) and resonant frequency (ω) of the Fe-1%Cu alloy, thermally treated at 773 K for 120 h, are shown in Fig. 1. The peak at about 310 K, also known as Snoek relaxation,[11] originates from the thermal activation of carbon impurities in the iron lattice. The peak position and full width at half maximum (~ 32 K) agree well with previous results[11] and correspond to typical observations for point-defect relaxation. The Snoek peak intensity agrees well with the reported carbon content in this alloy (~ 50 ppm). Interestingly, at a temperature around 122 K we observe large, steplike change in the internal friction coefficient, followed by a peak at the low-temperature side of the anomaly. This effect is accompanied by a sharp drop of the frequency as well. Generally, these types of discontinuities in the IF spectra can be associated with the existence of phase transition.[12] The singularities in Q^{-1} and ω define the phase-transition point while the steplike change in Q^{-1} originates from the difference between intrinsic damping in two phases.

The existence of a phase transition is confirmed by specific-heat measurements. The specific heat as a function of temperature for various thermally treated Fe-1%Cu alloys is presented in Fig. 2. The sharp anomaly is observed at about 123 K in very good agreement with the phase-transition temperature obtained from the internal friction experiment. The discontinuity is clearly observed in both experiments already for the sample aged for 0.5 h, see Figs. 2 and 3. From the relative sharpness of the transition, and from the fact that it strongly affects the macroscopic mechanical properties, we assign the $T_c = 122$ K to a first order structural phase transition.

Since the phase-transition anomalies depend on average cluster radius (aging time), see Figs. 2 and 3, we assume that the phase transition originates from the structural phase transition of Cu clusters, and analyze the IF and specific-heat anomalies on the basis of the Cu-precipitation kinetic model. In Fig. 4 we plot the change in IF coefficient, e.g., the magnitude of discontinuity defined as $\Delta Q^{-1} = Q^{-1}(117\ \text{K}) - Q^{-1}(127\ \text{K})$, the enthalpy change ΔH, and the Vickers hardness as a function of the aging time. Vickers hardness shows the typical behavior already observed in such alloys.[4] The peak hardening is observed at about 15 h, which corresponds to an average cluster radius of about 6 nm.[5] For aging times lower than 15 h the precipitates grow in size, causing the increase of hardness (also known as precipitation hardening). At higher aging times, the Cu clusters transform to the fcc structure and their number density decreases, causing a decrease in hardness (softening). This occurs due to stress lowering around the precipitates. Both ΔQ^{-1} and ΔH increase at the early stages of Cu-clusters growth and then saturate for the aging times above 120 h. The saturation is caused by the slowing down/the end of the precipitation process. Interestingly, ΔQ^{-1} and ΔH show very different behaviors at low aging times, as shown in the insets of Fig. 4. By

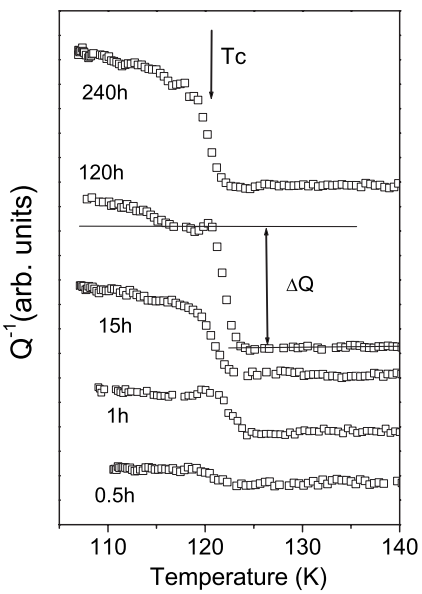

FIG. 3. Q^{-1} vs temperature for various aging times.

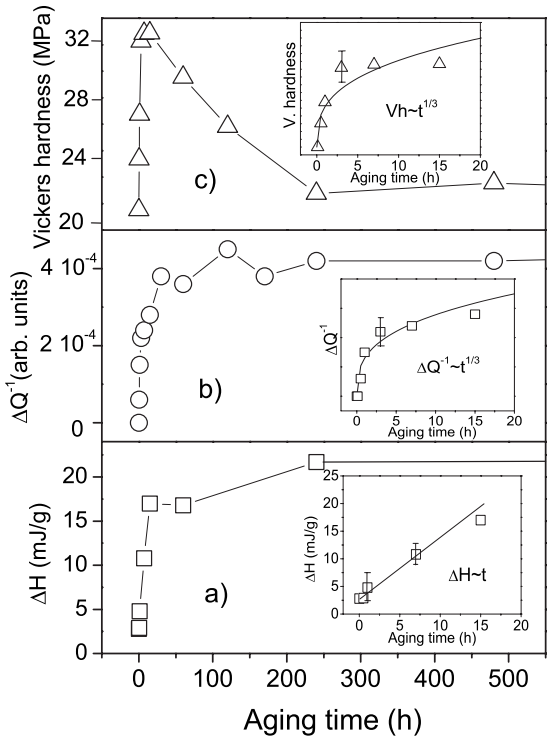

FIG. 4. (a) The change in the enthalpy, (b) the change in the internal friction coefficient, and (c) the Vickers hardness as a function of the aging time.

