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LETTER TO THE EDITOR

Magnetic properties of mechanically alloyed FeCu

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Abstract. The temperature dependence of saturation magnetization has been observed for an unstable FCC $Fe_{50}Cu_{50}$ solid-solution sample prepared by mechanical alloying. The unstable FCC $Fe_{50}Cu_{50}$ solid solution has a Curie temperature of 505 ± 5 K. At low temperatures the saturation magnetization is well approximated by the relationship $M(T) = M(0)(1 - BT^{3/2})$, where $M(0)$ = 108.7 emu g^{-1} and $B = 4.21 \times 10^{-5}$ $K^{-3/2}$. This holds over a large temperature range ($T/T_C < 0.4$) indicating the presence of long-wavelength spin-wave excitations and disordered atomic structure. On annealing the as-milled sample at annealing temperatures above about 500 K, decomposition of the metastable FCC $Fe_{50}Cu_{50}$ solid solution was observed. The magnetic moment of Fe atoms in the FCC $Fe_{100-x}Cu_x$ phases remains at about $2.35\mu_B$ for $50 < x < 61$, and drops rapidly to $0.544\mu_B$ for $x = 70.7$. This results in the 40% reduction of the saturation magnetization at zero temperature for the sample annealed at 673 K for 1 h when compared to that for the as-milled sample. The Curie temperature of the FCC $Fe_{29.3}Cu_{70.7}$ solid solution falls to about 200 K.

1. Introduction

In the equilibrium state, the solid solubility between Fe and Cu is negligible at room temperature and, for a wide composition range, Fe and Cu do not form solid solutions. In recent years, the formation of metastable $Fe_{100-x}Cu_x$ solid solutions with a wide range of composition by mechanical alloying has attracted much interest [1–5]. These solutions have the FCC structure when $x > 40$ and the BCC structure when $x < 20$. For $20 < x < 40$ two phases coexist. In our previous work [5, 6], an unstable FCC $Fe_{50}Cu_{50}$ solid solution was prepared by mechanical alloying of elemental Fe and Cu powder blends. The alloying process, the structure and the decomposition behaviour of the solid solution were studied using x-ray diffraction and Mössbauer spectroscopy. Initially, the milling process reduces the crystallite sizes of both elemental powders. After 20 h milling, some Fe particles are transformed into the FCC structure. Due to the structural similarity of the FCC Fe and FCC Cu phases, composites consisting of coherent Cu and Fe regions are formed. The increasing density of interfaces during further milling results in an interdiffusion of Cu and Fe. The alloying process was monitored by Mössbauer investigation, which showed an increasing Fe concentration in FCC Cu. After 50 h of milling, the Fe and Cu are alloyed on an atomic level to form an FCC $Fe_{50}Cu_{50}$ phase, in which many different environments of Fe atoms exist.

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The FCC $Fe_{50}Cu_{50}$ phase is unstable. In the initial state of decomposition, Fe atoms precipitate coherently in the FCC FeCu matrix as FCC Fe particles. At higher annealing temperatures the particle size increased, and the structure of the Fe particles transforms from FCC to BCC. A summary of results for the metastable FCC $Fe_{50}Cu_{50}$ solid solution (as-milled sample) and annealed samples is shown in table 1.

Magnetic properties of sputtered $Fe_{100-x}Cu_x$ films have been studied previously [16, 17]. However, little work has been reported for the FeCu solid solution prepared by mechanical alloying. Uenishi *et al* [2] observed for the FCC $Fe_{100-x}Cu_x$ phase from 40 to 60 at.% Cu that the magnetic moment per Fe atom at 77 K is sensitive to composition. It was also reported that the saturation magnetization at room temperature was the same for as-milled FCC $Fe_{50}Cu_{50}$ sample and the sample annealed at 760 K [3]. However, the experimental results concerning the magnetic properties of the FCC FeCu solid solution prepared by mechanical alloying are not completely understood. Therefore, in this letter, we extend our previous work [6] and report on a detailed study of the magnetic properties of the as-milled FCC $Fe_{50}Cu_{50}$ and annealed samples. A reasonable explanation of the temperature dependence of their saturation magnetization is presented.

Table 1. Our previous data for the as-milled FCC $Fe_{50}Cu_{50}$ and annealed samples: the lattice constant of the FCC phase, crystallite sizes of the FCC and BCC phases, the distribution of the iron in the various phases given in atomic per cent with respect to the total amount of Fe and the average hyperfine field of the FCC FeCu phase in the as-milled and annealed samples.

