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Experimental investigation of inhomogeneities, nanoscopic phase separation, and magnetism in arc melted Fe-Cu metals with equal atomic ratio of the constituents

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Composition gradient and phase separation at the nanoscale have been investigated for arc-melted and solidified with equiatomic Fe-Cu. Diffraction studies revealed that Fe and Cu exhibited phase separation with no trace of any mixing. Microscopy studies revealed that immiscible Fe-Cu form dense bulk nanocomposite. The spatial distribution of Fe and Cu showed existence of two distinct regions, i.e., Fe-rich and Cu-rich regions. Fe-rich regions have Cu precipitates of various sizes and different shapes, with Fe forming meshes or channels greater than 100 nm in size. On the other hand, the matrix of Cu-rich regions formed strips with fine strands of nanosized Fe. Macromagnetic response of the system showed ferromagnetic behavior with a magnetic moment being equal to about $2.13 \mu_B/\text{Fe atom}$ and a bulk like negligible value of coercivity over the temperature range of 5–300 K. Anisotropy constant has been calculated from various laws of approach to saturation, and its value is extracted to be equal to 1350 J/m^3 . Inhomogeneous strain within the Cu and Fe crystallites has been calculated for the (unannealed) sample solidified after arc-melting. Annealed sample also exhibited local inhomogeneity with removal of inhomogeneous strain and no appreciable change in magnetic character. However, for the annealed sample phase separated Fe exhibited homogenous strain. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Systems such as Fe-Cu,¹ Fe-Mg,² Co-Cr,³ etc., which exhibit miscibility gap have been studied extensively. Both experimental and theoretical studies have been carried out to clarify the physical mechanisms associated with the formation of non-equilibrium supersaturated solid solutions in these binary systems which possess positive heat of mixing.^{2,4,5} The Fe-Cu system has been investigated by several authors for full range of compositions using numerous experimental techniques.^{6,7} The Fe-Cu equilibrium binary phase diagram is composed of two separate phases, an fcc phase Cu and a bcc phase Fe, at room temperature.¹ Fe-Cu alloy is a system with a positive and high value of enthalpy of mixing at the middle of the phase diagram.^{4,8} Due to the relative simplicity, unmixing tendency, and large miscibility gap, Fe-Cu system serves as a benchmark case to study phase transformation kinetics.^{5,9–17} Various metastable synthesis techniques have been employed to form Fe-Cu alloys which can exhibit single phase fcc or bcc structures, depending on the relative ratio of the constituents.^{7,18,19} Metastable fcc Fe-Cu phases are found to decompose into fcc Cu and bcc Fe phases at 1000 K.¹⁹ Nevertheless, issues like Fe in Fe-Cu system exhibiting fcc structure, the so called γ -Fe, is still a

hot topic of discussion.^{20,21} Negligible mutual solubility of both the constituent elements in equilibrium state also requires a detailed investigation of presence of small fraction of intermetallic compounds. Commercially, bcc Fe having nanosized Cu precipitates exhibits an enhanced thermal stability and an increased hardness.^{22–24}

Simulations based on Monte Carlo (MC) technique revealed that in the alloys which exhibit unmixing tendency, trapping of vacancies at the matrix/precipitate interfaces or matrix diffusion can take place with the dissociation of small solute clusters within the precipitates. However, several other kinetic Monte Carlo simulations have suggested that in such alloys trapping of vacancies at the precipitate/matrix interfaces or within the precipitates may lead to the diffusion without dissociation of small solute clusters.^{13,14,25–29} As a consequence, it could favor the direct coagulation between precipitates and modify the precipitation kinetics. MC simulations based on the consideration that Cu atoms are more mobile compared with the Cu monomers revealed that mobility decreases as the cluster size increases.^{14,30}

