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Characterization of the metastable Cu-Fe nanoparticles prepared by the mechanical alloying route

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Abstract
Although Cu and Fe are immiscible under equilibrium conditions, they can form supersaturated solid solutions by mechanical alloying. In this paper, nano-structured of the metastable Cu-Fe phase containing 10, 15, 20 and 25% wt Fe were synthesized by intensive ball milling for 15h, in order to achieve a solid solution of Fe in Cu. The phase composition, dissolution of the Fe atoms into the Cu matrix, and the morphology of the milling products were studied by X-ray Diffraction (XRD), Energy Dispersive Spectrometer (EDS), and Field Emission Scanning Electron Microscope (FESEM) techniques, respectively. The mean crystallite size of the milled samples was determined by XRD peak broadening using the Williamson-Hall approximation. The XRD analysis results showed that the solid solubility of the Fe in the Cu was extended to 20%wt after milling for 15 h, and a homogeneous solid solution of $Cu_{80}Fe_{20}$ with a mean crystallite size of 19nm was obtained. The mean crystallite size decreased with increasing milling time and it was more evident in the initial stage of the milling. The Cu lattice parameter increased by dissolving the Fe into the Cu matrix probably due to the magneto-volume effect in the Cu-Fe alloys. The FESEM observations showed that the milling products were agglomerates consisting of uniform particles. The Vibrating Sample Magnetometer (VSM) results showed that the $Cu_{80}Fe_{20}$ powder has soft magnetic properties.

Keywords: *Cu-Fe, Mechanical alloying, Metastable, Nano-structure.*

1. Introduction

Binary Cu-base metastable alloys containing a bcc transition metal have been the subject of research for many years because of the limited solubility of these metals in Cu, which allows for high conductivity and strength in the alloys simultaneously [1]. Among them, the Cu-Fe alloys have attracted a lot of interest not only due to their high strength and high electrical conductivity [2], but also for their outstanding magnetic properties [3-5] and the lower price of Fe compared with the other metals such as W, Nb, V, and Ag [6]. The latter makes it possible to synthesize the Cu-Fe solid solutions on a large scale for their potential

applications. It has been proved that mechanical alloying is a useful method for synthesizing supersaturated solid solutions [7]. A considerable amount of work has been done on the synthesis of metastable Cu-Fe alloys and it has been shown that mechanical alloying can produce extensive solid solutions in these alloys [8, 9]. But most of the investigations had long milling durations which caused the formation of large particles. Limits of the solubility of the Fe in the Cu change considerably in the mechanically alloyed systems. Lots of studies have focused on the Cu-Fe alloying system with various compositions and showed that different structures were obtained for various compositions. For example Eckert *et al*., synthesized the nano-crystalline Fe_xCu_{1-x} powders with a wide range of composition and showed that the single phase fcc alloys and single phase bcc alloys are formed with x<60 and with x>80, respectively, after 24 h milling. For 60<x<80 both fcc and bcc phases coexist [10]. However, characterization of the metastable phases is still a challenging issue. In this paper, the supersaturated Cu-Fe solid solutions with different Fe contents were synthesized by mechanical milling for 15 h and the milling products were characterized using XRD, FESEM, EDS and VSM techniques.

2. Experimental

The starting materials were commercially pure Cu and Fe powders (99%, <150 μm). Mixtures of Cu and Fe having weight proportions of $Cu_{90}Fe_{10}$, $Cu_{85}Fe_{15}$, $Cu_{80}Fe_{20}$, and $Cu_{75}Fe_{25}$ were intensively milled in a planetary ball mill with steel vials and balls under argon atmosphere up to 15h. The ball to powder weight ratio and milling speed were 20:1 and 300 rpm, respectively. Phase composition and dissolution of the Fe into the Cu matrix were studied by XRD using a Philips PW-3710 diffractometer with Cu Kα radiation. The XRD peak broadening using the Williamson-Hall approximation was applied to determine the mean crystallite size of the milled powders. The morphology of the milling products was studied by Hitachi S4160 FESEM and the chemical composition of the samples was analyzed by the Bruker X-Flash silicon Drift type EDS detector. The magnetic properties of the $Cu_{80}Fe_{20}$ sample were investigated using the Vibrating Sample Magnetometer (VSM) apparatus under the maximum magnetic field of 10 kOe.