	As-milled	473 K	573 K	673 K	873 K
Lattice constant of the FCC FeCu phase (nm)	0.3643	0.3641	0.3637	0.3619	0.3618
Crystallite size of the FCC FeCu phase (nm)	*18*	*19*	*24*	*39*	*45*
Amount of Fe incorporated in the FCC FeCu phase	93.5	90.4	65.7	41.5	0.0
Average hyperfine field of the FCC FeCu phase at room temperature (kOe)	206	201	185	0	—
Amount of Fe incorporated in the FCC Fe phase	1.1	2.4	4.9	6.8	7.8
Crystallite size of the BCC Fe phase (nm)	—	10	13	37	49
Amount of Fe incorporated in the BCC Fe phase	5.4	7.2	29.4	51.7	92.2

2. Experimental details

For the preparation of FeCu alloys, powders of Fe (99.9%) and Cu (99.9%) with particle sizes smaller than 100 μm were mixed to a nominal composition of 50 at.% Fe and sealed in a vial in an Ar atmosphere (see [5] for details). After a milling time of 100 h, the sample consists of pellets of about 0.7 mm in diameter and about 0.3 mm in thickness. The compositions in the sample were determined by using scanning electron microscopy (SEM) with an energy-dispersive x-ray analysis (EDX) facility. About 0.9 at.% additional Fe and 0.35 at.% Cr could be determined, which originate from the abrasion of the vials and balls. The FCC structure of the as-milled sample was determined by x-ray diffraction. Annealing treatments of the samples were performed in silica tubes in a vacuum of 1.2×10^{-3} Pa at 473 K, 573 K, 673 K and 873 K for 1 h. The heating time and temperature were chosen to be consistent with our earlier study [6].

Magnetic measurements of the as-milled FCC $Fe_{50}Cu_{50}$ alloy and the annealed samples were carried out using a vibrating sample magnetometer (VSM) in a temperature range from 5 K to 295 K and in magnetic field of 1 T. Only the as-milled sample was measured at high temperature, up to 750 K, by heating at a rate of 5 K min^{-1}.

3. Results and discussion

The saturation magnetization ($M(T)$) of the as-milled FCC $Fe_{50}Cu_{50}$ alloy as a function of temperature, measured in a 1 T field, is shown in figure 1. The magnetization decreases with increasing temperature up to about 510 K. With further increase in temperature, the magnetization increases. By extrapolation of the curve below this minimum to zero magnetization the Curie temperature for the metastable FCC $Fe_{50}Cu_{50}$ solid solution is estimated to be T_C 505 ± 5 K. The temperature dependence of the saturation magnetization can be explained by the decomposition of the unstable FCC $Fe_{50}Cu_{50}$ alloy. As table 1 shows, all samples studied consist of three phases, FCC $Fe_{100-x}Cu_x$ with $x > 50$ (or FCC FeCu), FCC Fe and BCC Fe. The relative amount of each phase in the samples depends on the annealing temperature. When the annealing temperature reaches 473 K, the unstable FCC $Fe_{50}Cu_{50}$ phase begins to decompose into FCC FeCu, FCC Fe and BCC Fe phases. With higher annealing temperatures the amount of the BCC Fe phase rapidly increases at the expense of the Fe content in the FCC FeCu phase. It is known that the BCC Fe phase has a very high Curie temperature of 1042 K and a saturation magnetization at room temperature of 218.0 emu g^{-1} [7]. From this it can be evaluated that the saturation magnetization of the BCC Fe phase varies from about 208 emu g^{-1} at 500 K to about 185 emu g^{-1} at 750 K. However, for the FCC FeCu phase the saturation magnetization falls to zero above 505 K. Therefore, the temperature dependence of the saturation magnetization of the as-milled sample can be easily explained. Initially, the saturation magnetization of the FCC $Fe_{50}Cu_{50}$ decreases with increasing temperature. For temperatures above 500 K, the BCC Fe phase is formed. The amount of BCC Fe phase rapidly increases in the sample as the temperature is increased. This accounts for the increase of the saturation magnetization in the sample with temperature above 510 K.

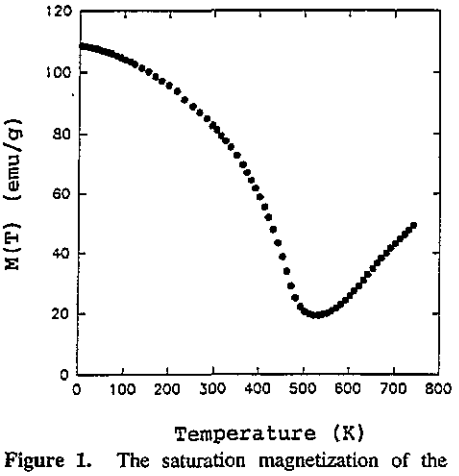

Figure 1. The saturation magnetization of the as-milled FCC $Fe_{50}Cu_{50}$ solid solution as a function of temperature.