Extensive researches in both experimental and theoretical areas have been conducted on Fe-Cu alloy both in equilibrium conditions and also in the metastable phase. In the equilibrium phase diagram, Fe and Cu are insoluble at

temperatures below about 700 °C. However, detailed experimental investigation related to the phase separation and precipitate formation at the nanoscale is missing. There are several questions to be addressed. For example, do the atoms form alloy on atomic scale?, which element prefers to precipitate?, are there any amorphous phases?, and what is the possibility of forming phases such as γ -Fe?, etc. There can exist phases or domains so small that they would be undetectable due to the resolution limit of the conventional characterization techniques. Furthermore, as far as the magnetic properties are concerned, most of the emphasis has been given to the metastable single phase Fe-Cu alloy.^{19,31–33} However, bulk equilibrium Fe-Cu two phase alloys still require more research, e.g., comparison of the magnetic behavior with bulk Fe. In this work, we present the results of our investigation of nanosized phase separation, precipitation, and magnetic response of arc-melted Fe-Cu alloys. Magnetic response includes both low and high temperature magnetic irreversibility. Observation of bulk like negligible coercivity at low temperature, application of the law of approach of saturation (LAS), strain exhibited by constituent components, and the effect of post-preparation annealing are presented in detail.

II. EXPERIMENTAL DETAILS

Bulk Fe-Cu alloy was prepared by melting equal atomic ratio of Fe and Cu metal pieces of 99.99% purity in an arc furnace on a Cu hearth provided with water cooling under argon flow. The mixture was melted several times to ensure chemical homogeneity. The weight loss was found to be negligible. The Bruker D8 Discover X-ray diffractometer using a Cu K_α radiation was used for the XRD studies. Beam was collimated to a spot size of 1 mm to scan the sample. In order to investigate inhomogeneities at microscopic scale, XRD scans were recorded on different spots by collimating the beam to a size of 0.1 mm. The microstructure of the sample was investigated with the help of cross-sectional transmission electron microscopy (TEM) technique. TEM samples were prepared by using focused-ion-beam (FIB), Model Helios450, FEI Company. These specimens were then analyzed with FEI Company's Titan G2 80-300 CT TEM by operating it at the electron energy of 300 keV. Bright-field TEM (BF-TEM) and selected area electron diffraction (SAED) techniques were utilized to investigate the morphology and microstructure of the sample. It is to be noted that the SAED patterns were acquired with a typical camera length of 460 mm, while the BF-TEM micrographs were recorded in the range of 20 000 $\times$ to 100 000 $\times$ magnification. On the other hand, the high-resolution TEM (HR-TEM) analysis of samples, used to study the microstructure of sample at the atomic scale, was performed in the magnification range of 500 000 $\times$ to 700 000 $\times$. The BF-TEM, SAEDs, and HR-TEM micrographs were recorded with a 4k $\times$ 4k charged-coupled devices (CCD) camera of Model US4000 from Gatan, Inc. The values of d-spacing present in the SAED micrographs were measured by applying Circular Hough Transform because of its higher accuracy and convenience for determining these values compared with

manual methods.³⁴ The high-resolution bright and dark field TEM techniques were utilized for imaging of the matrix as well as the precipitates. Finally, the energy-filtering TEM (EF-TEM) analysis of samples was performed in the same microscope by using a post-column energy-filter of model GIF TridiemTM 863 also from Gatan, Inc. The EF-TEM analysis allowed acquiring the elemental maps of Fe and Cu, which showed the spatial distribution of these elements in the samples. It should be noted that Cu and Fe maps were generated by acquiring their Cu-L_{2,3} and Fe-L_{2,3} edges, respectively. Moreover, the so-called 3-window method was utilized to generate these maps.³⁵ Arc-melted and solidified sample is termed as “unannealed sample” and post-solidification annealed sample is termed as “annealed sample.” Annealing of the sample was performed under a reducing atmosphere (95% N₂–5% H₂). Sample temperature was raised to 500 °C in 2 h. The temperature was then sequentially increased to 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C with raise time between the two successive temperatures being 1 h. For all the aforementioned temperatures, up to 900 °C, the dwell time was 2 h. However, the dwell time for 1000 °C was 6 h. Sample was then cooled to 500 °C with the same rates and dwell times as during the heating cycle. From 500 °C to room temperature, sample was allowed to cool naturally. The surface of the annealed disc resembled copper metal color, which is an indication of Cu-rich surface.

