Extended x-ray-absorption fine-structure studies of heat-treated fcc-Fe$_{50}$Cu$_{50}$ powders processed via high-energy ball milling

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The local structure and chemistry of a ferromagnetic fcc-Fe$_{50}$Cu$_{50}$ solid solution obtained through high-energy ball milling were measured before and after heat-treatment-induced decomposition using extended x-ray-absorption fine-structure measurements. The decomposition is first evident with the phase separation of α-Fe after a heat treatment at 523 K. Analysis of the residual fcc component revealed that the Fe atoms were predominantly surrounded by other Fe atoms, suggesting that the Fe has coalesced within the fcc structure. The Fe atoms within the fcc phase likely exist in low-spin clusters which provide an explanation for the reduced values of low-temperature magnetization previously measured in annealed samples [P. Crespo *et al.*, Phys. Rev. B **48**, 7134 (1993)].

Much research has been focused on the Fe$_x$Cu$_{1-x}$ system since it was shown that the miscibility of Fe in fcc-Cu can be greatly enhanced, $0 \leqslant x \leqslant 0.6$, through high-energy ball milling.[1–4] In recent work,[3,4] some of the authors have reported on the magnetic and structural properties of a ferromagnetic fcc-Fe$_{50}$Cu$_{50}$ solid solution processed using high-energy ball milling. Their findings indicate anomalous magnetic behavior for heat-treated samples in the intermediate stages of decomposition. Specifically, a significant decrease of the low-temperature magnetization relative to the value measured for the as-milled sample was observed in annealed samples where multiple phases are present. This behavior cannot be accounted for by a nucleation and growth decomposition where the alloy separates into pure fcc-Cu and bcc-Fe components. Alternatively, these authors have suggested a spinodal mechanism to describe the decomposition process. In an attempt to elucidate the decomposition mechanism in this material we have measured the average local structure and chemistry around the Fe and Cu sites before and after heat treatments using extended x-ray-absorption fine-structure (EXAFS) measurements.

Powder samples, having a nominal composition of Fe$_{50}$Cu$_{50}$, were fabricated by high-energy ball milling Fe powder with Cu foil for a period of 400 h in a Fritsch vibrating mill. X-ray-diffraction measurements of the milled powder revealed only Bragg peaks corresponding with a single fcc phase having a lattice parameter of 3.641 Å. Samples of the as-milled FeCu powders were annealed under flowing argon gas to temperatures ranging from 523 to 923 K at a rate of 20 K/min and were then allowed to cool. Details of sample processing and characterization, including results of x-ray-diffraction, Mössbauer effect, and magnetization measurements, have been reported in Ref. 4.

A portion of the as-milled and annealed powders were examined using the NRL materials analysis beamline, X23B, at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY). The x-ray-absorption spectra near the Fe and Cu K absorption edges were collected in conversion electron mode after attempts to employ the transmission mode failed due to our inability to grind the powder to the scale required for EXAFS measurements. In using the conversion electron technique we applied a generous amount of the powder over a still-wet coating of colloidal graphite on a substrate of commercial grade Al foil. As per this technique, the absorption spectra was measured as normalized sample current (see Ref. 5 for details of the operation and performance of the conversion electron cell used here).

Following established EXAFS analysis procedures[6] the fine structure extending from 20 to 600 eV above the absorption edges were first normalized to the edge step height and energy, then fitted with a cubic spline curve to remove a low-frequency background oscillation, and converted to photoelectron wave-vector (k) space. These data were then Fourier transformed to radial coordinates in order to obtain direct information of the structure and atomic symmetry around the Fe and Cu sites. Quantitative information of the local structure and chemistry around the Fe sites were obtained by further fitting the near-neighbor peak of the Fourier-transformed EXAFS data with empirical and theoretical standards. EXAFS data for the as-milled sample were fit using theoretical EXAFS spectra generated by the FEFF codes (ver. 3.11) developed by Rehr and co-workers.[7] Alternatively, the fitting of data collected from annealed samples, where multiple phases were present, was performed using empirical standards of bcc-Fe and fcc-FeCu (simulated using the Fe EXAFS collected from the as-milled sample). These empirical standards were chosen because the x-ray-diffraction measurements indicate that bcc-Fe precipitates from the solid solution upon heat treatment. We assume that the remaining fcc phase consists of both Fe and Cu atoms still in solution. All fits were performed in k-space using a least-squares-fitting algorithm.

