The phase transition in annealed mechanically alloyed Fe - Cu

The phase transition in annealed mechanically alloyed Fe–Cu

Li Yu-zhi†‡, Li Tie†‡, Zhang Yu-heng†‡§, Wu Li-wen†‖, Gao Chen†‖ and Liu Wen-han†‖

† Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China
‡ Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China
§ Chinese Centre of Advanced Science and Technology (World Laboratory), Beijing 100080, People's Republic of China
‖ Centre for Fundamental Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China

Abstract. Using Mössbauer spectra and x-ray diffraction patterns, annealed mechanically alloyed Fe–Cu has been investigated in this paper. It is found that in $Fe_{0.8}Cu_{0.2}$, after it has been milled, fcc-Cu has transformed into bcc-Cu, and some Cu atoms have diffused into the Fe. After the alloy has subsequently been annealed, it is found that bcc-Cu has transformed back into fcc-Cu, while the Cu atoms in the Fe have been separated. In $Fe_{0.6}Cu_{0.4}$, after being milled, an fcc-Fe-rich phase has been formed, and after the alloy has subsequently been annealed, this has transformed back to bcc-Fe. The shorter the milling time and the higher the annealing temperature, the faster the transformation. In $Fe_{0.5}Cu_{0.5}$, after it has been annealed, the fcc-Fe-rich phase has transformed to bcc-Fe also, and the fcc-Cu-rich phase remains when the annealing temperature increases. All of these results show that the fcc-Fe-rich phase in the milled samples is a metastable phase—it will transform to stable bcc-Fe when it is annealed— while the long-milling-product fcc-Cu-rich phase is a stable phase.

1. Introduction

Recently, ball-milling has been widely used to prepare new materials. It has been reported that it can be used to form amorphous compounds, solid solutions, and other phases. More recently, a lot of attention has been paid to the Fe–Cu system [3–11].

As Fe and Cu atoms have similar atomic radii, electronegativities and other electrochemical properties, in general solid-solution theory they should be readily miscible, but in fact they are almost immiscible [1]. Lots of investigations [2–11] have been presented that show that the structures of samples of Fe_xCu_{1-x} prepared by either vapour deposition [2] or mechanical alloying [3] depend on the proportion of Fe. Alloys with $x \leqslant 0.6$ are fcc and those with $x \geqslant 0.8$ are bcc, while the samples with intermediate compositions contain both structures [2]. All of these features have been demonstrated by lots of experiments, but the micro-structure of Fe–Cu ball-milled samples is still a puzzle.

Jiang *et al* [6] have studied the Mössbauer spectra of $Fe_{0.5}Cu_{0.5}$ milled for 0.5, 10, 20, 30, 50, 75 and 100 hours systematically, and demonstrated the existence of three phases in the samples: fcc-Fe–Cu solid solution (whose hyperfine magnetic field is 22 T); a bcc-Fe phase; and a fcc-Fe phase. The last two phases are found only for a few proportions.

Macri *et al* [7] have considered the Mössbauer spectra of $Fe_{0.5}Cu_{0.5}$ milled for 16 hours; they thought that the spectra should have a broadened sextet, a doublet and a singlet. The sextet should relate to the extended solid solution with a composition near to $Fe_{0.5}Cu_{0.5}$; the doublet should relate to a Cu-rich solid solution; and the singlet may be due to a γ-iron phase.

