Slater-Pauling curve of Fe-Cu solid solution alloys

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Magnetization measurement was performed on bulk samples of metastable solid solution alloys with bcc and fcc structures in the iron (Fe)-copper (Cu) system, which were prepared by mechanical alloying and shock compression. The saturation magnetic-moment (M_S) curve versus number of electrons per atom at 0 K was found to be reasonably similar to the Slater-Pauling curve of other transition-metal binary systems. The M_S curve shows a local maximum at about 26.2 electrons per atom similar to the cases of Fe-Co and Fe-Ni systems, and approaches zero at about 28.6 electrons per atom. Negative curvature is seen around the boundary between the mixed phase region (bcc and fcc) and the fcc phase in a Cu content of about 35 mol % (about 27.1 electrons per atom).

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The Slater-Pauling curve shows the fundamental magnetic nature of transition metals and their alloys.[1,2] However, the iron (Fe)-copper (Cu) system alloys are not included in the Slater-Pauling curve because the system is almost immiscible in the solid phase. Metastable solid solutions in the Fe-Cu system have been prepared in thin-film form by rapid quenching,[3] vapor deposition,[4,5] sputtering,[6] and ion-beam mixing methods.[7] Mechanical alloying (MA) experiments have frequently been carried out with this system for preparing metastable solid solution powders.[8–14] Magnetization measurements at low temperatures have been reported by many researchers, including Ma *et al.*,[12] Yavari *et al.*,[13] and Crespo *et al.*[14] measuring magnetizations of metastable alloy powders by superconducting quantum interference device. Chien *et al.*[5] estimated the saturation magnetic moments of the metastable films by Mössbauer spectroscopy experiment. Kneller[4] and Sumiyama *et al.*[15] measured the saturation magnetic moments of metastable films by torsion balance magnetometer. However, their magnetization results were not very consistent with the Slater-Pauling curve. The saturation magnetic moments of the Fe-Cu system alloys still remain controversial.

We prepared bulk samples of metastable solid solutions with body-centered-cubic (bcc) and face-centered-cubic (fcc) structures in the Fe-Cu system by using shock compression combined with MA treatment. In this study, the magnetization measurements were performed in magnetic fields up to 13 T and temperatures to 4 K to obtain the saturation magnetic moment at 0 K. By using bulk samples we can precisely measure the magnetization curves with a vibrating sample magnetometer (VSM).

The preparation methods and results of metastable solid solution powder preparation by MA treatment have been described earlier.[16] It was found that the metastable alloys prepared by MA treatments for 21 h had bcc or fcc structure in the Cu content regions of 0–25 mol % or 35–100 mol %, respectively, and consisted of a mixed phase between 25 and 35 mol % Cu content.[16] Figure 1 shows the atomic volume versus Cu content of the metastable solid solutions prepared by MA treatment for 21 h. The lattice parameters of the bcc and fcc phases were larger than those of pure Fe and Cu, respectively. The expansion of the bcc structure lattice with the amount of dissolved Cu atoms was reasonably explained by the atomic diameter of the Cu atom being larger than that of the Fe atom. However, the lattice parameter of the fcc phase shows a positive deviation from Vegard's law. The expansion of the fcc structure lattice may be attributable to magnetovolume effects.[10] Shock-compression recovery experiments conducted using a propellant gun[17] were described earlier.[16] Disk-shaped bulk samples with a diameter of about 12 mm and a thickness of 2–3 mm were obtained by shock compression. The morphology appeared almost as a uniform single phase over the entire surface, whose cross sections showed a metallic gloss. The x-ray diffraction (XRD) pattern did not change after shock compressions at a sufficiently low

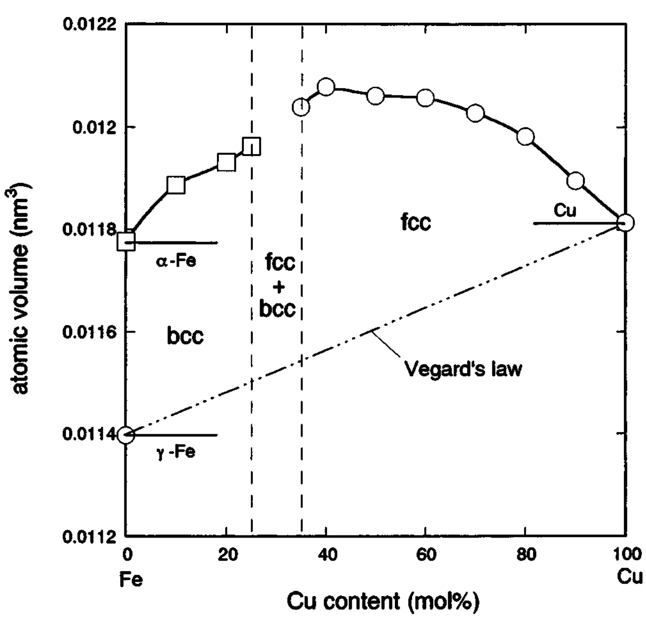

FIG. 1. Atomic volume versus Cu content of the fcc and bcc metastable solid solutions in the Fe-Cu system.

