RECOVERY OF IRON AND COPPER BY TWO LIQUID PHASES SEPARATION BETWEEN Fe-B AND Ag PHASES[1]

Hideki Ono-Nakazato[2]
Shingo Agawa[3]
Katsuhiro Yamaguchi[3]
Kenji Taguchi[4]
Tateo Usui[2]

Abstract

The two liquid phases separation is found in the Fe-Cu-B system, and the equilibrium relation of the phases separation is investigated at 1873, 1523 and 1425K. The equilibrium relation of the phase separation is also examined in the Fe-Cu-B-C system. Moreover, we have investigated the two liquid phases separation in the Fe-Ag-Cu-B system and have measured the copper distribution ratio between Fe-rich phase and Ag-rich phase at 1873 and 1523K. Through these studies, we discuss the separation and recovery of iron and copper from ferrous scraps by applying the two liquid phases separation.

Key words: Recycling; Separation; Iron; Scrap.

RECUPERAÇÃO DE FERRO E COBRE POR SEPARAÇÃO DE DUAS FASES LÍQUIDAS ENTRE AS FASES Fe-B e Ag

Resumo

A separação de dois líquidos no sistema Fe-Cu-B foi investigada e as relações de equilíbrio das fases formadas foram determinadas nas temperaturas de 1873, 1523 e 1425K. As relações de equilíbrio das fases separadas foram também examinadas no sistema Fe-Cu-B-C. Além disso, foi investigada a separação dos dois líquidos no sistema Fe-Ag-Cu-B, determinando a partição de Cu entre a fase rica em Fe e a fase rica em Ag nas temperaturas de 1873 e 1523K. Com base nestes resultados, foi discutida a separação de fases e a recuperação de ferro e cobre de sucatas ferrosas, por meio da aplicação da separação de duas fases líquidas.

Palavras-chave: Reciclagem; Separação; Ferro; Sucata.

1 *Technical contribution to the 7th Japan-Brazil Symposium on Dust Processin-Energy-Environment in Metallurgical Industries and 1st International Seminar on Self-reducing and Cold Bold Agglomeration, September 8-10 2008, São Paulo City – São Paulo State – Brazil*

2 *Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Japan*

3 *Graduate Student, Graduate School of Engineering, Osaka University, Japan*

4 *Formerly, Graduate Student, Graduate School of Engineering, Osaka University. Now at Corporate Research & Development Laboratories, Sumitomo Metals Industries, Ltd, Japan.*

1 INTRODUCTION

In recent years, interest in waste treatment and recycling has increased, due to environmental concerns. The shredder dust is produced from scrapped automobiles and home electric appliance by shredding and sorting. In particular, approximately 1.2 million tons of the automobile shredder residue (ASR) are generated in one year in Japan. Although the shredder dust has been conventionally dumped in landfill sites, it is essential to establish the treatment technology due to the the land pollution and the lack of the landfill sites. The metal in ASR is mainly composed of iron and copper, the contents of which are about 8 mass% and 4.4 mass%, respectively.[1] The amounts of iron and copper in ASR generated in one year in Japan are equivalent to approximately 0.15 mass% and 4 mass%, respectively, of the annual domestic consumption of iron and copper. Accordingly, it is very important to recover iron and copper from ASR.

An iron-copper binary system has a single liquid phase in molten state. It has been reported that it separates into Fe-rich and Cu-rich phases by the addition of C,[2-4] P,[5] Si[6] or Co.[7,8] In our previous study,[9] the two liquid phases separation was also found in the Fe-Cu-B system, and the equilibrium relation of the phase separation was investigated at 1873K. The lower temperature is considered to be more advantageous for separating the two liquid phases from both thermodynamics and the actual treatment. The liquidus temperature of Fe-Cu-B system is lowered by adding carbon, which is one of the most popular elements in steel. In the present study, the equilibrium relation of the phase separation is examined in the Fe-Cu-B and the Fe-Cu-B-C system at 1523 and 1425K.