III. RESULTS AND DISCUSSION

A. Structural analysis

Figure 1(a) shows room temperature XRD pattern of the arc-melted Fe-Cu alloy. Under equilibrium conditions, Fe and Cu are known to exhibit bcc and fcc structures, respectively. Reflections present in the pattern have been identified as (111), (200), and (220) crystal planes of Cu and (110) and (200) crystal planes of Fe lattice. The observation of these separate reflections suggests presence of phase separated Fe and Cu on the macroscopic scale. The values of lattice constant “*a*” for Fe and Cu metals are reported to be 2.860 Å (PCPDF # 870722) and 3.615 Å (PCPDF # 491568), respectively. Based on the peak position of (110) reflection, the values of “*a*” for Fe is calculated to be 2.868 Å. Similarly, the value of “*a*” for Cu, based on (111) reflections, is calculated to be 3.613 Å. Thus, the values of “*a*” for both metals are comparable with earlier reported values. It was expected that the values of “*a*” would change as a result of Fe and Cu mixing together. This similarity further suggests that both the elements retained their individual phases at the macroscopic level within the detection limit of the instrument. Although Fe and Cu concentrations were comparable, the peak intensities of the Cu (111) and Fe (110) reflections are found to be different, which indicates possible presence of inhomogeneity in the sample. To further investigate this aspect, XRD patterns were recorded at three different spots of the sample where X-ray beam was spatially small compared with the sample dimensions. The diffraction patterns from these spots are shown in Fig. 1(b). As is evident in these patterns, the recorded relative peak intensity ratio of

FIG. 1. (a) Room temperature XRD pattern of unannealed Fe-Cu. (b) Comparison of XRD patterns recorded at three different positions of the sample.

Cu (111) and Fe (110) reflections at these spots are different. This clearly shows presence of local phase inhomogeneities in the sample.

In order to further understand phase separation, inhomogeneities, and morphology, the sample was investigated in detail with TEM technique. BF-TEM micrographs, given in Figs. 2(a) and 2(b), show segregated region marked by “precipitates” in the micrograph. This finding corroborates the two phase formation that was observed with the XRD analysis. Moreover, the microstructures consist of large strips separated by very thin diffused regions. The strips regions have lengths in microns and their width vary between 50 and 100 nm, as shown in Figure 2(a). This indicates that one of the dimensions in the system is in the nanoscale range. However, the regions between these strips exhibit a distinct morphology where precipitates in a matrix can be observed (precipitates/matrix region). These precipitates regions could be Fe in Cu matrix or Cu in Fe matrix and are analyzed later. The SAED micrograph, shown

in Fig. 2(c), contains various diffractions spots that are forming Debye-Scherrer rings, indicating that the samples have a polycrystalline microstructure with both Cu and Fe grains randomly oriented with respect to the electron beam. Fig. 2(d) shows the Hough transform analysis applied to the SAED micrograph of Fig. 2(c) and is used to measure the distances of rings from the center. The measured distances represent the inter-planar d-spacing just like the case of XRD results. The results from Hough-transform analysis along with their corresponding crystal planes are given in Table I. As can be seen the measured interplanar distances correspond to various crystal planes due to elemental Fe and Cu. Together with XRD measurements, we do not find a conclusive evidence of the Fe and Cu alloying within the resolution and detection limit of both TEM and XRD techniques.

HRTEM micrographs along with its calculated fast-Fourier transform (FFT) are shown in Figs. 3(a) and 3(b), respectively. Here, two grains separated by grain-boundary (GB) were selected for FFT analysis. The FFT analysis of these grains revealed that one of the grains is of Cu with fcc crystal structure, while the other one is of α -Fe with bcc crystal structure. It further shows that the Cu grain was oriented along the [101] direction, while the α -Fe grain was also oriented along [101] direction. Therefore, HRTEM analysis allowed determining an orientation relationship between Cu and Fe grains, and it was found out to be α -Fe [101]//Cu [101]. In polycrystalline sample as in the present case, other orientations of Fe and Cu grains are also possible.