TABLE I. Chemical analytical results for zirconium, silicon, carbon, oxygen, and nitrogen contents.[a]

Chemical element		Zr[b] (wt %)	Si[b] (wt %)	O[c] (wt %)	N[d] (wt %)	C[e] (wt %)
Starting powders	Fe	<0.01	<0.01	0.29	<0.01	0.04
	Cu	<0.01	<0.01	0.64	0.01	0.33
Fe:Cu = 80:20 (in mol %)	MA treated (21 h)	1.05	0.11	2.24	0.63	0.10
	Shock-consolidated			2.14	0.62	0.18
Fe:Cu = 50:50 (in mol %)	MA treated (21 h)	1.45	0.44	1.85	1.98	0.20
	Shock-consolidated			1.84	1.93	0.45
Fe:Cu = 80:20 (in mol %)	MA treated (21 h)	1.05	0.11	2.24	0.63	0.10
	Shock consolidated			2.14	0.62	0.18

[a]The measurement errors for zirconium, silicon, nitrogen, oxygen, and carbon contents were less than 0.0001, 0.0001, 0.07, 0.02, and 0.01 wt %, respectively.

[b]Measured by inductively coupled argon plasma emission spectrophotometry with the SPS-1200 of Seiko Electric Co., Ltd.

[c]Measured by the Combustion in oxygen nondispersive infrared absorption method with the LECO Corp. TC-436.

[d]Measured by the inert-gas fusion thermal conductivity method with the LECO Corp. TC-436.

[e]Measured by the inert-gas fusion thermal conductivity method with the LECO Corp. WR-112.

pressure which was achieved by impact velocities of less than 1.0–1.3 km/s (impactor: 2024 Al).

The results of chemical analysis of Zr, Si, O, N, and C in the starting powder, the MA-treated (21 h) powders, and the shock-consolidated bulk samples in the 80:20, 50:50, and 80:20 mol % Fe-Cu systems are summarized in Table I. The Zr and Si contents in the MA-treated powders all increased from those in the starting materials (all <0.01 wt %) due to wear debris from the milling tools (zirconia [Y_2O_3-doped (3 mol %) ZrO_2] balls and silicon nitride (Si_3N_4) mill capsule). The impurity contents did not much change by the shock compression. The measured O contents increased from the average starting content of 0.78 wt %, which was calculated from those of pure Fe and Cu starting powder (0.29 and 0.64 wt %, respectively), by averagely 1.45 wt %. It was assumed that the most of O element existed as ZrO_2, Y_2O_3, CO_2, and most of the N element existed as Si_3N_4, NO_2, etc. The average increase in O content in the bulk samples calculated from the measured Zr and C contents was 1.42 wt %, which almost coincided with the above one calculated from the measured O contents. The average total impurity content of Zr, Si, C, N, O, etc. in the MA-treated powders was calcu-