In applying this two liquid phases separation to the separation and recovery of iron and copper from ferrous scraps, it is difficult to reuse Fe-rich phase as an iron resource as it is, because the Cu content of Fe-rich phase is not low enough. In the present study, we have noticed the liquid immiscibility of Fe-Ag system. We have investigated the two liquid phases separation in the Fe-Ag-Cu-B system and have measured the copper distribution ratio between Fe-rich phase and Ag-rich phase at 1873 and 1523K. Through these studies, the possibility of lowering the Cu content of Fe-rich phase is discussed.

2 MATERIALS AND METHODS

2.1. Separation of Fe-Cu-B and Fe-Cu-B-C Xystem into Two Liquid Phases

High purity electrolytic iron (purity: 99.98mass%) and reagent grade boron (purity: 99.8mass%) inserted in an alumina crucible (38-mm o.d., 45-mm height and 30-cm^3 volume) were inductively heated up to 1873 K in an Ar-H_2 atmosphere, and the Fe-3 to 5 mass%B alloys were prepared. Moreover, by adding carbon, the Fe-0.5 to 3.5 mass%B-3mass%C alloys were also made. The experimental apparatus consisted of a vertical $MoSi_2$ electric resistance furnace, which was connected to a proportional integral and derivative action (PID) controller with a Pt-6%Rh/Pt-30%Rh thermocouple. A mullite furnace tube (60-mm o.d., 52-mm i.d., 1000-mm long) was used. The prepared Fe-B or Fe-B-C alloy weighing 10g and reagent grade copper (purity: 99.0mass%) weighing 10g were put in an alumina crucible(15-mm o.d., 12-mm i.d., 100-mm height), and the alumina crucible was inserted in a graphite holder(42-mm o.d., 34-mm i.d., 150-mm height). Then, the sample was held for over 5h in an argon atmosphere at 1873, 1523 or 1425K, and the holding time was preliminary confirmed to be enough to attain the equilibrium between Fe-rich and Cu-rich phases.[9] After the equilibrium was attained, the sample was rapidly cooled by withdrawing from the furnace. The sample was cut vertically, and the immiscibility of the liquid Fe-rich and Cu-rich phases was observed from the vertical sections of samples in all the present experiments. The boron and copper contents of the Fe-rich phase and the boron and iron contents of the Cu-rich phase were analyzed by the inductively coupled plasma (ICP) emission spectrometry. The carbon content of the Fe-rich phase was also analyzed by the combustion method using a carbon analyzer.

Several phase diagrams of the Fe-B-C system are reported.[10-12] The initial compositions of Fe-Cu-B-C system were determined from the phase diagrams so that the Fe-rich phase after the phase separation of Fe-Cu-B-C system may become liquid at the experimental temperature. The liquidus temperature of some samples collected in the experiments carried out with Fe-Cu-B-C system were determined in the Fe-rich phase after the phase separation by using TG-DTA. The liquidus temperature of sample No.11, which experimental results are presented in Table 1, was 1365 K. It is preliminary confirmed that the liquidus temperature is lower than the present experimental temperature.

Table 1. Experimental results for the phase separation in Fe-Cu-B and Fe-Cu-B-C system.

No.	Temperature (K)	Fe-rich phase			Cu-rich phase	
		[mass%B]	[mass%C]	[mass%Cu]	[mass%B]	[mass%Fe]
1	1523	2.90	−	4.60	< 0.001	5.30
2		3.57	−	5.14	< 0.001	4.75
3		4.50	−	4.80	< 0.001	4.20
4		5.39	−	4.33	< 0.001	4.15
5	1523	0.56	3.04	7.33	< 0.001	4.09
6		1.11	2.60	5.79	< 0.001	3.96
7		1.70	2.99	4.55	0.002	3.43
8		2.21	2.92	4.12	0.010	3.08
9		3.25	2.72	3.90	0.013	2.86
10	1425	2.23	2.96	3.89	< 0.001	2.34
11		2.81	2.90	3.93	0.008	2.67