In order to confirm compositional gradient in the sample, to distinguish between strips and precipitate regions and to identify various regions compositionally, mapping was performed. Elemental maps were recorded from two selected regions that are shown in Fig. 2(a). Upper region shown in Fig. 2(a) was selected to analyze the strips, whereas lower region in the same figure was used to identify the precipitates/matrix region. Figs. 4 and 5 show those regions along with their Cu and Fe elemental maps. Respective elemental maps of Cu in these regions are shown in Figs. 4(b) and 5(b). Similarly, Figs. 4(c) and 5(c) show Fe elemental maps in these regions. Fe/Cu mapping images Red Green Blue (RGB) contrast [Fig. 4(d)] indicates that the strip regions are Cu-rich. Fe in these Cu-rich regions has very fine strand type structure. On the other hand, the precipitates/matrix regions are Fe-rich having Cu precipitates embedded in them, as shown in Fig. 5(d). Here, Fe is seen to form a mesh or

FIG. 2. (a) BF-TEM micrograph showing precipitates in the matrix as well as in alloys. (b) BF-TEM micrograph acquired at higher magnification. (c) SAED micrograph acquired for the same region shown in (b). (d) The Hough-transform analysis applied to the SAED micrograph of (c).

TABLE I. The values of the ring radius (R) and the interplanar spacing (d) extracted with the Hough transform analysis applied to the SAED micrograph of Fig. 2(c). Last column identifies various diffraction rings of the Fe and Cu lattices.

S. No	Radius (1/nm)	$d (= 1/\text{radius})$	Hough sum (weighted)	Profile peak	Centre X	Centre Y	Ring identification
1	3.744	0.267	7361	31	1037.287	1024.780	Moirés pattern
2	4.788	0.209	76 516	100	1040.155	1022.747	Cu(111)
3	5.308	0.188	30 263	40	1037.012	1022.467	Cu(200)
4	6.782	0.147	95 727	70	1039.537	1025.835	Fe(200)
5	7.550	0.132	6921	15	1036.870	1028.712	Cu(220)
6	8.370	0.119	46 241	33	1039.748	1021.116	Fe(211)
7	9.636	0.104	29 817	22	1041.839	1023.238	Cu(222)/Fe(220)
8	10.715	0.093	83 215	53	1039.827	1023.934	Cu(400)/Fe(310)
9	12.733	0.079	24 475	18	1038.909	1022.757	Cu(420)
10	13.730	0.073	20 345	17	1037.209	1026.456	Cu(422)

channel [see Figure 2(a)]. Cu islands of different shapes and various sizes are seen to be present between these Fe-rich regions. However, the presence of these clusters produces a discontinuity in Fe regions leading to reduction in the size of Fe regions to a nanoscale range at least in one dimension. Hence, the system after cooling from arc-melted state breaks into two regions. One of the regions is Fe-rich, where Fe forms matrix and Cu forms islands embedded in this matrix. The other region which is in the form of strips is Cu-rich carrying Fe strands. The sizes of Fe strand in these strips are also in nanoscale regime with typical sizes < 10 nm (Fig. 4(d)). Hence, the immiscible Fe-Cu forms dense bulk nanocomposites.