Information of the local structure and chemistry around the Fe and Cu sites is contained in the Fourier transform of their respective EXAFS data. These data for the as-milled sample are presented in Fig. 1 with similar data collected
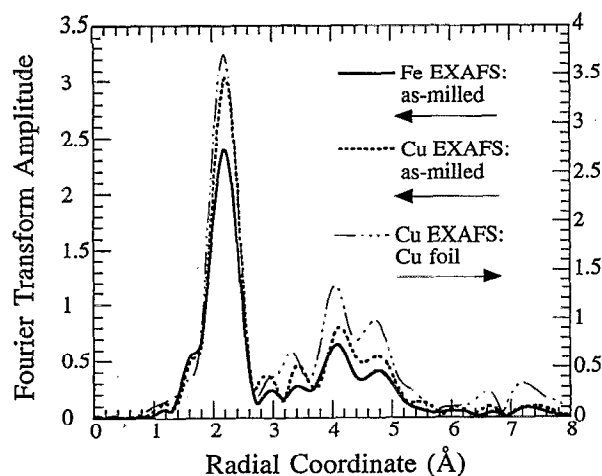
FIG. 1. Fourier-transformed Fe and Cu EXAFS from the as-milled $Fe_{50}Cu_{50}$ sample. Similar data collected from a fcc-Cu standard are shown for comparison. All data were transformed using k^2-weighting and k-ranges of 2.5–12.5 $Å^{-1}$. Electron phase-shift corrections have not been included, therefore radial distances do not correspond directly with bond lengths.

FIG. 2. Fourier-transformed Fe EXAFS data for the as-milled sample and those samples annealed at T=523, 723, 823, and 923 K. All data were transformed using k^2-weighting and k-ranges of 2.5–12.5 $Å^{-1}$. Electron phase-shift corrections have not been included, therefore radial distances do not correspond directly with bond lengths.

from a Cu foil used here to represent the fcc structure. Data corresponding with the as-milled sample are shown to resemble closely the fcc structure of the Cu standard in both the relative amplitude and radial distance of Fourier peaks appearing over the range of 1–5 Å. Slight changes in relative amplitude and distance of these Fourier peaks between the milled sample data and the fcc Cu standard can be attributed to the increased structural disorder of the milled powder and the smaller diameter of the Fe atom, respectively.

Fitting of the near-neighbor peak of the EXAFS data presented in Fig. 1 using FEFF generated EXAFS spectra indicates that the first coordination shell around both the Fe and Cu atoms consists of a mixture of Fe and Cu atoms which reflect a stoichiometry of $Fe_{48}Cu_{52}$, a result consistent within the uncertainty of the EXAFS fitting analysis with the nominal composition of the starting powder mixture. This analysis establishes that atomic level mixing has occurred around Fe and Cu sites due to the ball milling operation and indeed an fcc solid solution exists. Attempts to include a bcc component to the fit resulted in a significant deterioration of the least-squares-fitting parameter, as did attempts to simulate coherent fcc-Fe clusters within the Cu matrix. Further details of this analysis will be presented elsewhere.