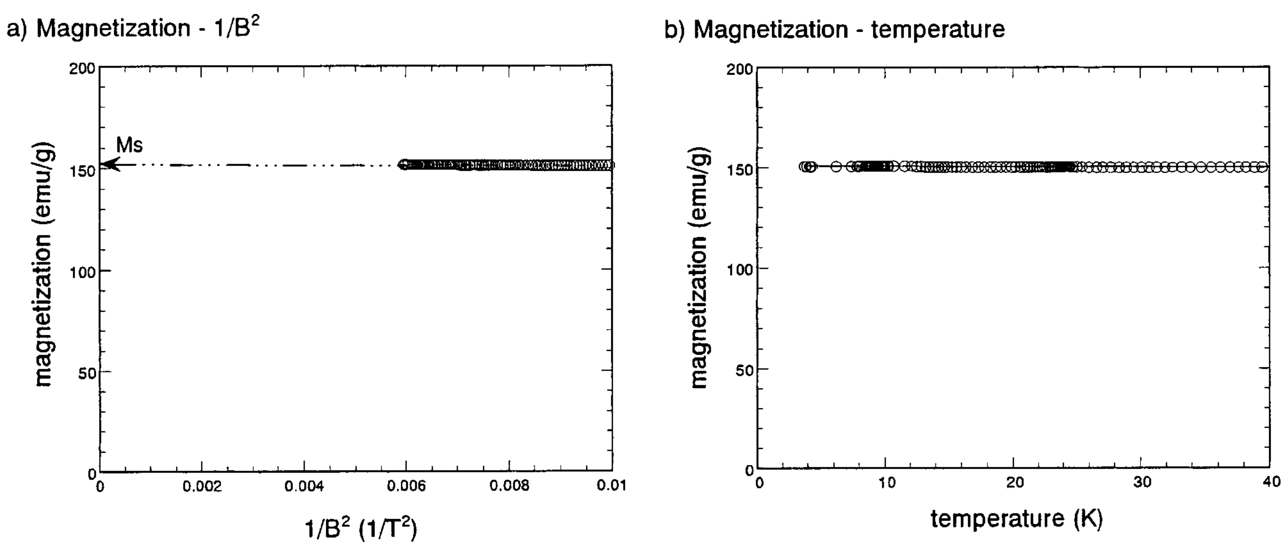

FIG. 2. Magnetization measurement results of the bcc metastable bulk alloy with 75:25 Fe-Cu ratio. (a) Magnetization curve versus $1/B^2$ at 4 K. (b) Magnetization curve versus temperature at 10 T.

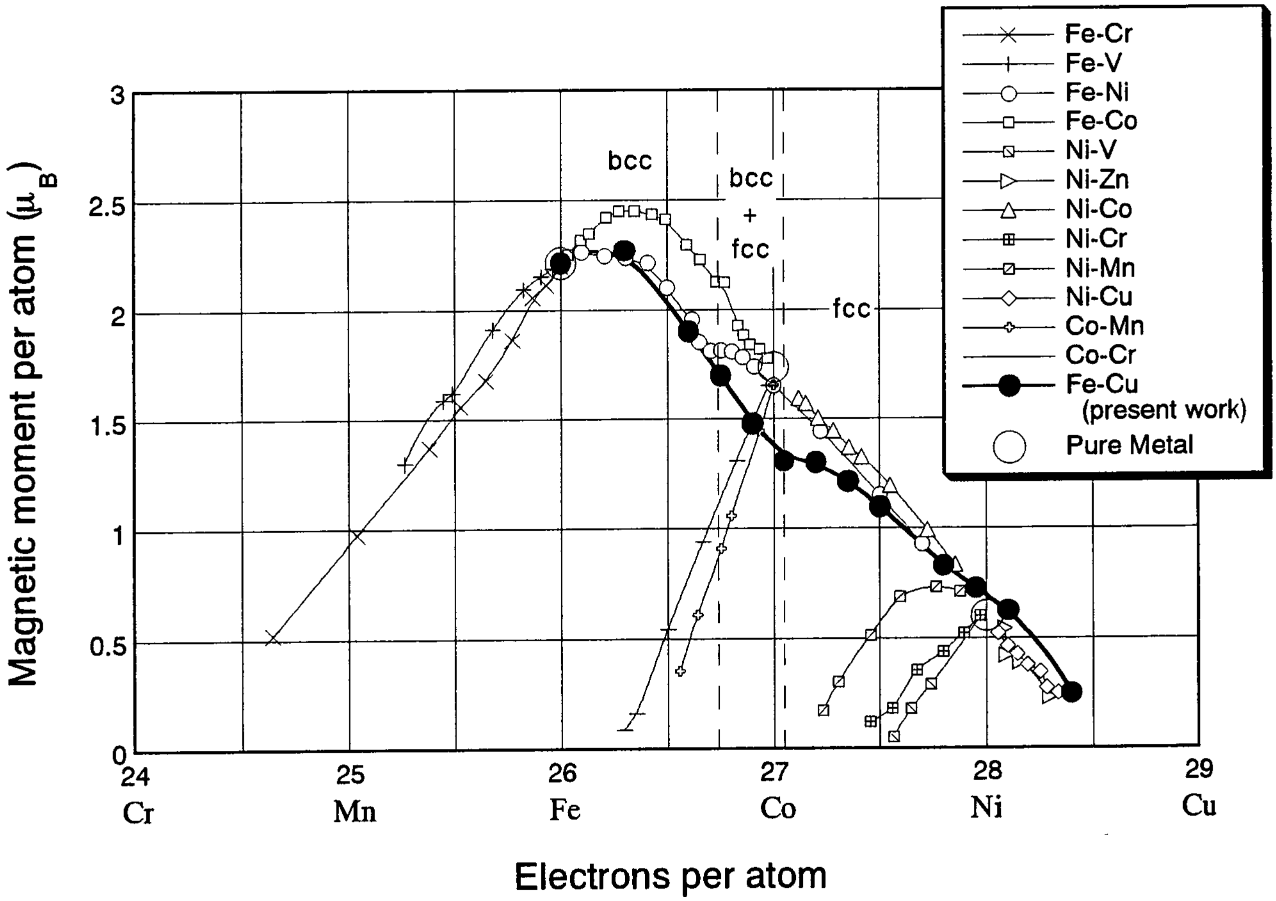

FIG. 3. Saturation magnetic moment (M_S) per atom versus the number of electrons per atom at 0 K of the transition metals and their alloys (Slater-Pauling curve).