B. Magnetic properties

Figure 6(a) shows the magnetic hysteresis $M(H)$ loops of the sample measured at 5 K and 300 K. The values of the saturation magnetization (M_S) are 107 and 104 emu/g at 5 K and 300 K, respectively. The M_S value at 5 K corresponds to a magnetization of $2.13 \mu_B/\text{Fe atom}$. Both loops exhibited zero coercivity (H_c) and remanence. Absence of coercivity and remanence is commonly reported in materials synthesized with nanometric dimensions.³⁶ Here, as discussed in Section III A, in Cu-rich strips regions Fe exists in the form of strands. Similarly, in Fe-rich regions with Fe forming mesh or channel type structure and Cu as precipitates, the dimensions of the Fe regions are less than 100 nm at least along one direction. Both of these could possibly lead to a superparamagnetic behavior and to the observed lack of

remanence and coercivity. It can be argued that the magnetic components (due to Fe-rich regions) of the sample are in superparamagnetic state with blocking temperature (T_b) lying below 5 K. In order to accept or reject this hypothesis, M versus H/T plots for 5 and 300 K are shown in Fig. 6(b). It is well known that in the superparamagnetic regime, i.e., $T_b < T < T_C$, the nanoparticles follow Langevin paramagnetism, and the difference is that the classical moment μ is giant.³⁷ Here, T_C is Curie temperature, and for the present case, its value for bulk Fe is 1044 K.³⁷ Practically, superparamagnetic state can be confirmed if the reduced magnetization curves plotted as a function of H/T super impose over a wide range of temperatures T , i.e., $T_b < T < T_C$. Present system, even though with nanoscopic dimension, does not follow this criterion, as shown in Fig. 6(b). Therefore, it can be inferred from the magnetic analysis that the system does not exhibit superparamagnetism, even though the value of H_c is negligibly small. As far as the observed negligible coercivity is

FIG. 3. (a) HRTEM micrograph showing Cu and Fe grains that are separated by a Grain-Boundary (GB). (b) The calculated FFT of same micrograph showing $\alpha\text{-Fe}[101]/\text{Cu}[101]$ orientation relationship.

FIG. 4. The EFTEM-analysis of a strip region, with (a) showing bright field image of a selected area to be used for elemental mapping, (b) Cu elemental map, (c) Fe elemental map, and (d) RGB elemental map with Cu in green and Fe in red color.

FIG. 5. EFTEM analysis of an area containing precipitates, with (a) showing bright field image of a selected area to be used for elemental mapping, (b) Cu elemental map, (c) Fe elemental map, and (d) RGB elemental map with Cu in green and Fe in red color.

concerned, we can compare our results with the ones reported in literature. For the case of pure bulk iron, commercial polycrystalline iron, and single domain iron particles, H_c is reported to be equal to 12.6×10^{-3} , 12.6×10^{-1} , and 126 Oe, respectively.³⁸ Similarly, Ambrose *et al.*³⁹ also reported a small value of coercivity (~ 10 Oe) for bulk iron. Hence, when compared with the bulk reported values, negligible coercivity in the present case is not surprising as the overall morphology of Fe in this system is complex where iron is interfaced with Cu. These negligible values of coercivity and remanence (as shown in Fig. 6(a)) are likely due to the particular domain configuration (discussed earlier) as a result of minimization of the demagnetizing energy in these complex Fe structures.

Observation of negligible coercivity with the absence of superparamagnetism served as a motivation to investigate high temperature magnetization response, the anisotropy

FIG. 6. (a) $M(H)$ loops measured at 5 K and 300 K. (b) M vs H/T plots extracted from $M(H)$ loops measured at 5 K and 300 K. (c) The $M(T)$ behavior in 1000 Oe magnetic field. (d) The $M(T)$ behavior around 800 K.

constant, and effects of post annealing on various properties of sample. Magnetization as a function of temperature $M(T)$ was recorded in the presence of 1000 Oe field and results are shown in Figure 6(c). During the heating cycle, magnetization was found to change from 27.9 to 26.98 emu/g as the temperature increased from 300 to 1000 K. The variation in values of magnetization is small in this wide range of temperature ($300 \text{ K} < T < 1000 \text{ K}$) and matches well with the results reported by Ambrose *et al.*³⁹ In their report, they observed a sharp drop in the magnetization for temperatures greater than 1000 K and magnetization was found to vanish around 1050 K. Furthermore, we observe a small hump around 650 K in heating curve, which might be due to the compositional gradient, i.e., possible presence of small fraction of Fe in Cu or Cu in Fe. This aspect will be discussed later when the results of annealed samples will be presented. In addition to this, irreversibility in the magnetization curves between the subsequent thermal cycles is observed around 800 K as shown in Fig. 6(c). In the temperature range between 800 K and 900 K, the magnetization recorded during heating is slightly higher than the one recorded during cooling as shown in Fig. 6(d). This behavior can be ascribed to various factors, such as the exhibition of martensite-austenite $\alpha \rightarrow \gamma$ phase transition in Fe which is known to occur around 900 K,^{32,33} interaction between the Fe cluster,^{40,41} and due to the presence of inhomogeneities such as Cu impurities in Fe. Again we will discuss this point later in context with the analysis of the annealed sample.