3. Results and Discussion

The XRD patterns of the samples milled for 15 h are shown in Figure 1. It is obvious that only the Cu diffraction peaks exist in the patterns of all the samples, except for $Cu_{75}Fe_{25}$, in which a very small peak of Fe is observed. It illustrates that up to 20%wt Fe can be dissolved in the Cu after milling for 15h. Figure 2 shows the diffraction patterns of the $Cu_{80}Fe_{20}$ sample milled for various times. By increasing the milling time, the average intensity of the peaks decreased and the peaks are broadened due to the crystallite refinement. In addition, the displacement of the Cu peak positions to smaller angles by increasing the milling time due to the expansion of the Cu lattice parameter occurs. This is related to the dissolution of the Fe in the Cu, although it is not in agreement with the smaller atom size of the Fe compared with the Cu.

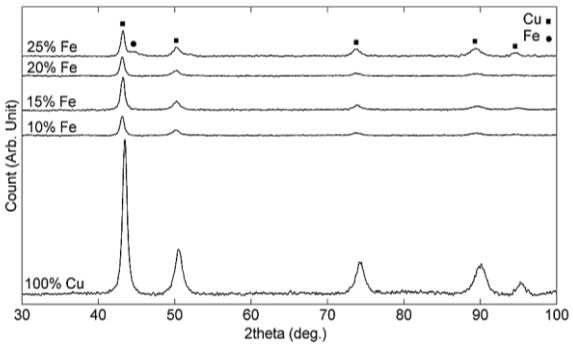

Fig. 1. XRD patterns of the Cu-Fe solid solutions with different Fe content (%wt.) milled for 15h

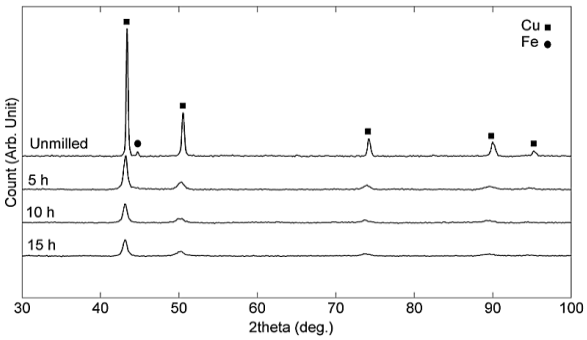

Fig. 2. XRD patterns of the $Cu_{80}Fe_{20}$ powders milled for various times

Expansion in the Cu lattice parameter could be attributed to the magneto-volume effect in the Cu-Fe alloys, which is due to the stronger core-core repulsion between the Cu atoms when the magnetic Fe nanoparticles are alloyed into the Cu matrix [11]. These results show the formation of the supersaturated $Cu_{80}Fe_{20}$ solid solution in the 15h milled sample. The changes in average crystallite size and lattice parameter by milling time for all samples are shown in Figure 3(a) and (b) respectively. Mean crystallite size decreased by increasing milling time and decreasing Fe content. The average crystallite size of the $Cu_{80}Fe_{20}$ supersaturated solid solution formed after milling for 15h was calculated to be about 19nm. The $Cu_{80}Fe_{20}$ sample was also milled for 30 h and according to Figure 3, further milling (>15 h) had negligible effect on both the lattice parameter and the mean crystallite size of this sample. It shows the complete dissolution of the Fe in the Cu in a 15 h milled $Cu_{80}Fe_{20}$ sample and it is the evidence for the steady state of mechanical alloying after 15 h. According to Figure 3(b), lattice parameter for all samples increased by increasing milling time except for sample $Cu_{95}Fe_5$. It can be said that small amount of Fe in this sample in not enough to result in magneto-volume interaction and increasing the lattice parameter. The FESEM images of the different samples milled for 15h are shown from Figure 4(a) to 4(d). It can be seen that the powders consist of agglomerations of nanoparticles. As shown in Figure 4c, the particles of the $Cu_{80}Fe_{20}$ sample are more uniform compared with the other samples and its average particle size is about 25nm. The corresponding EDS results of the $Cu_{90}Fe_{10}$, $Cu_{85}Fe_{15}$, and $Cu_{80}Fe_{20}$ samples, which are supposed to be uniform solid solutions, are summarized in Table 1. The given values are the average composition of the elements at different points. As can be seen, the composition of the elements after 15h milling is very close to the initial composition, which means that the impact energy of the milling has provided the required energy for the diffusion of the Fe into the Cu in a non-equilibrium state and alloying has occurred between these immiscible elements.

