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Changes in vibrational entropy during the early stages of chemical unmixing in fcc Cu–6% Fe

Hillary L. Smith [a,*], B.C. Hornbuckle [b], L. Mauger [a], B. Fu [b], S.J. Tracy [a], G.B. Thompson [b], M.S. Lucas [c], Y. Xiao [d], M.Y. Hu [e], J. Zhao [e], E. Ercan Alp [e], B. Fultz [a]

[a] Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA
[b] Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA
[c] Air Force Research Laboratory, Wright-Patterson AFB, OH 45433, USA
[d] HPCAT, Geophysical Laboratory, Carnegie Institute of Washington, Argonne, IL 60439, USA
[e] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

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Abstract

A nanocrystalline face-centered cubic (fcc) solid solution of 6% Fe in Cu was prepared by high-energy ball milling, and annealed at temperatures from 200 to 360 °C to induce chemical unmixing. The chemical state of the material was characterized by three-dimensional atom probe microscopy, Mössbauer spectrometry and X-ray powder diffractometry. The unmixing was heterogeneous, with iron atoms forming iron-rich zones that thicken with further annealing. The phonon partial density of states (pDOS) of ^{57}Fe was measured by nuclear resonant inelastic X-ray scattering, showing the pDOS of the as-prepared material to be that of an fcc crystal. The features of this pDOS became broader in the early stages of unmixing, but only small changes in average phonon frequencies occurred until the body-centered cubic (bcc) phase began to form. The vibrational entropy calculated from the pDOS underwent little change during the early stage of annealing, but decreased rapidly when the bcc phase formed in the material.

Keywords: Nanocrystalline material; Microstructure formation; Vibrational entropy; Atom probe tomography; Fe–Cu alloy

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1. Introduction

The chemical entropy of mixing has the well-known configurational contribution

$$S_{\mathrm{cfg}} = -k_{\mathrm{B}}[(1-c)\ln(1-c) + c\ln c], \tag{1}$$

which can be obtained from the statistics of a random solid solution. (Here c is the mole fraction of solute in a binary mixture, and is the mole fraction of iron in the present work.) It is best understood when the solid solution is referenced to pure elements, for which $S_{\mathrm{cfg}} = 0$. When unmixing occurs on a small spatial scale, however, there may be a substantial volume fraction of material of intermediate compositions, and these compositional inhomogeneities evolve during an unmixing transformation.

The vibrational entropy S_{vib} also evolves during unmixing [1], and for a binary alloy it is:

$$S_{\mathrm{vib}}(T) = 3k_{\mathrm{B}}\int_0^{\infty}[(1-c)g_{\mathrm{Cu}}(\varepsilon) + c\,g_{\mathrm{Fe}}(\varepsilon)] \times [(1+n_\varepsilon) \times \ln(1+n_\varepsilon) - n_\varepsilon \ln n_\varepsilon]d\varepsilon, \tag{2}$$

where $n_\varepsilon(T) = [\exp(\varepsilon/(k_{\mathrm{B}T})) - 1]^{-1}$ is the Planck occupancy factor at the temperature T. In the present study, $g_{\mathrm{Cu}}(\varepsilon)$ and $g_{\mathrm{Fe}}(\varepsilon)$ are phonon partial densities of states (pDOS) for Cu and Fe atoms normalized to 1, and the mole fraction of iron is c. Here the interface is assumed to make no contribution to S_{vib}, but this can be checked experimentally. There has been some work on the change of vibrational entropy of unmixing [1], but very little work

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* Corresponding author. Tel.: +1 (484)883 7518.
E-mail address: HLS@caltech.edu (H.L. Smith).

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on how it might depend on small-scale compositional inhomogeneities in the material.

Vibrations of small crystals have been studied for many years. Calculations for both isolated nanocrystals [2,3] and nanocrystals with rigid constraints [4] established the characteristic enhancement in the number of modes at low energies that has been observed in all subsequent calculations of the density of states (DOS) for nanomaterials, and observed in inelastic neutron scattering experiments since 1995, following the upsurge of interest in nanostructured materials [5–11]. Subsequently, nuclear resonant inelastic X-ray scattering (NRIXS) has become an established technique for probing the pDOS of a resonant atom (typically ^{57}Fe) in nanostructures [12–22]. In addition to the enhancement of vibrational spectral intensity at low energies, nanostructures usually show a broadening of their Van Hove singularities, especially the peak from longitudinal modes near the top of the vibrational spectrum [14]. Numerous experiments have been undertaken to identify the specific origins of the unique phonon spectra of nanocrystals, and to decouple competing effects including the nature of surface atoms, low-coordinated interfacial atoms, and oxide surfaces [17,21,22]. The vibrational dynamics of nanostructures remains an active area of research.

