Note

Activity Coefficient of Cu in the Fe–C–Cu–S Alloy Saturated with Graphite at 1473 K

Yun LEI,* Takeshi YOSHIKAWA and Kazuki MORITA

Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8505 Japan.

(Received on September 13, 2012; accepted on November 12, 2012)

KEY WORDS: activity coefficient; Cu removal; carbon-saturated iron; thermodynamics.

1. Introduction

Steel scrap is one of the main raw materials for producing iron and steel. However, recycled steel scrap is generally mixed or coated with Cu, which induces surface hot shortness in steel during hot-rolling or forging processes. Therefore, a practical process for the removal of Cu from steel scrap is required. Sulfide slagging of molten iron is considered as a promising method for removal of Cu on an industrial scale, and the development of this process using FeS–Na₂S fluxes has been attempted.^{1,2)} The distribution ratio of Cu between the sulfide fluxes and the carbon-saturated iron melt (L_{Cu}) is an important parameter contributing to the process-efficiency and has been investigated mainly at 1473 K and 1673 K.^{1,2)} As the dependence of the Cu distribution ratios on temperature was found to be insignificant, the slagging process should be operated at lower temperatures in order to suppress the erosion of ladle lining³⁾ and to decrease the energy consumption.

The activity coefficient of Cu in the carbon-saturated iron (Fe–C_{satd.}) alloy which is an important parameter to be considered while studying the removal of Cu in slagging reactions, has been investigated at various temperatures.^{1,2,4–7)} However, there are limited data at temperatures close to the eutectic point of the Fe–C system (1427 K).⁸⁾ Imai and Sano¹⁾ determined the activity coefficient at 1473 K, which is the lowest value reported thus far. However, this value reported by Imai and Sano is not sufficiently determined because the contribution of S to the activity coefficient of Cu in the Fe–C_{satd.} alloy was not considered in their study, and the maximum concentration of Cu was limited to 2.2 mol%, which is much smaller than the solubility of Cu (3.3 mol%) in the Fe–C_{satd.} alloy.

Therefore, in the present study, we determined the activity coefficient of Cu in Fe–C_{satd.} alloys at 1473 K for various Cu and S concentrations.

2. Experimental

The activity coefficient of Cu in Fe–C_{satd.} was determined from the distribution of Cu between Ag–Cu and Fe–C_{satd.}–

Cu alloys with and without S addition. This method was chosen because of the immiscibility of these two alloys and the negligible solubility of C in the Ag–Cu alloy.

The Ag–Cu alloy was prepared by melting predetermined quantities of high-purity (99.99 mass%) Ag and Cu shots in an induction furnace. The Fe–C_{satd.} alloy was prepared by melting electrolytic iron (purity: 99.99 mass%) in a graphite crucible at 1473 K under an atmosphere of purified Ar for 3 h in a SiC electric resistance furnace. Two grams of prepared Ag–Cu alloy and two grams of prepared Fe–C_{satd.} alloy were charged into a graphite crucible and kept at 1473 K in a purified Ar atmosphere for 24 h which was predetermined to be sufficient for equilibration.

To determine the effect of S on the activity coefficient of Cu, 2 g each of the prepared Ag–6 mass%Cu and Fe–C_{satd.} alloys were added along with preset amounts of FeS (purity >99 mass%) powder into a graphite crucible and maintained at 1473 K under an atmosphere of purified Ar for 24 h. These conditions were predetermined to be sufficient for the equilibrium. The Ag–6 mass%Cu alloy was used because it allows the incorporation of only small amounts of Fe, resulting in the negligible contribution of Fe to the thermodynamic properties of the Ag–Cu alloy.

After equilibration, the crucible was quickly withdrawn from the furnace, and the two immiscible alloys were carefully separated. The amount of Cu and Ag in the two immiscible alloys and that of Fe in the Ag–Cu alloy were determined by inductively coupled plasma-atomic emission spectrometry. The carbon content in the Fe–C_{satd.} alloy and the amount of S in both alloys were analyzed by a LECO combustion analyzer.