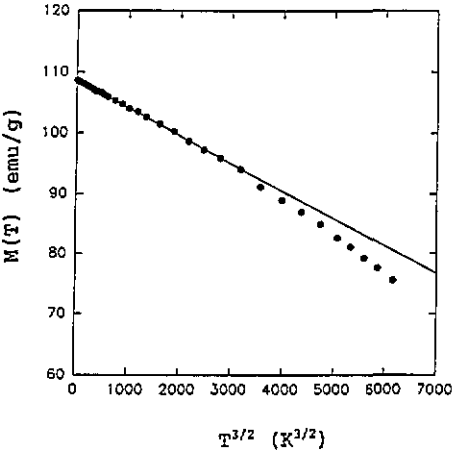

Figure 2. The saturation magnetization as a function of $T^{3/2}$ for the as-milled FCC $Fe_{50}Cu_{50}$ solid solution. The solid line was fitted using $M(T) = M(0)(1 - BT^{3/2})$ with $M(0)$ = 108.7 emu g^{-1} and B = 4.21 × 10^{-5} $K^{-3/2}$.

The saturation magnetization for the as-milled FCC $Fe_{50}Cu_{50}$ alloy at temperatures lower than 340 K has been plotted as a function of $T^{3/2}$ in figure 2. From this plot,

it is clear that the data lie on a straight line with $M(0) = 108.7$ emu g^{-1} and a slope of -0.00457 emu g^{-1} K$^{-3/2}$ over a large temperature range (up to about 200 K or $0.4T_C$). This indicates the excitation of long-wavelength spin waves in the sample at low temperature. According to Bloch's law, $M(T)/M(0) = 1 - BT^{3/2}$, or $(1 - M(T)/M(0)) = B_{3/2}(T/T_C)^{3/2}$. The values of the parameters B and $B_{3/2}$ for the as-milled FCC $Fe_{50}Cu_{50}$ alloy are listed in table 2, along with data for some amorphous alloys and crystalline Fe and Ni. B and $B_{3/2}$ values for the as-milled FCC $Fe_{50}Cu_{50}$ alloy are many times larger than those for Fe and Ni, but are similar to those for the amorphous alloys. It has been found that the disordered atomic structure in amorphous alloys leads to an increase in the spin-wave density of states at low excitation energies [10, 11]. Consequently, the larger values of B and $B_{3/2}$ in the unstable FCC $Fe_{50}Cu_{50}$ solid solution imply that the atomic structures are very disordered. This is in good agreement with our previous results obtained by Mössbauer spectroscopy measurements [5, 6].

Table 2. The coefficients B and $B_{3/2}$, and Curie temperature T_C, for the as-milled FCC $Fe_{50}Cu_{50}$ solid solution with data for various amorphous alloys and crystalline Fe and Ni.

Sample	$B_{3/2}$	B (10^{-6} K$^{-3/2}$)	T_C (K)	Reference
$Fe_{80}B_{20}$	0.40	22	685	[8]
$Fe_{75}P_{15}C_{10}$	0.36	23	619	[8]
$Fe_{80}P_{16}BC_3$	0.36	25	590	[8]
$Fe_{40}Ni_{40}P_{14}B_6$	0.47	38	537	[8]
$Fe_{29}Ni_{38}P_{14}B_6Si_2$	0.48	65	377	[8]
Crystalline FCC $Fe_{50}Cu_{50}$	0.478	42.1	505	present work
Crystalline Fe	0.114	3.4	1042	[9]
Crystalline Ni	0.117	7.5	627	[9]

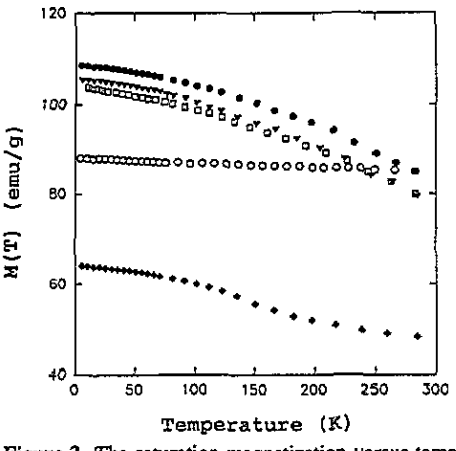

Figure 3. The saturation magnetization versus temperature for the as-milled FCC $Fe_{50}Cu_{50}$ solid solution (●) and samples annealed at 473 K (▼), 573 K (□), 673 K (♦) and 873 K (○), respectively.