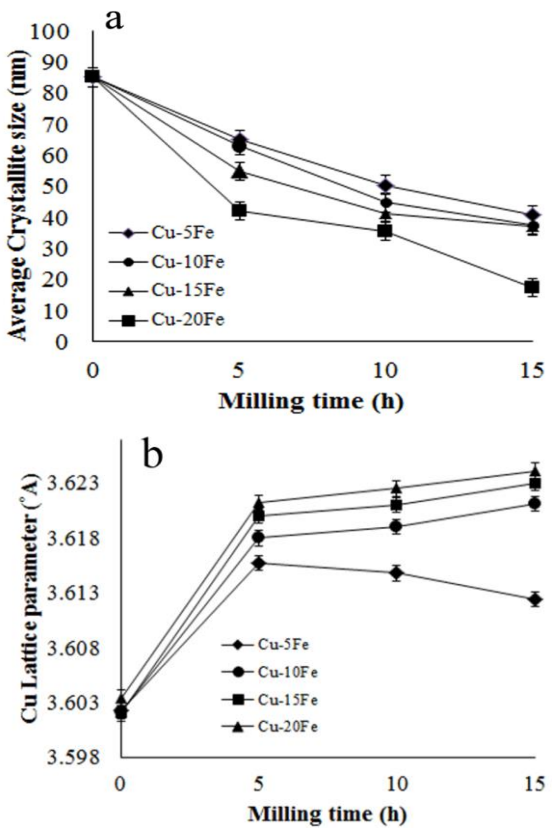

Fig. 3. a) Average crystallite size, and b) lattice parameter of samples for various milling times

Table 1. EDS analysis of the samples correspond to the images of Fig. 4

	$Cu_{90}Fe_{10}$	$Cu_{85}Fe_{15}$	$Cu_{80}Fe_{20}$
%Cu-K	88.71	84.14	79.21
%Fe-K	10.98	14.87	19.95

The magnetic properties of the $Cu_{80}Fe_{20}$ powder were also investigated using the VSM apparatus to make sure that there is not any un-dissolved Fe in this sample. Figure 5 shows the hysteresis loop of magnetization for the $Cu_{80}Fe_{20}$ powder milled for 15h. The saturation magnetization of the sample was 7emu/g, which is in agreement with the previous works which shows that the sample powder is supersaturated solid solution [9]. The measured coercive field (H_c) was about 27Oe, which indicates that the supersaturated $Cu_{80}Fe_{20}$ powder has soft magnetic properties. However, they have smaller magnetization due to the smaller Fe content.