increasing the aging time, the enthalpy change exhibits the linear dependence, $\Delta H \sim t$, see inset of Fig. 4(a). On the other hand, the change in internal friction coefficient can be fully described by a cubic root dependence on aging time, $\Delta Q^{-1} \sim t^{1/3}$. The calculated curves are shown as full lines in insets of Fig. 4. If T_c can be associated to the phase transition of copper clusters, the change in internal friction coefficient and the change in enthalpy as a function of Cu-cluster radius must obey the laws of precipitation kinetics. The validity of the Lifshitz, Slyozov, and Wagner (LSW) distribution law[13] is already confirmed experimentally in thermally aged Fe-1.3%Cu alloys.[6] In this case, the growth of Cu clusters can be described by the kinetics of coarsening and the LSW function predicts that the cluster diameter varies as the cubic root of the aging time, $R \sim t^{1/3}$. As a consequence, the internal friction and specific-heat experiments give $\Delta Q^{-1} \sim R$ and $\Delta H \sim R^3$.

Following the proposed scenario of the phase transition, the enthalpy change can be related to the transformed volume of the precipitates which is proportional to the third power of the precipitate radius. This agrees with the present experimental observations. In the case of the internal friction experiment the physical picture is a bit more complicated. Two effects can give a linear dependence of ΔQ^{-1} on R; (a) dislocation-defect interaction and (b) thermoelastic effect; within the former scenario, $\Delta Q^{-1} \sim R$ originates from a linear dependence of stress field on the precipitate radius. the combination of small Cu cluster sizes with their large number density is responsible for the formation of Guinier-Preston (GP) zones with large stress field, capable of strong dislocation pinning.[14,15] Dislocation motion occurs by dislocation cutting through the GP zone and/or via shearing of Cu clusters by dislocations. In this case, the dislocation-precipitation interaction, and the increase in stress exhibit a linear dependence on precipitate radius, $\sigma \sim RU_s\pi/bL$, where U_s is the change in precipitate (GP zone) surface energy (due to precipitate/zone shearing), b is Burgers vector, and L is the average distance between precipitates.[16] Essentially, the linear dependence of ΔQ^{-1} as a function of precipitate radius originates from the one-dimensional character of the dislocation structure. If the motion of dislocations is the main source of damping at low temperatures, the drop of the IF coefficient, i.e., the decrease in damping, at temperatures above 122 K can be associated to the decrease in dislocation mobility.[17] This effect can occur if the phase transition increases the effective stress (in the direction from low T to high T) which blocks dislocation motion. Therefore, $T_c = 122$ K may be regarded as an order-disorder type of phase transition caused by thermal fluctuations, analogous to the size-triggered bcc(9R)-fcc phase transition, with fcc being the low-T-ordered phase. However, even though the model correctly predicts the linear dependence of the IF coefficient as a function of R, very few dislocations are expected to be mobile at 100 K since the main contribution in bcc metals comes from screw dislocations with an activation energy of about 1 eV.[18]

The other possibility is that geometrical factors, such as the presence of precipitates, influence the phonon mean-free path affecting the damping via thermoelastic effect.[19] At low temperatures the phonon mean-free path in Fe-1%Cu may become comparable with mean distance between Cu nanoclusters so the phase transformation of Cu clusters could affect it. If the phase transition of Cu clusters acts by decreasing the phonon mean-free path, a change in damping is expected across the phase transition with a linear dependence on the cluster radius. Similarly as in the previous scenario, the low-temperature Cu-cluster phase might be regarded as an ordered structure, noncoherent with the iron lattice, which increases the phonon scattering with respect to the high-temperature phase. Besides, the nature of the transition remains an open issue. Additional low-temperature experiments, such as x-ray diffraction, resistivity measurements, or yield strength measurements (tensile tests), are needed to address the question of the order parameter, and to distinguish between these two proposed explanations of the internal friction result.

Moreover, it is important to note that the vacancies also affect the precipitation kinetics. Despite the fact that experimental data in Fe-Cu alloys show very good agreement with classical theories of nucleation growth and coarsening, recent theoretical calculations suggest that vacancies can modify the precipitation kinetics.[20] It is argued that the segregation of vacancies at the precipitate interface increases the precipitate mobility, allowing direct precipitate coagulation (the classical coarsening model assumes that precipitate size changes by the emission or absorption of individual solute atoms). Our experimental data show the validity of the LSW kinetics model. It is however possible that a more detailed study at very short aging times (below 1 h) is required to access the regime with different precipitation kinetics. Questions related to these issues are the subject of ongoing research.

To conclude, we observed a phase transition at $T_c = 122$ K in Fe-1%Cu alloy which is assigned to the structural phase transition of Cu clusters. The specific-heat measurements and the temperature-dependent internal friction spectra exhibit typical phase-transition-type discontinuities which are found to depend on the average Cu-cluster radius. The enthalpy and the change in internal friction coefficient across the phase transition exhibit cubic and linear dependence on the precipitate radius, respectively, in agreement with the LSW transformation kinetics model of Cu clusters.

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*mkonstan@sckcen.be

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