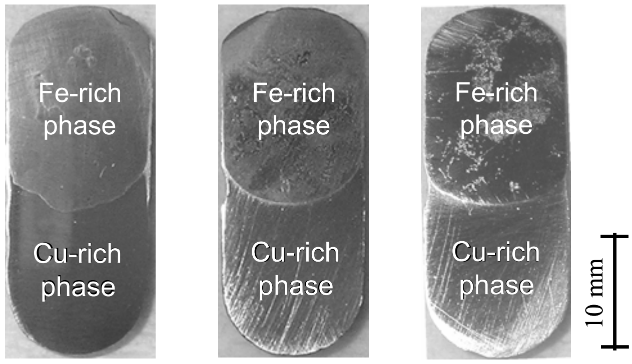
2.2 Separation of Fe-Ag-Cu-B System into Two Liquid Phases

The prepared Fe-5mass%B alloy and the high purity electrolytic iron totally weighing 10g, reagent grade silver (purity: 99.0mass%) weighing 20g and reagent grade copper (purity: 99.0mass%) weighing 1g were put in the alumina crucible. The boron content was adjusted by changing the mass ratio of the Fe-5mass%B alloy and the electrolytic iron. The alumina crucible was inserted in the graphite holder. Then, the sample was held for over 5h in an argon atmosphere at 1873 or 1523K. After the equilibrium was attained, the sample was rapidly cooled by withdrawing from the furnace. The sample was cut vertically, and the immiscibility of the liquid Fe-rich and Ag-rich phases was observed from the vertical sections of samples in all the present experiments. The boron, copper and silver contents of the Fe-rich phase and the boron, copper and iron contents of the Ag-rich phase were analyzed by the inductively coupled plasma (ICP) emission spectrometry. In the experiments at 1523K, the boron content of Fe-rich phase was adjusted over about 3 mass% so that the Fe-rich phase may become liquid at the experimental temperature. Subsequently, the similar experiments were carried out by changing the copper content from 0.1 to 1 g under a fixed mass ratio of Fe-B alloy, electrolytic iron and silver.

3 RESULTS AND DISCUSSION

3.1 Separation of Fe-Cu-B and Fe-Cu-B-C System into Two Liquid Phases

Cross-sectional views of several samples (Nos. 2, 6 and 10) are shown in Figure 1. It is found that all the experimental samples are clearly separated into two liquid phases, the upper and bottom layers of which are Fe-rich and Cu-rich phases, respectively. The experimental results are shown in Table 1. Under all the present experimental conditions, two liquid phases which are composed of Fe-rich phase in the top layer and Cu-rich phase in the bottom layer were confirmed by observing a cross section of the samples after the experiments.



(a) No.2 (b)No.6 (c) No.10

Figure 1. Images of separation into two liquid phases for several samples from Fe-Cu-B and Fe-Cu-B-C system (sample Nos. 2, 6 and 10).

3.2 Effect of a Drop in Temperature on the Phase Separation of Iron and Copper

In the Fe-Cu-B system, the effects of the boron content of the Fe-rich phase on the copper content of the Fe-rich phase and the iron content of the Cu-rich phase are shown respectively in Figs. 2(a) and 2(b) at 1523 K. It is found from Fig. 2 that both the copper content of the Fe-rich phase and the iron content of the Cu-rich phase gradually decrease with increasing the boron content of the Fe-rich phase. The previous experimental results at 1873 K[9] are also plotted in Figure 2. The copper content of the Fe-rich phase and the iron content of the Cu-rich phase at 1523 K are 4.60 mass% and 5.30 mass%, respectively, in the case of $[\text{mass\%B}]_{(\text{in Fe})}$=2.90 (No. 1). The contents are about 1 to 2 mass% lower than those at 1873 K. It is found that the two liquid phases separation is enhanced at the lower temperature.