At equilibrium, the activity of Cu in the two immiscible phases is identical, and the following relationships are established.

$$a_{Cu}^{Fe-C_{satd.}-Cu-(S)} = a_{Cu}^{Ag-Cu-(S)} \quad \dots\dots\dots (1)$$

$$\gamma_{Cu}^{Fe-C_{satd.}-Cu-(S)} = \gamma_{Cu}^{Ag-Cu-(S)} \cdot (X_{Cu}^{Ag-Cu-(S)} / X_{Cu}^{Fe-C_{satd.}-Cu-(S)}) \quad \dots\dots\dots (2)$$

Here, a_{Cu}^i , γ_{Cu}^i , and X_{Cu}^i represent the activity, the activity coefficient, and the mole fraction of Cu, respectively, in the i melt. According to Eq. (2), the value of $\gamma_{Cu}^{Ag-Cu-(S)}$ is necessary to determine $\gamma_{Cu}^{Fe-C_{satd.}-Cu-(S)}$. Hultgren *et al.*⁹⁾ reported the thermodynamic properties of Ag–Cu alloy in the entire composition range. The activity coefficient of Cu at 1473 K in Ag–Cu alloy can be expressed as Eq. (3).

$$\ln \gamma_{Cu}^{Ag-Cu} = (X_{Ag}^{Ag-Cu})^2 \cdot (1.22 - 0.22 \cdot (X_{Ag}^{Ag-Cu})) \quad \text{at 1473 K} \quad \dots\dots\dots (3)$$

The contribution of S to the activity coefficient of Cu in the Ag–Cu alloy was disregarded due to the insufficient content of S.

3. Results and Discussion

The experimental results obtained when Fe–C_{satd.} and Ag–Cu alloys were in equilibrium at 1473 K are listed in **Table 1**. Raghavan¹⁰⁾ reported the phase relations at a Fe-rich corner in the phase diagram of the C–Cu–Fe system, and the contents of Cu and C in this Fe phase at 1473 K were reported to take the values of 4.56 mass% and 4.10 mass%,

* Corresponding author: E-mail: leiyn2008@163.com
DOI: <http://dx.doi.org/10.2355/isijinternational.53.538>

Table 1. The experimental results indicating the Cu distribution between Fe–C_{satd.}–Cu(S) and Ag–Cu–(S) alloys at 1473 K.

No.	Ag–Cu–(S) alloy, mass%				Fe–C _{satd.} –Cu–(S) alloy, mass%					$\gamma_{\text{Cu}}^{\text{Ag}}$	$\gamma_{\text{Cu}}^{\text{Fe–C}_{\text{satd.}}}$
	Ag	Cu	Fe	S	Fe	Cu	C	Ag	S		
1-1	99.2	0.77	0.047	0	95.4	0.11	4.42	0.066	0	2.64	42.3
1-2	97.9	2.06	0.056	0	95.3	0.27	4.37	0.058	0	2.54	42.3
1-3	96.0	3.93	0.062	0	95.2	0.49	4.26	0.052	0	2.41	41.8
1-4	94.1	5.87	0.066	0	94.9	0.72	4.34	0.050	0	2.29	40.0
1-5	87.8	12.1	0.12	0	94.4	1.27	4.30	0.042	0	1.97	38.6
1-6	77.9	21.8	0.31	0	93.8	1.90	4.31	0.045	0	1.63	36.1
1-7	63.7	35.9	0.39	0	93.4	2.42	4.17	0.040	0	1.33	34.9
1-8	48.5	50.7	0.81	0	92.9	2.87	4.20	0.043	0	1.16	33.3
1-9	31.9	66.9	1.1	0	92.6	3.27	4.14	0.031	0	1.06	32.4
1-10	16.2	82.0	1.8	0	91.8	3.93	4.21	0.032	0	1.01	29.5
1-11	0	97.4	2.6	0	91.6	4.26	4.12	0	0	1.00	29.7
1-12	94.7	5.25	0.067	0.03	95.0	0.65	4.35	0.038	0.061	2.33	40.7
1-13	94.8	5.03	0.14	0.082	95.0	0.62	4.30	0.038	0.21	2.33	40.5
1-14	95.0	4.95	0.027	0.064	95.2	0.63	4.14	0.048	0.42	2.34	39.5
1-15	94.8	5.13	0.028	0.072	95.2	0.67	4.04	0.053	0.62	2.33	38.3
1-16	95.3	4.68	0.023	0.05	95.3	0.63	4.02	0.048	0.85	2.36	38.3
1-17	95.1	4.80	0.022	0.043	95.3	0.66	3.98	0.047	1.2	2.35	37.6

respectively. Yamaguchi and Takeda¹¹⁾ investigated the miscibility gap in the Fe–Cu–C system at 1453 K. They reported that the contents of Cu and C in the Fe-rich phase were 4.60–4.64 mass% and 4.11–4.16 mass%, respectively, and that of Fe in the Cu-rich phase was 3.04–3.49 mass%. The values obtained in the present study in sample (1-11) agreed with the aforementioned reported values. The effect of Ag on the thermodynamic properties of the Fe–C_{satd.} alloy was found to be negligible because of the extremely small Ag content. The effect of Fe on the activity coefficient of Cu in the Ag–Cu alloy could be neglected because of its small content in the Ag–Cu alloy.