In reference [8], we included a study of the two groups' samples. The first set had $x = 0.6$ and had been milled for 10, 40, and 160 hours, and the second set had a milling time of $t = 160$ hours and values of x of 0.8, 0.6, and 0.5 respectively. We pointed out that, corresponding to their hyperfine-magnetic-field distributions derived from the Mössbauer spectra, and by considering the results of extended x-ray-absorption fine-structure (EXAFS) and x-ray diffraction studies [11], the structures of these samples can be divided into three types according to the different hyperfine-magnetic-field regions: bcc-Fe $((30\text{--}32) \pm 2$ T$)$; a fcc-Fe-rich solid-solution phase $((21\text{--}24) \pm 6$ T$)$; and a fcc-Cu-rich solid-solution phase $(<10$ T$)$.
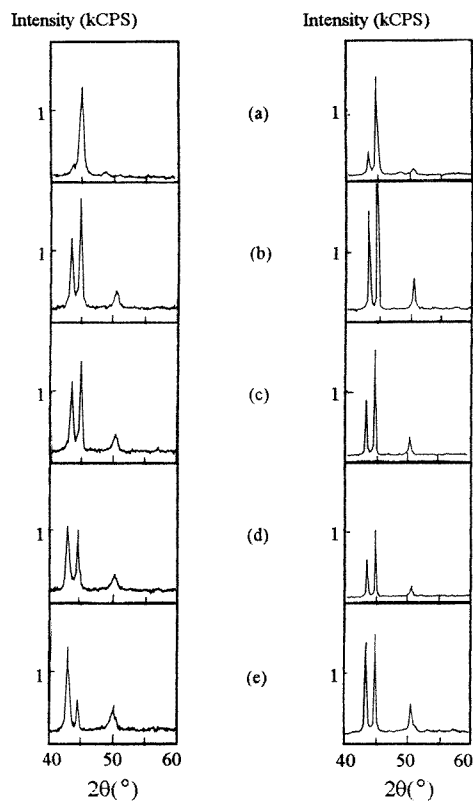

Figure 1. X-ray diffraction patterns for Fe_xCu_{1-x} milled for t hours and annealed at different temperatures; left: 330 °C; right: 500 °C; (a) $x = 0.8$, $t = 160$; (b) $x = 0.6$, $t = 10$; (c) $x = 0.6$, $t = 40$; (d) $x = 0.6$, $t = 160$; (e) $x = 0.5$, $t = 160$; ●: bcc-Fe; ○: bcc-Cu; ■: fcc-Fe rich; □: fcc-Cu.

Some studies [9, 7, 10] have shown that the product from ball-milling Fe–Cu is metastable. In this work, the two groups' samples—detailed above—were studied via differential scanning calorimeter (DSC) measurements first and then annealed in order to

investigate the micro-structure of the samples and the tendencies in the thermal treatment.

Table 1. Fitting parameters of the Mössbauer spectra from the mechanically alloyed Fe_xCu_{1-x} samples annealed at different temperatures.

			$Fe_{0.8}Cu_{0.2}$ 160 h	$Fe_{0.6}Cu_{0.4}$ 10 h	$Fe_{0.6}Cu_{0.4}$ 40 h	$Fe_{0.6}Cu_{0.4}$ 160 h	$Fe_{0.5}Cu_{0.5}$ 160 h
330 °C	Sextet I	IS (mm s^{-1})	0.00	0.00	0.00	0.00	0.00
		QS (mm s^{-1})	0.00	0.00	0.00	0.00	0.00
		HWH (mm s^{-1})	0.14	0.16	0.15	0.15	0.14
		H_{hf} (T)	33.1	32.9	33.1	33.0	33.1
		A (%)	54	94	80	62	30
	Sextet II	IS (mm s^{-1})	0.02				
		QS (mm s^{-1})	0.01				
		HWH (mm s^{-1})	0.27				
		H_{hf} (T)	31.7				
		A (%)	46				
	Sextet III	IS (mm s^{-1})			−0.11	−0.09	0.06
		QS (mm s^{-1})			0.10	0.00	0.03
		HWH (mm s^{-1})			0.52	0.51	0.54
		H_{hf} (T)			21.9	23.0	22.4
		A (%)			12	30	59
	Sextet IV	IS (mm s^{-1})					0.09
		QS (mm s^{-1})					0.00
		HWH (mm s^{-1})					0.15
		H_{hf} (T)					3.7
		A (%)					8
	Singlet	IS (mm s^{-1})		−0.06	−0.07	−0.14	−0.08
		HWH (mm s^{-1})		0.24	0.29	0.29	0.25
		A (%)		6	8	8	3
500 °C	Sextet	IS (mm s^{-1})	0.00	0.00	0.00	0.00	0.00
		QS (mm s^{-1})	0.00	0.01	0.01	0.01	0.01
		HWH (mm s^{-1})	0.17	0.15	0.14	0.13	0.14
		H_{hf} (T)	33.0	33.0	33.0	33.0	33.0
		A (%)	100	99	98	95	87
	Singlet	IS (mm s^{-1})		0.02	0.04	0.01	−0.08
		HWH (mm s^{-1})		0.18	0.24	0.24	0.15
		A (%)		1	2	5	13