Bulk Fe exhibits temperature dependence of anisotropy constant ($K(T)$), which approaches zero around 1000 K with a relatively small variation in the value of K within the range $77 \text{ K} < T < 300 \text{ K}$.⁴² Effective anisotropy of randomly oriented cubic crystals is proportional to the coercivity.⁴³ However, as reported by Perez *et al.*⁴⁴ response of the nanostructured Fe samples was strikingly different where coercivity decreases drastically from 550 Oe to 50 Oe as the temperature increases from 10 K to 75 K. In the same study, law of approach to saturation was used to extract anisotropy constant, which was calculated to be $2.5 \times 10^5 \text{ J/m}^3$, which is an order of magnitude larger than that of the bulk counterpart.⁴⁴ They attributed this increase in K to the presence of oxides at the interfaces. Tartaj *et al.*⁴⁵ extracted anisotropy constant of Fe nanocrystals of size 4–7 nm dispersed in spherical silica particle of diameter 150 nm and concluded that K depends on the nature of coating shell. In their studies, the value of anisotropy constant calculated from the blocking peak was found comparable with that of bulk value.

As discussed earlier, anisotropy constant for the nanostructures has been reported to be different as compared with their bulk counterpart. This motivated us to extract the values of anisotropy constant for the current system by exploiting the theories of approach to saturation. These approaches require the applied field to be larger than the coercive field. The rotation of the magnetization of the various components or domains in polycrystalline magnets increases the magnetization, and system approaches saturation as the applied field increases. In general, magnetization (M) as function of field (H) can have several terms, as proposed by Brown,⁴⁶ and can be expressed as

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{a}{H} - \frac{b}{H^2} - \dots \right] + \chi_p H + c\sqrt{H}. \quad (1)$$

The coefficient “ a ” was referred by Brown as due to the strain in the crystal lattice. However, Neel claimed that it is related to non-magnetic regions present within samples.⁴⁷ The coefficient “ b ” is related to the magnetocrystalline anisotropy of the sample. For a collection of cubic anisotropy axes being oriented in random directions, the coefficient b is related to anisotropy constant by the expression

$$b = \frac{8K_1^2}{105\mu_0^2 M_S^2}. \quad (2)$$

Here, K_1 represents the first cubic anisotropy constant. The linear term in Equation (1) is understood to be due to Pauli paramagnetism, and the coefficient χ_p is referred to as the Pauli susceptibility. The term proportional to $H^{1/2}$, as described by Holstein and Primakoff⁴⁸ is related to the effect of thermal or spin-wave excitations that give rise to the incomplete alignment of the moments. Various forms of LAS have been used to fit the experimental data using method of least squares, and values of anisotropy constant were extracted using Eq. (2). The different forms used for fitting are

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{b}{H^2} \right], \quad (3)$$

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{a}{H} - \frac{b}{H^2} \right], \quad (4)$$

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{b}{H^2} \right] + c\sqrt{H}, \quad (5)$$

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{b}{H^2} \right] + \chi_p H, \quad (6)$$

$$\mu_0 M(H) = \mu_0 M_S \left[1 - \frac{a}{H} - \frac{b}{H^2} \right] + \chi_p H. \quad (7)$$