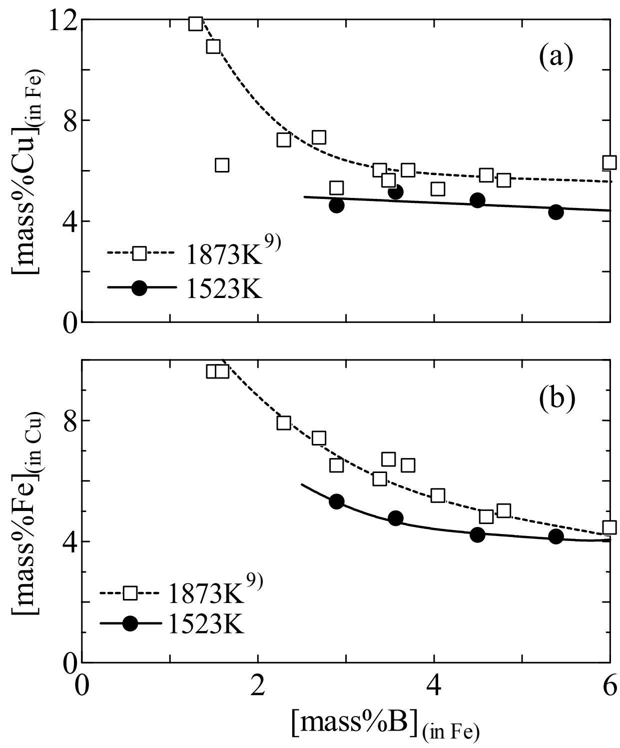


Figure 2. Effect of boron content of the Fe-rich phase on copper content of the Fe-rich phase and iron content of the Cu-rich phase.

3.3 Effect of Carbon on the Phase Separation of Iron and Copper

Figure 3 shows the effects of boron content of the Fe-rich phase on the copper content of the Fe-rich phase and on the iron content of the Cu-rich phase in the Fe-Cu-B and the Fe-Cu-B-3mass%C systems at 1523 K. From Figure 3(a), it can be seen that the copper content of the Fe-rich phase in the Fe-Cu-B-3mass%C system is smaller than that in the Fe-Cu-B system at the same boron content. It is found from Figure 3(b) that the iron content of Cu-rich phase in the Fe-Cu-B-3mass%C system is about 2 to 3 mass% lower than that in the Fe-Cu-B system. These results indicate that the carbon addition to the Fe-Cu-B system widens the miscibility gap and is more effective for the separation of iron and copper. The isothermal cross-sectional phase diagrams of the Fe-Cu-B and Fe-Cu-B-3mass%C systems at 1523 K are respectively drawn in Figure 4 from the present experimental results.