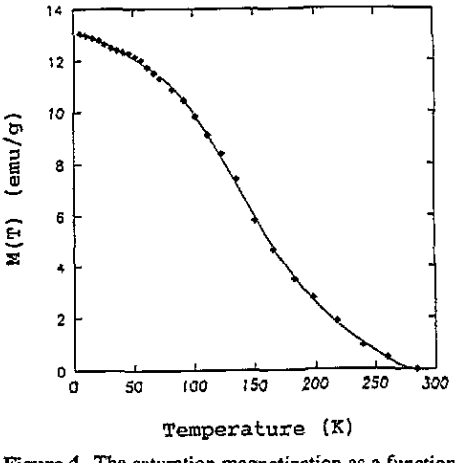

Figure 4. The saturation magnetization as a function of temperature for the FCC $Fe_{29.3}Cu_{70.7}$ phase in the sample annealed at 673 K for 1 h. The data were obtained by extracting the contribution of the BCC Fe phase from the original data.

Figure 3 shows the curves of saturation magnetization versus temperature for the as-milled FCC $Fe_{50}Cu_{50}$ alloy and the samples annealed at 473 K, 573 K, 673 K and 873 K for 1 h, respectively. It is clearly seen that the value of the magnetization at zero temperature $M(0)$ depends on the annealing temperature, and that the value does not vary linearly with the annealing temperature. After low-temperature annealing ($\leqslant$ 573 K), the magnetization is slightly reduced (less than 5%) compared to that for the as-milled sample. However, for the sample annealed at 673 K, the magnetization is about 40% less than that for the as-milled sample. By further increasing the annealing temperature to 873 K, the value of magnetization was increased to 87.9 emu g^{-1}. Although the saturation magnetization at room temperature is the same for the as-milled sample and the sample annealed at 873 K, in agreement with the result obtained by Yavari *et al* [3], their magnetization behaviours at low temperature are very different. The saturation magnetization versus temperature curve for the sample annealed at 873 K is very flat from 5 K to 285 K. This is characteristic of the BCC Fe phase. From the data in table 1, it is known that the sample annealed at 873 K consisted of three phases: FCC Cu, FCC Fe and BCC Fe phases. Therefore, by assuming no magnetic moment for the Cu atoms, it can be obtained that the FCC Fe phase also has a negligible contribution to the saturation magnetization of the sample. This is consistent with the antiferromagnetic state of the FCC Fe phase.

Under the assumption that the pure Cu does not precipitate, by using the data in table 1 for the distribution of Fe atoms in various phases, the Fe concentration dependence of saturation magnetization per Fe weight in the FCC $Fe_{100-x}Cu_x$ alloys can be evaluated, as shown in table 3. It can be seen that the magnetic moment of the Fe atoms in FCC $Fe_{100-x}Cu_x$ alloys has a large value of about $2.35\mu_B$ down to $x = 60.4$. This then drops rapidly to about $0.544\mu_B$ for $x = 70.7$. Based on experimental data and the band theory of ferromagnetism for Fe alloys [12–15], it has been proposed that an Fe atom with a larger atomic volume has a larger magnetic moment. The lattice constant of the FCC $Fe_{100-x}Cu_x$ alloys with $50 < x < 61$ is about 0.364 nm, which is comparable to those observed for the ferromagnetic FCC Fe alloys [12, 14]. On the other hand, for $x = 70.7$ the lattice constant is only 0.3619 nm. Therefore, it is expected that the Fe atom has a large magnetic moment in FCC $Fe_{100-x}Cu_x$ for $50 < x < 61$ and a small magnetic moment for $x = 70.7$. A similar result has been also reported in other mechanically alloyed $Fe_{100-x}Cu_x$ samples [2] and in sputtered $Fe_{100-x}Cu_x$ films [16].

Table 3. The saturation magnetization at zero temperature $M(0)$, the Fe concentration and the magnetic moment of the Fe atom for the FCC $Fe_{100-x}Cu_x$ phase in the as-milled and annealed samples. The saturation magnetization at zero temperature per alloy weight is also given.

	As-milled	473 K	573 K	673 K
Fe percentage in the FCC $Fe_{100-x}Cu_x$	48.3	47.5	39.6	29.3
$M(0)$ per alloy weight (emu g^{-1})	108.7	105.7	103.7	64.2
$M(0)$ per Fe weight (emu g^{-1})	235.7	232.3	238.1	54.4
Magnetic moment of Fe atom (μ_B/atom)	2.358	2.323	2.382	0.544

For the sample annealed at 673 K for 1 h, it was found [6] that the FCC $Fe_{29.3}Cu_{70.7}$ phase is in a paramagnetic state at room temperature. In order to obtain the Curie temperature of this phase, the saturation magnetization data for the sample annealed at 673 K were extracted from the contribution of the BCC Fe phase. The temperature dependence of the saturation magnetization of the FCC $Fe_{29.3}Cu_{70.7}$ phase can be obtained, as shown in figure 4.

The Curie temperature, estimated from the plot, is about 200 K for this phase, which is in good agreement with the result obtained from the sputtered $Fe_{100-x}Cu_x$ films [16, 17].

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