The activity coefficients of Cu in the Fe–C_{satd.}–Cu(S) alloy, with reference to pure liquid Cu, were determined from Eqs. (1)–(3), and the values are summarized in Table 1.

The activity coefficient of Cu in the Fe–C_{satd.}–Cu–S alloy can be expressed by Eqs. (4)–(5).

$$\ln \gamma_{\text{Cu}} = \ln \gamma_{\text{Cu}}^* + \ln \gamma_{\text{Cu}}^{\text{Cu}} + \ln \gamma_{\text{Cu}}^{\text{S}} = \ln \gamma_{\text{Cu}}^* + \varepsilon_{\text{Cu}}^{\text{Cu}} \cdot X_{\text{Cu}} + \varepsilon_{\text{Cu}}^{\text{S}} \cdot X_{\text{S}} \quad (4)$$

$$\varepsilon_{\text{Cu}}^j = (\partial \ln \gamma_{\text{Cu}} / \partial X_j)_{X_j \rightarrow 0, a_c = 1} \quad (5)$$

In the above equation, γ_{Cu} is the activity coefficient of Cu in the Fe–C_{satd.} alloy, γ_{Cu}^* is the activity coefficient of Cu in the Fe–C_{satd.} alloy in its infinitely dilute solution and $\ln \gamma_{\text{Cu}}^{\text{Cu}}$ and $\ln \gamma_{\text{Cu}}^{\text{S}}$ are the contributions of Cu and S, respectively, to the activity coefficient of Cu in the Fe–C_{satd.} alloy. $\varepsilon_{\text{Cu}}^j$ is the interaction parameter of component j on Cu in the Fe–C_{satd.} alloy, which includes the effect of changes in the C content for carbon saturation condition.

First, the self-interaction of Cu in the Fe–C_{satd.} alloy was evaluated from the results for samples (1-1)–(1-11). **Figure 1** shows the activity coefficient of Cu in the Fe–C_{satd.} alloy as a function of the concentration of Cu. The activity

Fig. 1. Relationship between the activity coefficient of Cu and Cu concentration in the Fe–C_{satd.} alloy at 1473 K.

coefficient decreased with increase in the Cu concentration present in the alloy and can be expressed by Eq. (6).

$$\ln \gamma_{\text{Cu}} = 3.76 - 11.45 \cdot X_{\text{Cu}} \quad (6)$$

For comparison, the activity coefficients of Cu in the Fe–C_{satd.}–Cu alloy determined by Imai and Sano¹⁾ by equilibrating Fe–C_{satd.}–Cu alloy with Pb alloy at 1473 K under an atmosphere of Ar have also been included in Fig. 1. These reported values agreed well with the results of the present study at low Cu concentrations ($X_{\text{Cu}} < 0.01$) but showed a significant difference at higher Cu concentrations.

The activity coefficient of Cu in Fe–C_{satd.} alloy in its infinitely dilute solution was found to take the value of 43 at 1473 K, revealing a large positive deviation from ideality. The data on infinitely dilute solutions have been previously reported by Imai and Sano,¹⁾ Wang *et al.*,²⁾ Koros and Chipman,⁴⁾ Schenck *et al.*,⁵⁾ Choudary *et al.*,⁶⁾ and Yamaguchi *et al.*,⁷⁾ and are summarized in **Fig. 2**. A rough estimation

Fig. 2. Temperature dependence of the activity coefficient of Cu in its infinitely diluted solution in the Fe-C_{satd.} alloy.

Fig. 3. Contribution of S to the activity coefficient of Cu in the Fe-C_{satd.}-Cu-S alloy at 1473 K.

of the values, with the assumption of regular solution behavior ($RT \ln \gamma_{Cu}^* = \text{constant}$), is represented by the plot in broken line in Fig. 2, which agrees well with the reported values.