Fitting of both the Fe and Cu EXAFS data found a Cu—Fe(Fe—Cu) bond of 2.60±0.02 Å, significantly larger than the sum of the Goldsmidt radii (assuming a coordination of 12), 2.55 Å. However, this result is consistent with x-ray-diffraction measurements of the as-milled powder[2] which indicate a larger lattice parameter for the solid solution, a_0=3.641 Å, than that of fcc Cu, a_0=3.615 Å. The Fe—Fe and Cu—Cu bonds are measured to be 2.53±0.01 Å. Taken together, the resulting EXAFS lattice parameter, 3.627±0.02 Å, matches within the EXAFS fitting uncertainty to the value obtained by XRD. The distorted bond distance of the Cu—Fe correlation is apparently responsible for the distorted lattice measured by XRD. However, at this time we can only speculate that the repulsion between the Fe and Cu atoms arises
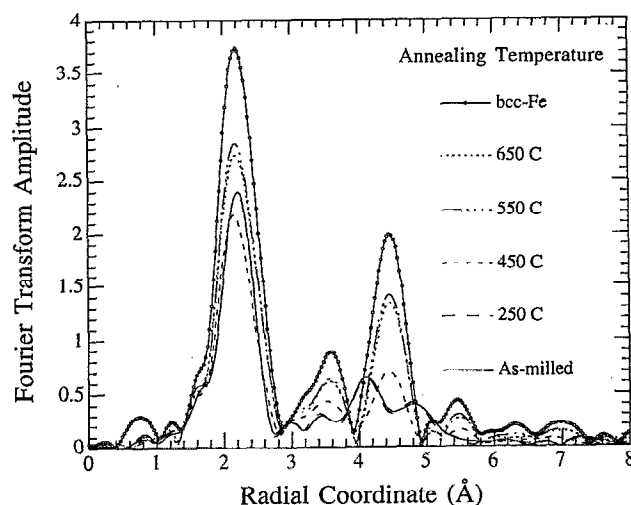
from an electronic interaction brought about by the filled d-band of Cu interacting with the unfilled d-band of Fe.

Figure 2 depicts the Fourier-transformed Fe EXAFS data for the as-milled and annealed samples illustrating the evolution of local structure around the Fe site as a function of heat-treatment temperature. All the data presented in Fig. 2 are shown on the same x and y axes without offset or normalization to allow for the direct comparison between samples annealed at different temperatures. The as-milled sample and the sample annealed at 523 K have nearly identical transform profiles, indicating that the local structure around the Fe atoms remains largely unchanged after this low-temperature anneal. However, the data corresponding with the sample annealed at 723 K displays significant changes in the Fourier features appearing over the r range of 3–5 Å (uncorrected for electron phase shifts). This transform illustrates features common to both bcc and fcc structures, indicating that the Fe atoms exists in both phases after this heat treatment. Evidence for the bcc phase is seen in the large peak appearing near 3.5 Å which corresponds with the cube-diagonal unit-cell site and the body-centered site of the adjacent cell. Anneals at still higher temperatures are seen to further advance the chemical and phase separation: The Fourier-transformed data for samples annealed at 823 and 923 K closely match the bcc Fe transform presented in Fig. 2 in both relative amplitude and radial distance of Fourier peaks.

Information of the local chemical environment at different stages of decomposition would be very useful in providing insight to the nature of the decomposition mechanism and in turn assist in our understanding of the magnetic properties. However, because the photoelectron backscattering amplitudes of the Cu and Fe atoms are similar, it is difficult to extract information of the local chemistry from a qualitative inspection of the data presented in Fig. 2. To this end, we have performed a quantitative fitting analysis of the near-

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neighbor Fourier peak for all samples whose data appear in Fig. 2. Because the Fe atom may occupy more than one inequivalent site in these partially decomposed samples, depending upon the nature of the decomposition and the annealing temperature, it is difficult to fit the EXAFS data using only FEFF generated EXAFS spectra. This difficulty arises from the increasing number of independent variables (used in fitting) corresponding with each inequivalent site. Hence, we chose to fit these data using empirical standards of bcc-Fe and fcc-FeCu. Through this approach multiple inequivalent Fe sites in the annealed samples are simplified to two, those existing in bcc and fcc symmetries. This modeling does not take into account the variation in local chemistry around the absorbing atom. It does, however, provide a means of measuring the relative fraction of atom which occupies those sites differentiated by symmetry made possible by the differences in local atomic symmetry between the bcc and fcc structures.