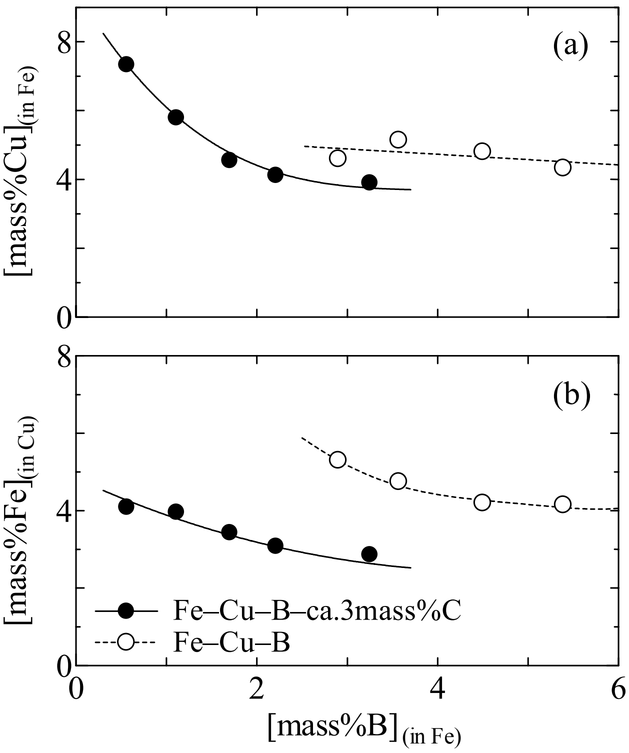


Figure 3. Effect of boron content of the Fe-rich phase on copper content of the Fe-rich phase and iron content of the Cu-rich phase at 1523 K.

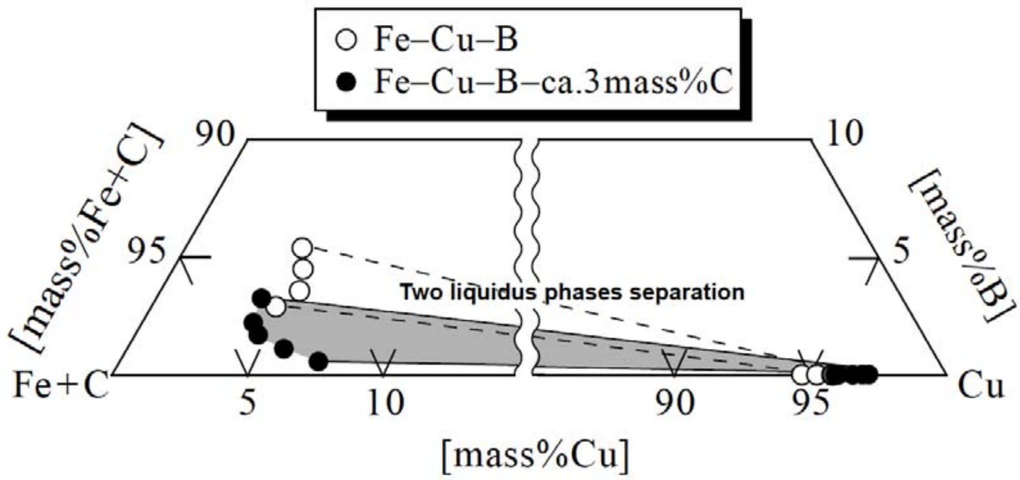


Figure 4. Region of two liquid phases for Fe-Cu-B-C system at 1523 K.

We consider the recovery of iron and copper from Fe-Cu alloy by using the two liquid phases separation. The recovery ratios of iron and copper, R_{Fe} and R_{Cu} (mass%), are defined by the following equations:

$$R_M = \frac{m_M}{m_M^{\circ}} \times 100 \text{ (mass\%) (M: Fe, Cu)} \qquad \ldots (1)$$

where m_M° and m_M denote the mass of M(=Fe, Cu) in the initial Fe-Cu alloy and in the M-rich phase after the separation by the boron and/or carbon additions, respectively. The recovery ratios of iron and copper from (a) Fe-30mass%Cu, (b) Fe-

20mass%Cu and (c) Fe-10mass%Cu alloys are calculated according to the following procedure:

1. The amounts of boron and carbon which are added in the initial Fe-10, 20 and 30 mass%Cu alloys weighing m°_{T} =($m^{\circ}_{Fe} + m^{\circ}_{Cu}$) (kg) are determined.
2. After the boron and/or carbon additions, the mass of iron contained in the Fe-rich phase, m°_{Fe}, and the mass of copper contained in the Cu-rich phase, m°_{Cu}, are calculated from the phase diagram shown in Figure 4.
3. The recovery ratios of iron and copper can be determined by using Eq. (1).
4. The procedure in Steps 1 to 3 is repeated for sample No. 1 to 11 in Table 1.

The calculation results for samples No. 1 to 11 are tabulated in Table 2. It is found that more than 80 mass% of recovery ratio of copper can be almost obtained from (b) Fe-20 mass%Cu alloy.