2. Experiments and analysis

The DSC measurements were made using a Shimadzu DSC-50. Exothermic peaks appear at temperatures between 300 and 500 °C. This indicates that the phase transition temperatures are between 500 °C and 300 °C. Therefore, the annealing temperatures were chosen as 330 and 500 °C to get the phase transition to proceed and the variation of the micro-structure to commence. To avoid oxidation, the samples were annealed in a vacuum for one hour. Then all of the samples were characterized using a RIGAKU-MAX-γA rotating-target x-

Table 2. A comparison of the hyperfine magnetic fields in mechanically alloyed Fe_xCu_{1-x} samples annealed at different temperatures.

	Annealing temperature (°C)	H_1 (T)	A_1 (%)	H_2 (T)	A_2 (%)	H_3 (T)	A_3 (%)
$Fe_{0.8}Cu_{0.2}$	No*	30 ± 4	96	17	3	4	1
(160 h)	330	33	51				
		32	49				
	500	33	100				
$Fe_{0.6}Cu_{0.4}$	No	32 ± 2	67	24 ± 6	21	0–10	12
(10 h)	330	33	94			0	6
	500	33	99			0	1
$Fe_{0.6}Cu_{0.4}$	No	32 ± 2	33	24 ± 6	59	0–10	8
(40 h)	330	33	80	22	12	0	8
	500	33	98			0	2
$Fe_{0.6}Cu_{0.4}$	No	32 ± 2	7	24 ± 6	86	0–10	7
(160 h)	330	33	62	23	30	0	8
	500	33	95			0	5
$Fe_{0.5}Cu_{0.5}$	No	~ 31	8	21 ± 5	78	0–10	14
(160 h)	330	33	30	22	59	3.7	8
						0	3
	500	33	87			0	13

* All of the data for unannealed samples are taken from reference [8].

ray diffractometer (Cu Kα, $\lambda = 1.54$ Å) and an Oxford MS-500 Mössbauer spectrometer (^{57}Co/Pd).

Figure 1 represents the x-ray diffraction patterns of the annealed samples. Figure 2 shows the experimental and fitted Mössbauer spectra of the annealed samples. The Mössbauer spectra were taken at room temperature and fitted by the Gauss–Newton method; the fitting parameters are listed in table 1.

First, let us analyse the results for $Fe_{0.8}Cu_{0.2}$.

In the unmilled sample, the structure of Fe is bcc and that of Cu is fcc. After the sample has been milled for 160 hours, the x-ray diffraction patterns show that there is only a bcc peak: the fcc peak has disappeared [11]; also the hyperfine magnetic field of the Mössbauer spectra is 30 ± 4 T [8]. Comparing this result with that for α-Fe, it can be seen that the field has decreased and the peak width has become broad. This means that some Cu atoms have diffused into the Fe. In this sample, the atomic proportion of Cu is 20%; it is impossible for all of the Cu atoms to diffuse into Fe, so where did the remainder go? From the results of EXAFS studies [11], we know that the Cu–Cu neighbour distance is 6.6 Å; hence, it is reasonable to consider that Cu has been changed to bcc-Cu.