The results of the fitting analysis of the annealed samples are presented graphically in Fig. 3. The inset plot illustrates the experimental Fourier-filtered Fe EXAFS data of the near-neighbor region and the best-fit calculation for the sample annealed at 723 K. The as-milled sample and the sample annealed at 523 K are measured to contain only an fcc component to the near-neighbor environment of Fe. After an anneal at 723 K, however, 30% of the sample exists in a bcc phase with 70% remaining in the fcc phase. Anneals at 823 and 923 K further advance the decomposition with a bcc atom fraction growing to 68% and 72%, respectively. The error bars presented in Fig. 3 represent a 100% increase in the goodness of fit parameter, indicating a significant deterioration relative to the best fit. The increase in error bar for samples annealed at 823 and 923 K is attributed to the gradual change in chemistry of the residual fcc phase with increasing annealing temperature. In these samples the empirical fcc-FeCu standard becomes a poor simulation of the fcc component.

The observed magnetic behavior reported in Refs. 3 and 4 cannot be explained by a simple nucleation of fcc-Cu and bcc-Fe from the as-milled fcc solid solution. The decrease of low-temperature magnetization (relative the value of the as-milled powder) with the appearance of the bcc phase suggests that a significant amount of Fe must exist in a low-spin state, either as small clusters of fcc-Fe or dilute Fe in fcc-Cu. To investigate this hypothesis, we have isolated the fcc component of a partially decomposed sample, namely the sample annealed at 723 K which was found previously to have a 30% bcc component. EXAFS modeling of the fcc component of this sample using FEFF generated theoretical EXAFS spectra indicates that the average environment of the Fe sites in this phase is dominated by Fe neighbors at a ratio of 10:1. In theory, with 30% of the Fe in the bcc phase, the fcc phase should have a composition near $Fe_{20}Cu_{80}$, if it were to remain a solid solution. If this was the case the local environment of Fe would be dominated by Cu neighbors at a ratio of 4:1. This result provides evidence that the Fe atoms in the
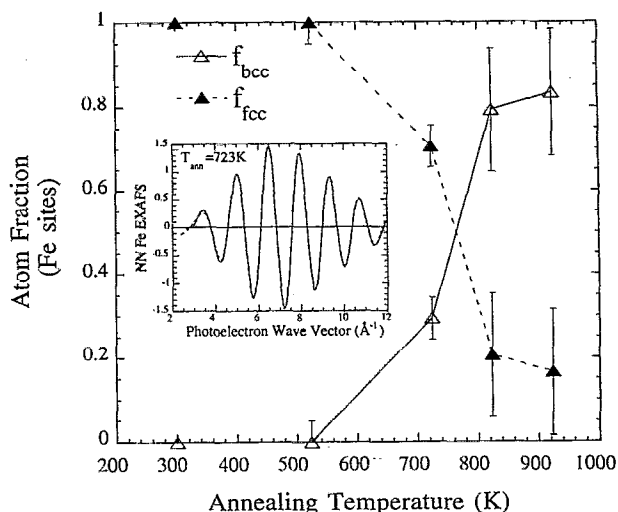

FIG. 3. Atomic fraction of Fe atoms occupying bcc and fcc sites in heat-treated samples as a function of annealing temperature. Results were derived from EXAFS fitting of the near-neighbor (NN) region of the Fourier-transformed data presented in Fig. 2 using empirical standards. The inset plot illustrates the experimental Fourier-filtered NN Fe EXAFS data for the sample annealed at 723 K and the best-fit calculation. Error bars reflect a 100% increase in the least-squares-fitting parameter. The lines connecting the data points are presented to illustrate the qualitative trend with annealing temperature.

residual fcc phase have coalesced within the Cu matrix during the heat-treatment-induced decomposition. Furthermore, it is likely that these fcc clusters of Fe are sufficiently small so as to exist in a low-spin state, thus providing an explanation for the reduced magnetization at low temperatures reported in Refs. 3 and 4.

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