Table 2. The calculated recovery ratios of iron and copper from (a) Fe-30mass%Cu, (b) Fe-20mass%Cu and (c) Fe-10mass%Cu alloys.

Sample No.	(a) Fe-30%Cu		(b) Fe-20%Cu		(c) Fe-10%Cu	
	R_{Fe}(%)	R_{Cu}(%)	R_{Fe}(%)	R_{Cu}(%)	R_{Fe}(%)	R_{Cu}(%)
1	97.9	88.6	98.9	80.3	99.7	55.4
2	98.1	87.1	99.0	77.7	99.7	49.5
3	98.3	87.9	99.1	79.0	99.7	52.5
4	98.3	89.0	99.1	81.0	99.7	57.0
5	98.5	81.1	99.3	67.3	99.9	26.0
6	98.5	85.3	99.2	74.6	99.8	42.5
7	98.7	88.5	99.3	80.1	99.8	55.0
8	98.8	89.5	99.3	82.0	99.8	59.2
9	98.9	90.0	99.4	82.8	99.8	61.1
10	99.1	90.1	99.5	83.0	99.8	61.6
11	98.9	90.0	99.4	82.7	99.8	60.9

1.4 Separation of Fe-Ag-Cu-B System into Two Liquid Phases

The boron content of Ag-rich phase was under 0.001 mass% for all the samples. At 1873K, the Cu content of Fe-rich phase was 1.78 mass% when the B content of Fe-rich phase equals to 0. The copper content of Fe-rich phase decreases as increasing the B content of Fe-rich phase, and the Cu content of Fe-rich phase becomes 1.00 mass% when the B content of Fe-rich phase increases to 3.96 mass%. The effect of B content of Fe-rich phase on the copper distribution ratio, $L_{Cu}\left(=[\text{mass\%Cu}]_{(\text{in Ag})}/[\text{mass\%Cu}]_{(\text{in Fe})}\right)$, at 1873 and 1523 K is shown in Figure 5. It is found from Figure 5 that the value for L_{Cu} at 1523 K is larger than that at 1873 K. Subsequently, under the condition of a fixed B content, about 3 mass%, of Fe-rich phase, the variation of Cu distribution ratio with the Cu content was investigated. The results are shown in Figure 6. It is found that the copper distribution ratio shows a constant value in spite of the variation of Cu content. In the two liquid phases separation in Fe-Cu-B system, the Cu content of Fe-rich phase is 4.6 mass% when the B content of Fe-rich phase is 2.9 mass%. It is possible to reduce the copper content of Fe-rich phase by using silver as a solvent of Cu and by lowering the Cu activity.

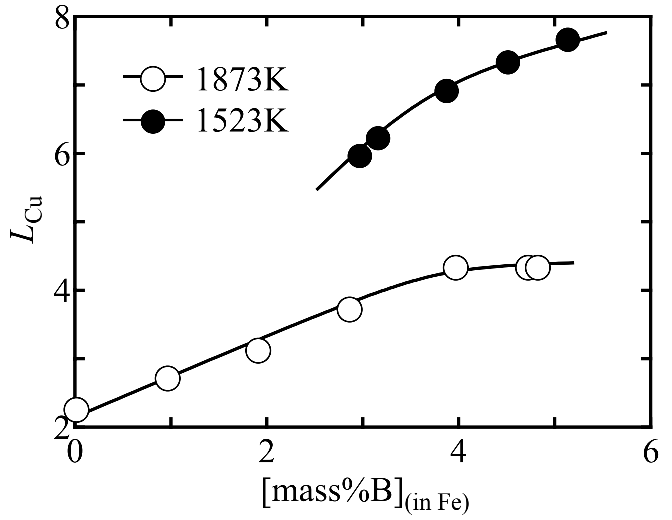


Figure 5. Effect of boron content of Fe-rich phase on L_{Cu}.