lated to be 5.5 wt %. The impurity contents can be reduced by shortening the MA-treated time, because the alloying finished within 12 h in this system.[16] However, these oxide and nitride impurities would not very much disturb the magnetic property of the metastable bulk samples, because they are nonmagnetic materials.

Magnetic hysteresis measurements were carried out using the VSM apparatuses combined with a conventional magnet (Riken Denshi Co. Ltd. BHV-30HT) and a superconducting magnet (Oxford Instruments, Mag. Lab. VSM), whose maximum magnetic field were 1.5 and 15 T, respectively. We used rectangular bulk samples [about $3\times3\times(2-3)$ mm^3] with a weight of a few hundred milligrams. The magnetization curves (up to 1.5 T) at room temperature of the bcc metastable bulk alloy in the 80:20 Fe-Cu system, and the fcc metastable ones in the 50:50 and 20:80 Fe-Cu systems all showed ferromagnetic hysteresis loops, while the fcc pure Fe (γ-Fe) was antiferromagnetic. The atomic volumes of the fcc and bcc solid solutions were $(11.90-12.10)\times10^{-3}$ nm^3 and $(11.89-11.93)\times10^{-3}$ nm^3, respectively, which were larger than those of γ-Fe (11.40×10^{-3} nm^3)[18] and α-Fe (11.77×10^{-3} nm^3), respectively, as shown in Fig. 1. The appearance of ferromagnetism in the fcc solid solutions can take place due to lattice expansion according to the Bethe-Slater curve.

For the experiment using a superconducting magnet, we initially increased the magnetic field to 13 T at 4 K, and then decreased it to 10 T. After that, the sample was heated to room temperature (about 300 K) in a field of 10 T. Figure 2 shows the result of a typical magnetization measurement on the bcc metastable bulk alloy with 75:25 Fe-Cu ratio. The VSM system was calibrated using pure nickel (Ni) with the

TABLE II. Summary of the M_S values per atom versus the Cu content or number of electrons per atom at 0 K of the metastable alloys in the Fe-Cu system.

Cu content (mol %)	10	20	25	30	35	40	45	50	60	65	70	80
Electron number per atom	26.3	26.6	26.75	26.9	27.05	27.2	27.35	27.5	27.8	27.95	28.1	28.4
M_S value (μ_B)	2.26	1.89	1.69	1.47	1.30	1.30	1.21	1.09	0.83	0.73	0.62	0.25

same dimensions, and a reported value of saturation magnetization at 4 K (58.57 emu/g).[19] The saturation magnetization (I_S) at 4 K of the sample was determined by extrapolating the magnetization (I) curve versus $1/B^2$ (B: the magnetic field) to an infinite field, as shown in Fig. 2(a). Then, the I_S at 0 K was obtained by extrapolating the I_S data at 4 K using the gradient of I versus temperature at 10 T [Fig. 2(b)]. The I_S values were corrected by considering the average total impurity content mentioned above.

Figure 3 shows the saturation magnetic moment (M_S) per atom [Bohr magneton (μ_B)] versus the number of electrons per atom at 0 K of the metastable alloys in the Fe-Cu system. The M_S values were summarized also in Table II. The M_S curve shows a local maximum at about 26.2 electrons per atom, which is similar to the cases in the Fe-Co and Fe-Ni systems. It decreases with increasing Cu concentration, and approaches zero at about 28.6 electrons per atom. The present result is consistent with other binary systems in the Slater-Pauling curve. Negative curvature is seen on the saturation magnetic moment around the boundary between the mixed phase region (bcc and fcc) and the fcc phase in a Cu content of about 35 mol % (about 27.1 electrons per atom). This result is similar to the case in the Fe-Ni system, in which the invar effect appears.

In this study, it was found that the Fe-Cu solid solution, which was primarily immiscible, also showed the Slater-Pauling curve reasonably similar to the other transition-metal systems. The features of M_S data of this system must be basically understood by the energy-band theory, except in the mixed phase region. However, theoretical calculation of the Slater-Pauling curve of the Fe-Cu system has been reported only in the bcc phase region.[2] We expect that the present data will offer useful information for the discussion of magnetism of transition-metal alloys. The invar effect is now under study.

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