After the annealing, the Mössbauer spectrum of the sample shown in figure 2 is quite similar to that for α-Fe. The fitting results show that the magnetic field is 32–33 T in the sample annealed at 330 °C, and that when the annealing temperature becomes 500 °C the field is only 33 T, while the peak width is narrow. These results indicate that annealing has made the Cu atoms in bcc-Fe separate. In figure 1, it is obvious that the diffraction peaks at $2\theta = 44.7°$ are for Fe(110), while a peak $2\theta = 44.5°$ overlaps that for the sample annealed at 330 °C. From the analysis above, it should be arising from bcc-Cu. As the
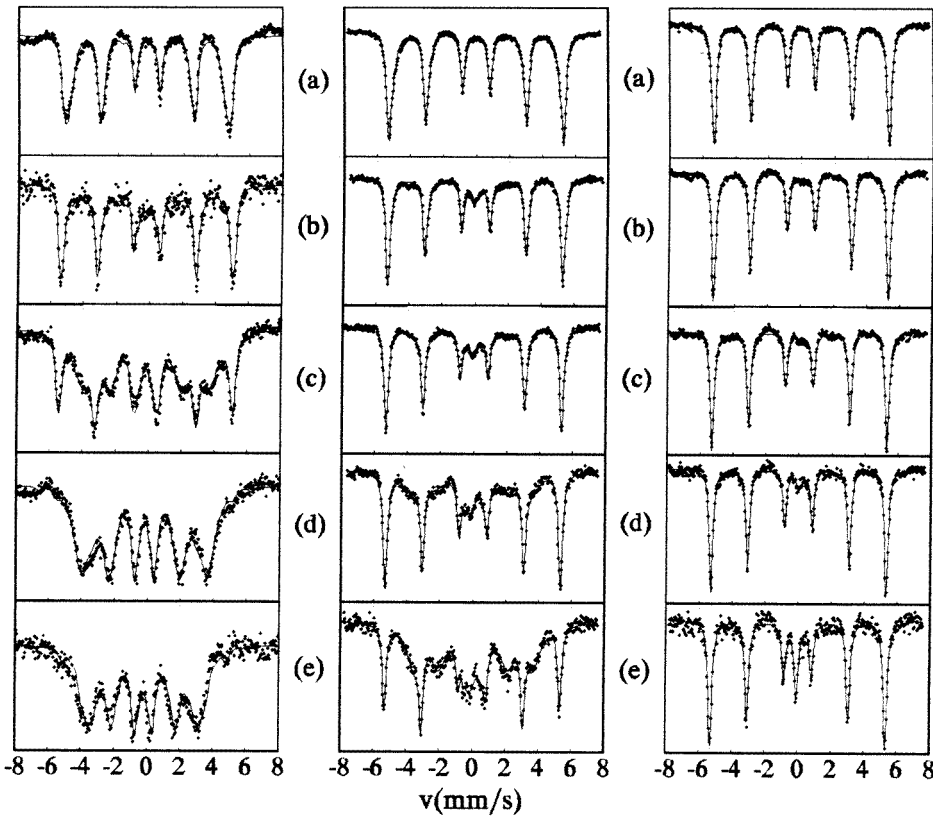
Figure 2. Experimental and fitted Mössbauer spectra of Fe_xCu_{1-x} milled for t hours and annealed at different temperatures; left: unannealed; middle: 330 °C; right: 500 °C; (a) $x = 0.8$, $t = 160$; (b) $x = 0.6$, $t = 10$; (c) $x = 0.6$, $t = 40$; (d) $x = 0.6$, $t = 160$; (e) $x = 0.5$, $t = 160$.

equation $2d \sin\theta = \lambda$ shows, the crystal lattice size is 2.89 Å, which is a little more than that of bcc-Fe: 2.87 Å. This is consistent with the EXAFS data [11]. When the annealing temperature reaches 500 °C, the position at $2\theta = 43.3°$ also has a strong peak, and it seems likely that the position at 50.3° will produce a peak. In $Fe_{0.8}Cu_{0.2}$, Fe exhibits only the bcc structure; hence, the diffraction peaks at 43.3° and 50.3° can only be arising from the fcc-Cu(111) and (200). In other words, the Cu has again assumed a fcc structure after the annealing.