The fits to the $M(H)$ data in the high field regions with the various forms of law of approach to saturation are shown in Fig. 7. As can be seen, all the equations give good fits to the experimental data. The values of anisotropy constant K_1 were obtained by using various LAS [Eqs. (3)–(7)] and then extracted from Eq. (2) as shown in Fig. 8. The variation in the possible value is so wide that nearly any value of K_1 is possible given an appropriate choice of fitting function and range of the magnetization data chose for the fit. Apart from the relatively large variations shown by Eq. (3), the values of K_1 by all the remaining equations are almost similar. As the range of the magnetization data chosen to the fit the $M(H)$ curve increases, the error decreases. The value of the K_1 is extracted to be equal to 1350 J/m^3 using emu per gram of Fe. This value is lower compared with that of the bulk counterpart [$4.7 \times 10^4 \text{ Jm}^{-3}$].³⁷

It has been reported that the values of K_1 depend on interface⁴⁹ or finite size of the magnetic system.⁵⁰ In case of magnetic nanoparticles, surface anisotropy contributes to the overall anisotropy of particles, which arises due to the lower

FIG. 7. Various fits of law of approach to saturation to the experimental $M(H)$ data.

coordination and broken symmetry at surface.^{51,52} Rusponi *et al.*⁵³ reported that the atoms residing at the edge of the two dimensional cobalt islands contribute significantly to the anisotropy. Another study based on the micro-SQUID measurement revealed that the anisotropy of cobalt clusters embedded in matrix can be varied by changing the cluster matrix interface.⁵⁴ In the present studies low value of the K_1 seems to result from the Fe/Cu interface with a possibility of interface alloying. However, it not possible to comment on K_1 dependence on the interaction between the nanoscopic Fe regions. Another feature in the present study is the small variation in values of M_S and similar functional form of $M(H)$ loops recorded at 5 and 300 K. This is expected to yield similar values of anisotropy constant at these temperatures. This trend matches with that for pure Fe where the value of K_1 measured at 50 and 300 K are reported to be similar.⁴² Furthermore, the complex configuration of nano-metric size Fe may lead to the domain configuration, which minimized the demagnetization energy of the system and hence resulted in the observed low H_c and K_1 values.

FIG. 8. Anisotropy constant K_1 variation obtained from the various LAS equations versus $M_{\min}/M_{\max}$.

C. Effect of annealing

In order to homogenize the sample, annealing in reducing atmosphere (5% H_2 –95% Ar) was performed at high temperatures close to the melting point of Cu (detail is given in Section II). Figure 9(a) shows the room temperature XRD pattern and Fig. 9(b) shows the XRD patterns recorded at three different spots of the annealed sample. As is evident in these patterns, the peak intensity ratio corresponding to Cu (111) and Fe (110) reflections at these separate spots are different. Thus, similar to the unannealed case, Fe and Cu retained their individual phases on the macroscopic scale, and the peak intensity of the Cu (111) and Fe (110) reflections remained different even though the concentrations of Fe and Cu were comparable. This confirms the presence of local phase inhomogeneities even in the annealed sample, and preferential orientation remains similar to that of the unannealed sample.

In order to explore finer structural differences between the as-prepared and annealed samples, high resolution XRD patterns of the as-prepared and annealed samples for the most intense peaks, i.e., (110) and (111) peaks, are shown in Fig. 10. Full width at half maxima is much smaller for annealed sample compared with the unannealed sample for both Fe and Cu reflections, which indicates the possible increase in the grain size and/or reduction of homogenous strain upon annealing. There is no significant change in the peak position of Cu for the annealed sample, and the value of lattice parameter ($a = 3.612 \text{ \AA}$) matches well with that of unannealed case ($a = 3.613 \text{ \AA}$). However, there is a shift in the position of (110) peak of Fe toward higher 2θ values upon annealing, and the value of “ a ” is found to be equal to $2.864 \text{ \AA}$ which is slightly smaller than the value in unannealed case. This shift in the peak position of Fe towards higher 2θ values (i) rules out the possibility of Cu substitution into Fe and (ii) indicates the emergence of homogeneous strain in Fe lattice. Similar to the unannealed case, there is no mixing of Fe and Cu (i.e., alloying) in the annealed sample as well.