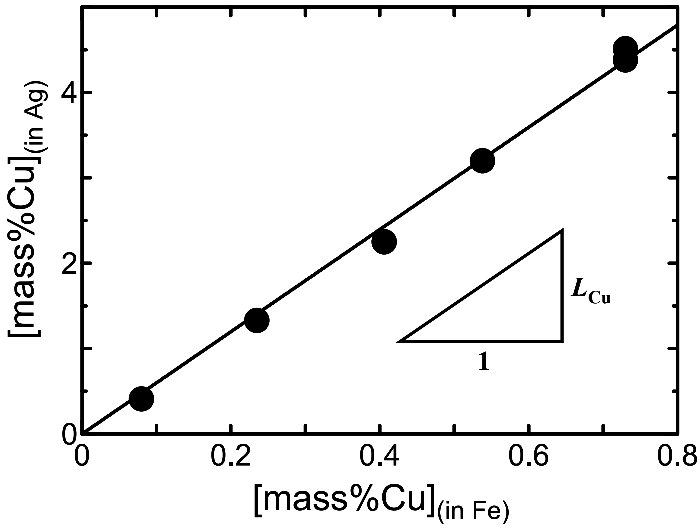


Figure 6. Relationship between copper content of Fe-rich and Ag-rich phases at 1523K. [mass%B]$_{(in\ Fe)}$ =3)

4 CONCLUSIONS

The phase separation in the Fe-Cu-B, Fe-Cu-B-C and Fe-Ag-Cu-B system has been investigated at 1873, 1523 and 1425K. The conclusions are as follows:

(1) In the Fe-Cu-B system, the copper content of the Fe-rich phase and the iron content of the Cu-rich phase at 1523 K are 4.60 and 5.30 mass%, respectively, in the case of [mass%B]$_{(in\ Fe)}$=2.90. The contents are about 1 to 2 mass% lower than those at 1873 K.

(2) In the Fe-Cu-B-3mass%C system, the copper content of the Fe-rich phase and the iron content of the Cu-rich phase are lower than those in the Fe-Cu-B system. The carbon addition widens the miscibility gap and is effective for the separation of iron and copper.

(3) By the boron and/or carbon additions, it is almost possible to recover more than 80 mass% of copper from Fe-20mass%Cu alloy.
(4) It is possible to reduce the copper content of Fe-rich phase by using silver as a solvent of Cu and by lowering the Cu activity.

REFERENCES

1 Y. Kitagawa: *JRCM NEWS*, No. 200 (2003), 2.
2 K. Yamaguchi and Y. Takeda: *Metall. Rev. MMIJ*, **15** (1998), 26.
3 S. E. Amara, A. Belhadj, R. Kesri and S. H. Thibault: *Z. Metallkd*., **90** (1999), 116.
4 K. Marukawa, T. Tanaka and S. Hara: *Eng. Mater.*, **48** (2000), 62.
5 T. Yoshida, S. Ueda and K. Yamaguchi: *CAMP-ISIJ*, **17** (2004), No. 4, P3.
6 M. Hino, T. Nagasaka and T. Washizu: *J. Phase Equilibria*, **20** (1999), 179.
7 A. Munitz: *J. Mater. Sci*., **30** (1995), 2901.
8 A. Munitz, R. Abbachian, C. Cotler and C. Shacham: *High Temp. Mater. and Process*, **15** (1996), 187.
9 K. Taguchi, H. Ono-Nakazato and T. Usui: *ISIJ Int.*, **46** (2006), 29.
10 P. Villars, A. Prince and H. Okamoto: Handbook of Ternary Alloy Phase Diagrams Vol.5, ASM International, Metal Parks, Ohio, (1995), 5333.
11 E. Schümann and S. X. Li: *GIESSEREIFORSCHUNG*, **37** (1985), 121.
12 M. Hasebe and Y. Nishizawa: *J. Jpn. Inst. Met.*, **38** (1974), 46.