It can be concluded from the above that when $Fe_{0.8}Cu_{0.2}$ has been milled for 160 hours, some Cu atoms will have diffused into the bcc-Fe, and the other Cu atoms (perhaps most of them) will have been transformed to bcc-Cu; after the annealing, the Cu atoms in bcc-Fe will be separated, and bcc-Cu will have been transformed back into fcc-Cu.

Now, let us consider the $Fe_{0.6}Cu_{0.4}$ milled for 10, 40 and 160 hours.

From reference [8], it can be established that in the milled samples there are three phases: the bcc-Fe, the fcc-Fe-rich and the fcc-Cu-rich phases. As the Fe atomic radius is similar to that of Cu atoms, the diffraction peaks from the latter two fcc phases will overlap, but they can still be distinguished from each other by their different magnetic fields: the fcc-Fe-rich sample has a field of 20–24 T, and the fcc-Cu-rich phase has a field below

10 T. Hence, the variation of the hyperfine magnetic fields during the annealing process will reflect the structure changes. Figure 2 shows the Mössbauer spectra of the unannealed samples and the corresponding annealed ones. The unannealed samples were fitted using the Le Caer and Dubois method [8], and their magnetic fields can be divided into three regions: 32 ± 2 T (that is, the centre is at 32 T and the distribution region is about 4 T); 24 ± 6 T; and 0–10 T. Hence, we referred to the results of reference [8] and fitted the Mössbauer spectra for the annealed samples shown in figure 2 as two sextets and one singlet. Sextet I has the magnetic field of α-Fe (33 T); sextet II has a field of 22–23 T. According to the results of reference [8], they correspond to a bcc-Fe phase and a fcc-Fe-rich phase respectively. The singlet corresponds to a fcc-Cu-rich solid solution which is similar to the Nd-rich phase in $Nd_{15}Fe_{77}B$ alloys [13]. The details are listed in table 1. For easier comparison, the variations of the magnetic fields are contrasted in table 2.

From table 2, it can be seen that during annealing at 330 °C, the proportion of the high-field phase (bcc-Fe) increases rapidly: the increases are 27, 47 and 55% respectively for the samples milled for 10, 40 and 160 hours. However, the proportion of the medium-field phase decreases rapidly; the decreases are of 21, 47 and 56%, respectively. It can be observed that the degree of increase is similar to the degree of decrease. This means that the fcc-Fe-rich phase should have transformed to bcc-Fe, and that the longer the milling proceeds, the greater the change will be—while the fcc-Cu phase changes little. When the annealing temperature reaches 500 °C, it is found that the fcc-Fe-rich phase has changed to bcc-Fe completely, and the proportion of fcc-Cu-rich phase has decreased.

In figure 1, the diffraction peaks of the three samples of $Fe_{0.6}Cu_{0.4}$ milled for different times and annealed at 330 °C appeared at $2\theta = 44.7, 43.3$ and $50.3°$. It is certain that the peak at $44.7°$ arises from bcc-Fe. Its intensity is strong and it is very sharp, which indicates that the annealed sample has more and larger bcc-Fe crystal grains. The other two peaks may indicate the addition of the fcc phases: the Fe-rich, Cu-rich and fcc-Cu phases. During the annealing at 500 °C, all of these peaks stay at their positions. Their intensity in figure 1(c) and 1(d) varies: one (at $44.7°$) increases and other two decrease; this is especially marked for the sample of $Fe_{0.6}Cu_{0.4}$ milled for 160 hours. This reflects the substantial change in the proportion of fcc-Fe-rich phase in these samples when the annealing temperature is increased from 330 to 500 °C.

As in the report above, after the annealing, the fcc-Fe-rich phases in the milled samples of $Fe_{0.6}Cu_{0.4}$ have transformed back to bcc-Fe, with a few atoms precipitating. The process depends on the milling time and the annealing temperature. For a given annealing temperature, the shorter the milling time, the greater the proportion transformed (21/21, 47/59, 56/86). For a given milled sample, the higher the annealing temperature, the faster the transformation.