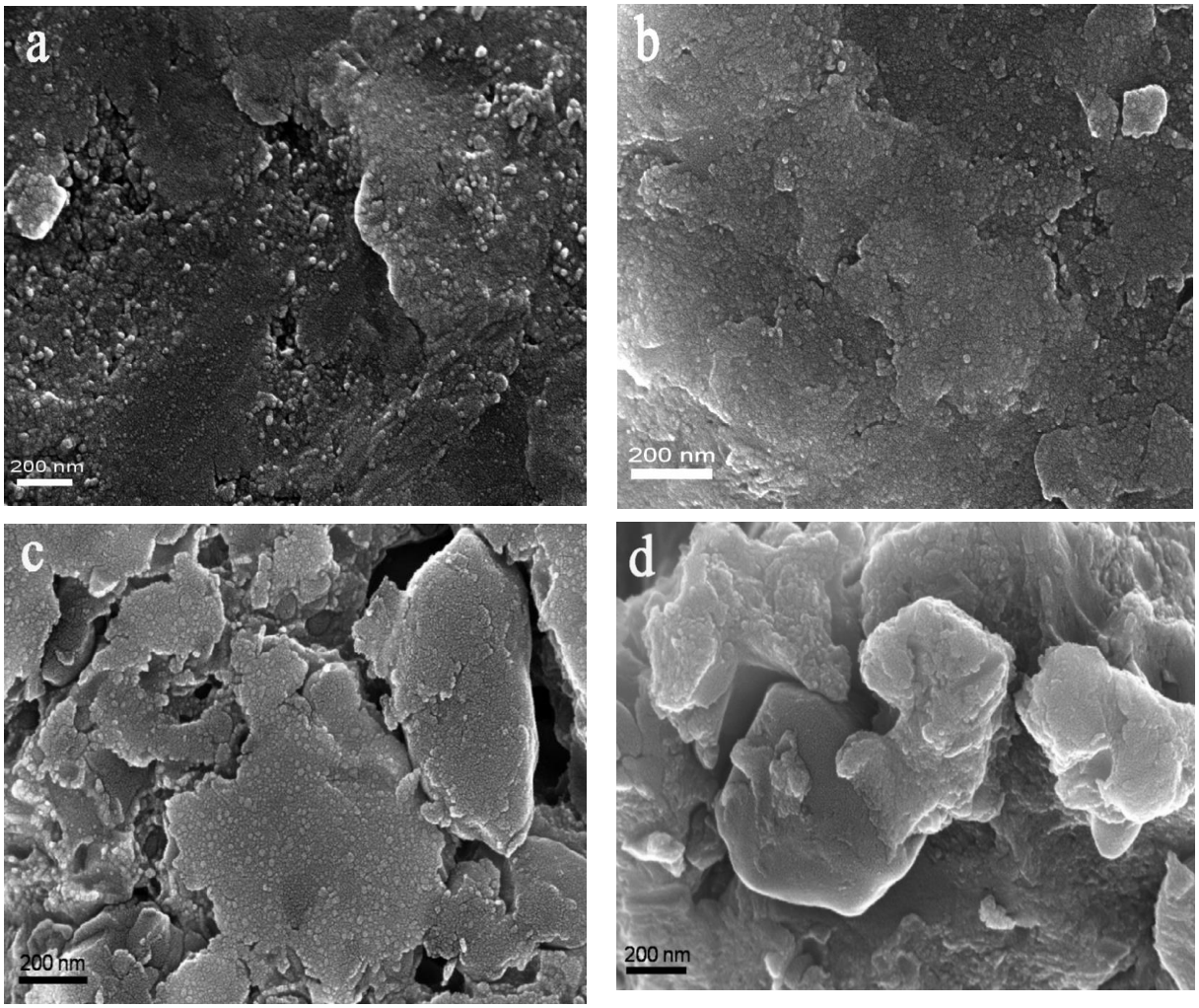

Fig. 4. FESEM images of (a) $Cu_{90}Fe_{10}$, (b) $Cu_{85}Fe_{15}$, (c) $Cu_{80}Fe_{20}$, (d) $Cu_{75}Fe_{25}$ milled for 15h

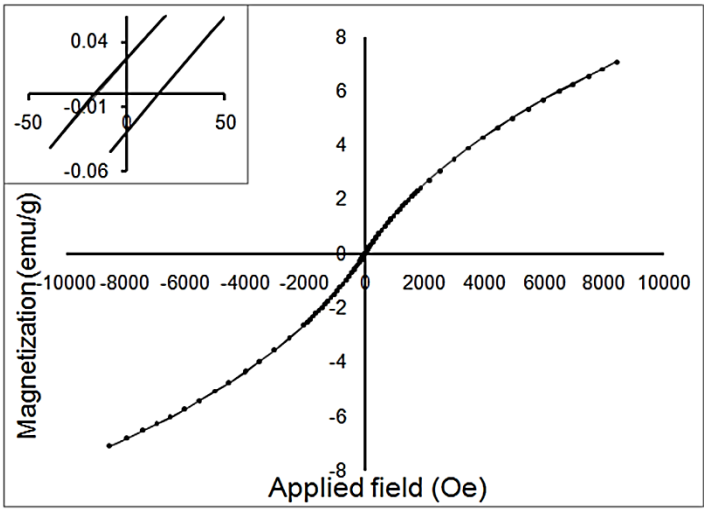

Fig. 5. Hysteresis loop of 15 h milled $Cu_{80}Fe_{20}$ powder (The inset plot is the enlarged view of the loop at the center)

4. Conclusions

In this paper, the nanoparticles of the metastable Cu-Fe phase containing 10, 15, 20 and 25%wt Fe were synthesized by intensive ball milling. The XRD results showed that the solid solubility of the Fe in the Cu was extended to 20%wt after milling for 15h, and a homogeneous $Cu_{80}Fe_{20}$ solid solution with a mean crystallite size about 19 nm was achieved. The FESEM images indicated that the $Cu_{80}Fe_{20}$ powders milled for 15h consist of uniform particles with average size of about 25nm. Magnetization measurements demonstrated the soft magnetic behavior for the supersaturated $Cu_{80}Fe_{20}$ powder.

Acknowledgment

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