Next, the interaction of S on Cu in Fe-C_{satd.} alloy was evaluated from the results obtained from samples (1-12)–(1-17) by rearranging Eq. (4) to Eq. (7) as shown below.

$$\ln \gamma_{Cu} - \ln \gamma_{Cu}^* - \epsilon_{Cu}^{Cu} \cdot X_{Cu} = \epsilon_{Cu}^S \cdot X_S \quad \text{..... (7)}$$

The relationship between the left hand side of Eq. (7) and the S concentration of the Fe-C_{satd.} alloy, as expressed in Eq. (7), is shown in Fig. 3. The increase in S concentration led to the decrease in the activity coefficient of Cu in the Fe-C_{satd.} alloy, which was disregarded by Imai and Sano.¹⁾ The interaction parameter (ϵ_{Cu}^S) obtained by linear regression was found to take the value of -4.74 . ϵ_{Cu}^S in molten iron was reported as -2.35 at 1873 K.¹²⁾ The attractive interaction of S on Cu in the Fe-C_{satd.} alloy is stronger than that in molten steel. The change in the activity coefficient of Cu in the Fe-

C_{satd.} alloy by the sulfur addition can be expressed as the following equation,

$$d \ln \gamma_{Cu} = \frac{\partial \ln \gamma_{Cu}}{\partial X_S} dX_S + \frac{\partial \ln \gamma_{Cu}}{\partial X_C} \cdot \frac{\partial X_C}{\partial X_S} dX_S \quad \text{..... (8)}$$

where the first and second terms of the right hand side of Eq. (8) correspond to the original Cu-S interaction and the contribution of change in the carbon content, respectively. Since the interaction between Cu and C, $\partial \ln \gamma_{Cu} / \partial X_C$, is speculated to be repulsive from the positive value of the interaction parameter in molten iron (3.19 at 1873 K¹³⁾ and $\partial X_C / \partial X_S$ is negative as seen in Table 1, the change in the carbon content affects the attractive interaction. In addition, both activity coefficients of Cu and S in carbon saturated iron are larger than those in molten iron, resulting in relatively their larger interaction in carbon saturated iron. Hence, the stronger affinity between Cu and S in carbon saturated iron can be explained from the above two aspects.

Accordingly, the activity coefficient of Cu in the Fe-C-Cu-S alloy saturated with graphite was obtained as the following equation.

$$\ln \gamma_{Cu} = 3.76 - 11.45 \cdot X_{Cu} - 4.74 \cdot X_S \quad (0 \leq X_{Cu} \leq 0.033, 0 \leq X_S \leq 0.018) \quad \text{..... (9)}$$

4. Conclusions

The distribution of Cu between Ag-Cu and Fe-C_{satd.} alloys with and without S addition at 1473 K was investigated. The activity coefficient of Cu in the Fe-C_{satd.} alloy was determined as the following equation.

$$\ln \gamma_{Cu} = 3.76 - 11.45 \cdot X_{Cu} - 4.74 \cdot X_S \quad (0 \leq X_{Cu} \leq 0.033, 0 \leq X_S \leq 0.018)$$

REFERENCES

- 1) T. Imai and N. Sano: *Trans. Iron Steel Inst. Jpn.*, **28** (1988), 999.
- 2) C. Wang, T. Nagasaka, M. Hino and S. Ban-ya: *ISIJ Int.*, **31** (1991), 1300.
- 3) Y. Lei, Y. Uchida, T. Yoshikawa and K. Morita: *CAMP-ISIJ*, **25** (2012), 931, CD-ROM.
- 4) P. J. Koros and J. Chipman: *Trans. Metall. Soc. AIME*, **206** (1956), 1102.
- 5) H. Schenck and W. Spieker: *Arch. Eisenhüttenwes.*, **30** (1959), 641.
- 6) U. V. Choudary, J. A. Serkin and G. R. Belton: *Metall. Trans.*, **6B** (1975), 399.
- 7) K. Yamaguchi, H. Ono and T. Usui: *Tetsu-to-Hagané*, **96** (2010), 531.
- 8) J. Chipman: *Metall. Mater. Trans. B*, **3** (1972), 55.
- 9) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelly: *Selected Values of the Thermodynamic Properties of Binary Alloys*, ASM, Metals Park, Ohio, (1973), 48.
- 10) V. Raghavan: *J. Phase Equilib.*, **23** (2002), 251.
- 11) K. Yamaguchi and Y. Takeda: *Shigen-to-Sozai*, **113** (1997), 1110.
- 12) G. K. Sigworth and J. F. Elliott: *Met. Sci.*, **8** (1974), 298.
- 13) T. Fuwa and J. Chipman: *Trans. Metall. Soc. AIME*, **215** (1959), 708.