Finally, let us discuss $Fe_{0.5}Cu_{0.5}$.

Mössbauer spectra show that the proportion of bcc-Fe phase increases during an annealing at 330 °C, while the proportion of fcc-Fe-rich phase decreases. When the annealing temperature increases to 500 °C, the proportion of fcc-Fe-rich phase decreases to 0, and the proportion of bcc-Fe phase increases from 30% to 87%. The increase of the proportion of fcc-Fe-rich phase of 57% approaches the decrease of 59%. This result is similar to the result for $Fe_{0.6}Cu_{0.4}$. Comparing with $Fe_{0.6}Cu_{0.4}$, the intensity of the x-ray diffraction peak at $43.3°$ is stronger, and the proportion of fcc-Cu-rich phase is greater (11–13%).

3. Conclusion

By combining various thermal treatments of different compositions of Fe_xCu_{1-x} for different milling times, we have established the following results.

(i) When the Fe proportion is $x = 0.8$, after milling fcc-Cu is found to have transformed to bcc-Cu, and some Cu atoms diffuse into the Fe. After subsequent annealing, it is found that the bcc-Cu has transformed back to fcc-Cu, while the Cu atoms in Fe are separated.

(ii) When the Fe proportion is decreased to 0.6, after milling it is found that a fcc-Fe-rich phase has been formed; on subsequent annealing, this transforms back to bcc-Fe. The shorter the milling time and the higher the annealing temperature, the faster the transformation.

(iii) When the Fe proportion is 0.5, after annealing it is found that the fcc-Fe-rich phase has transformed to bcc-Fe also, and the fcc-Cu-rich phase is unchanged when the annealing temperature increases.

All of these results show that the fcc-Fe-rich phase in milled samples is a metastable phase—it will transform to stable bcc-Fe during annealing—while the long-milling-product fcc-Cu-rich phase is a stable phase.

Acknowledgments

References

[1] See, e.g.,
   Campbell S J and Clark P E 1974 *J. Phys. F: Met. Phys.* **4** 1073
   Kubaschewski O 1982 *Iron-Binary Phase Diagrams* (Berlin: Springer)
[2] Chien C L, Liou S H, Kofaut D, Yu W, Egami T and McGuire T R 1986 *Phys. Rev.* B **33** 3247
[3] Yavari A R, Desre P J and Benameur T 1992 *Phys. Rev. Lett.* **68** 2235
[4] Ambrose T, Gavrin A and Chien C L 1993 *J. Magn. Magn. Mater.* **124** 15
[5] Eckert J, Holzer J C, Krill C E III and Johnson W L 1993 *J. Appl. Phys.* **73** 2794
[6] Jiang J Z, Gonser U, Gente C and Bormann R 1993 *Appl. Phys. Lett.* **63** 1056
[7] Macri P P, Rose P, Frattini R, Enzo S, Principi G, Hu W X and Cowlam N 1994 *J. Appl. Phys.* **76** 4061
[8] Li Tie, Li Yu-zhi, Zhang Yu-heng, Gao Chen, Wei Shi-qiang and Liu Wen-han 1995 *Phys. Rev.* B **52** 1120
[9] Ma E, Atzmon M and Pinkerton F E 1993 *J. Appl. Phys.* **74** 955
[10] Crespo P, Hernando A and Escorial A G 1994 *Phys. Rev.* B **49** 13 227
[11] Wei Shi-qiang, Yin Shi-long, Liu Wen-han, Liu Fang-xin, Gao Chen, Yang Yuan-zheng, Dong Yuan-da and Hu Tian-dou 1994 *Acta Phys. Sinica* **43** 1630
[12] Hernando A, Crespo P, Barandiaran J M, Escorial A G and Yavari R 1993 *J. Magn. Magn. Mater.* **5–8** 124
[13] Li Zheng-wen, Ping Jue-yun, Ma Ru-zhang and Pan Shi-ming 1988 *Appl. Sci. Sinica* **6** 323