The present investigation on iron unmixing from a face-centered copper (fcc) copper matrix was performed to measure the iron phonon pDOS, $g_{\mathrm{Fe}}(\varepsilon)$, from which we obtain the contribution of Fe atoms to the vibrational entropy with Eq. (2). A previous study on dilute ^{57}Fe in fcc Cu used a similar method to identify the vibrational spectrum of fcc Fe [23], but in the present work we examine carefully a series of samples annealed from as-prepared material, studying the state of chemical unmixing by three-dimensional atom probe tomography (APT), the crystal structure by X-ray diffractometry, the magnetic state by Mössbauer spectrometry, and correlate these changes in the phonon spectrum to chemical and structural changes of the nanostructure. Our goal is to better understand how the vibrational entropy changes with chemical unmixing, for which we find the dominant effect to be the formation of regions of bcc Fe.

2. Experimental

Powders of Cu and 5.6 at.% ^{57}Fe were mixed with 5 wt.% stearic acid and sealed in a steel vial in a high-purity argon atmosphere. Ball milling was performed with a Fritsch Planetary Mono Mill for 92 h at 400 rpm using a steel ball-to-powder weight ratio of 92:1. After milling, the material was sonicated in isopropyl alcohol, centrifuged and decanted to remove the stearic acid. The materials were sealed in a quartz ampoule under vacuum, and annealed by ramping to temperature over 30 min, heating constantly for 1 h at ±4 °C and immediately cooling. The samples were then enclosed in Kapton sample holders for X-ray diffraction (XRD), Mössbauer spectrometry, and NRIXS measurements. The same material was used for APT.

XRD patterns were collected for all samples using Cu Kα radiation. Rietveld analyses were used to determine lattice parameters, crystal size and root-mean-squared strain and corresponding errors. The Cu powder used for sample synthesis was also characterized by XRD at room temperature and analyzed in the same manner. Mössbauer spectrometry was performed at room temperature with a conventional constant acceleration system with a radiation source of ^{57}Co in a Rh matrix. Velocity and isomer shift calibrations were performed with reference to the room-temperature α-Fe spectrum.

APT analysis was performed on specimens from three different annealing temperatures and the as-prepared material using a Cameca Local Electrode Atom Probe (LEAP 3000XSi™). Specimens were prepared using a dual electron beam-focused ion beam (FIB) site-specific extraction technique [24]. The lifted-out specimen wedge was attached to 2 μm × 2 μm × 100 μm Si mounting pillars for handling and then subsequently annular ion milled to form the required needle shape geometry. In the final milling step, the accelerating voltage of the FIB was reduced to 5 keV to limit the Ga ion implantation and surface damage while sculpting the specimen tip radius to ~100 nm [25]. The sculpted tips were then placed into the LEAP analysis chamber at a base pressure of $<10^{-10}$ Torr. All specimens were run at 30 K using laser-assisted field evaporation pulse energies of 0.3 nJ, a pulse rate of 250 kHz and a target evaporation of 0.5%.

The datasets were reconstructed using standard software. For the as-prepared and 260 °C annealed samples, a core methodology, commonly called an "envelope clustering method", was performed [26]. In this method, the data sets of atoms are statistically determined to be either spatially random or nonrandom. If the distribution is nonrandom, a maximum separation distance, $d_{\max}$, is defined to capture a minimum number of solute atoms and is used to search for clusters in the dataset. We used a $d_{\max}$ of 0.61–0.65 nm, with a minimum number of 33 Fe atoms, to define a cluster. For the 310 and 360 °C samples, the chemical partitioning was significant and did not require the envelope clustering analysis. Instead, isoconcentration surfaces were used to delineate the segregation. The isoconcentration surface value was determined by finding the cross-over composition value between the Fe-enriched and Fe-depleted portions of the interdiffusion compositional curve. Hence, the isoconcentration surface created by this value determined the composition within the surface (cluster) and outside the surface (matrix).

NRIXS was performed at beamlines 3-ID-B and 16-ID-D at the Advanced Photon Source of the Argonne National Laboratory [27–29]. The incident photon energy was tuned to 14.4125 keV, the nuclear resonance energy of ^{57}Fe, and data were collected in scans of incident photon energy from −80 to +80 meV around the elastic peak. All measurements were performed at room temperature. The monochromator resolution function was measured in situ using a single avalanche photodiode detector in the