Peak broadening in nanostructures arises due to the crystal size and inhomogeneous strain.^{55,56} The broad and symmetric peaks associated with Fe and Cu for the unannealed sample show presence of inhomogeneous strain. The unannealed sample is also strained due to the rapid solidification of the alloy from the molten state with the Fe and Cu nano regions randomly distributed, as shown by the electron microscopy studies. Inhomogeneous strain in the unannealed

FIG. 9. (a) Room temperature XRD pattern of annealed Fe-Cu sample. (b) The comparison of XRD patterns recorded at three different spots of sample.

FIG. 10. High resolution XRD pattern of unannealed and annealed Fe-Cu sample.

sample can be estimated by comparing its XRD peak FWHM with that of annealed sample. Annealing leads to the reduction the FWHM due to removal of inhomogeneous strain, and FWHM is primarily due to crystal size only. Hence, subtraction of FWHM of the annealed sample from the FWHM of the unannealed sample yields broadening ($\Delta\beta$) associated with the inhomogeneous strain of the unannealed sample. This procedure also subtracts contribution from the instrument broadening. Using this procedure, the broadening due to the inhomogeneous strain in Cu and Fe for the unannealed sample was obtained to be equal to 0.0017 and 0.0031, respectively. The relationship between the mean inhomogeneous strain (ϵ) and the peak broadening is $\Delta\beta = 4\epsilon \tan \theta$. Inhomogeneous strain in the unannealed sample within the Cu and Fe crystallites is calculated to be equal to 0.0045 and 0.0078, respectively. However, as the sample is annealed, Fe exhibits strain which is homogeneous, as evident from the shift of the peak towards larger 2θ values. It also seems that post annealing yielded reorientation of the crystals. Unlike Cu, signature of homogeneous strain in annealed sample for the Fe region requires additional orientation dependent structural investigation.

Figure 11(a) shows the $M(H)$ loops of the annealed sample measured at 5 K and 300 K. Similar to unannealed sample, both low and high temperature loops exhibited zero coercivity and remanence. Both loops have different slope and saturation fields. This fact points towards the presence of an easy magnetization axis in the sample, and the value of anisotropy increases with lowering the temperature. Partial alignment observed from XRD data after the annealing also led to the observation of change in the hysteresis (measured at 5 K and 300 K) compared with that of the unannealed sample as shown in Fig. 6(a). Magnetization as a function of temperature was recorded in the presence of 1000 Oe field and the results are shown in Figure 11(b). Irreversibility in the magnetization curves between the subsequent thermal cycles is also observed around 800 K and matches well with that of the unannealed case. Similar to the behavior in the unannealed case, $M(T)$ values during the heating cycle are slightly higher than during cooling in the temperature range between 800 K and 900 K.

FIG. 11. (a) $M(H)$ loops of annealed sample measured at 5 K and 300 K. (b) The $M(T)$ behavior of sample in presence of 1000 Oe magnetic field.

In summary, we have probed local phase separation in Fe-Cu. In Fe-rich regions, Cu appears in clusters of various sizes and shapes, while in the Cu-rich regions Fe appears in the form of strips. The magnetic moment of Fe atom is comparable with that of the bulk. However, the values of the anisotropy constant are less than that of the bulk and the difference has been attributed to the presence of the complex environment for the Fe atom and reduced dimensions. There was no observable change in the magnetic response with the post synthesis annealing of the sample. For both as-solidified and annealed samples, 20% decrease in the value of magnetization is observed between room temperature and 1000 K. Missing signature of superparamagnetism revealed ferromagnetic character with negligible bulk like coercivity. Magnetic irreversibility was observed between 800 K and 900 K, which matches with the martensite-austenite $\alpha \rightarrow \gamma$ phase transition temperature of bulk Fe.

¹See <http://www.crct.polymtl.ca/fact> for SGTE alloy databases.

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