Surface Tension of Liquid Fe-Cr-O Alloys at 1823 K

JOONHO LEE, KOJI YAMAMOTO, and KAZUKI MORITA

The surface tension of liquid Fe-Cr-O alloys has been determined by using the sessile drop method at 1823 K. It was found that the surface tension of liquid Fe-Cr-O alloy markedly decreases with oxygen content at constant chromium content, and the surface tension at a given oxygen content remains almost constant, regardless of the chromium content. When the surface tension of liquid Fe-Cr-O alloys is plotted as a function of oxygen activity, with an increase in the chromium content, the surface tension shows a much steeper decrease with respect to oxygen activity. The surface tension of liquid Fe-Cr-O alloys at 1823 K is given as follows: $\sigma = 1842 - 279 \ln (1 + K_O a_O)$. Here, assuming a Langmuir-type adsorption isotherm, the adsorption coefficient of oxygen, $K_{O(Fe\text{-}Cr)}$, as a function of chromium content, was shown to be $K_O = 140 + 4.2 \times [\text{wt pct Cr}] + 1.14 \times [\text{wt pct Cr}]^2$.

I. INTRODUCTION

KNOWLEDGE of surface tension of liquid iron in the presence of surface-active elements such as oxygen and sulfur is important to the understanding of the processing of liquid steel, because the surface-active elements would preferentially occupy the surface sites and considerably decrease the surface tension.

For example, the nitrogen absorption (or desorption)[1–12] kinetics is related to the surface tension of liquid steels. When the interfacial chemical reaction in nitrogen absorption is the rate-determining step, surface-active elements occupy the reaction sites, so that the reaction only (or preferentially) occurs on the vacant sites. If we consider a thermodynamic equilibrium [1] among the surface-active element i in the bulk, the sites occupied by i ($\underline{i}$), and the vacant sites ($\_$), the equilibrium constant is given by Eq. [2].[13]

$$\mathrm{i} + (\_) = (\underline{\mathrm{i}}) \qquad [1]$$

$$\frac{\theta_i}{(1 - \theta_i) a_i} = K_i \qquad [2]$$

where θ_i is the fraction of the surface sites occupied by the surface-active element i, a_i is the activity of i normalized to 1 wt pct as the standard state, and K_i is the adsorption coefficient of i. The adsorption coefficient K_i can be obtained from the information of the change of the surface tension with respect to a_i.

The gas bubble behavior in front of an advancing solid-liquid interface[14,15] is another example. In front of an advancing solid-liquid interface in the continuous casting process, the behavior of gas bubbles is determined by the surface tension gradient, which, in turn, is determined by the concentration gradient of the surface-active element in the boundary layer. Therefore, the surface tension of liquid steels needs to be expressed as a function of the concentration (or activity) of the surface-active element.

Belton expressed the surface tension, σ, of a liquid metal containing a surface-active element as a function of the activity of the surface-active element using Eq. [3].[13]

$$\sigma = \sigma^P - \mathrm{R}T\Gamma_i^{sat} \ln (1 + K_i a_i) \qquad [3]$$

where σ^P is the surface tension of pure metal, R is the gas constant, T is the temperature, and Γ_i^{sat} is the surface adsorption of i at saturation. Hence, if we determine the values of σ^P, Γ_i^{sat}, and K_i for a given metal (or alloy) at a given temperature, we may anticipate the interfacial behavior of liquid steel (nitrogen adsorption, bubble behavior, *etc*.).

It is probable that knowledge of the surface tension of liquid Fe-Cr-O alloy is necessary in order to better understand the processing of stainless steels containing oxygen. Numerous researchers have reported on the surface tension of liquid Fe-Cr alloys,[16–23] but these results show considerable discrepancies of more than 300 mN/m. There have been a number of studies of the effect of oxygen on the surface tension of pure liquid iron.[24–31] However, no research had been published on the surface tension of liquid Fe-Cr-O alloys, except that of Mukai *et al*.[16] on the surface tension of liquid Fe-16 wt pct Cr-O alloys. In the present work, the surface tension of liquid Fe-10 and 30 wt pct Cr-O alloys with varying oxygen concentration was measured at 1823 K by the sessile drop method, combined with modern image processing techniques.

II. EXPERIMENTAL

The sessile drop method was employed in the present investigation.[32,33] Experiments were carried out using a SiC electric resistance furnace in purified argon gas (or that with either a trace or 25 pct hydrogen gas for the alloys with lower oxygen content less than 0.01 wt pct). Experiments flowing 25 pct H_2-Ar gas were performed, as the chemical reaction at the metal surface is the rate-determining step. Thus, the effect of oxygen was estimated from the bulk composition obtained by the chemical analysis after experiments. Details are presented in the Appendix. Cubes of alloy samples weighing about 1 to 2 grams were polished with a grinder and washed in acetone by an ultrasonic cleaner and dried before being placed on ceramic substrates. (The Fe-Cr alloys were made by melting high-purity electrolytic iron (>99.99 pct purity) and high-purity electrolytic

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Manuscript submitted May 23, 2004.

chromium (>99.99 pct purity) in alumina crucibles using an induction furnace, in gas mixtures of 10 pct H_2-Ar at 1873 K. Some selected alloys were analyzed for chromium and oxygen contents.) A high-purity alumina (99.6 pct purity) plate was used as the substrate in this study. After a sample was settled at the center of the furnace, the reaction chamber was sealed and evacuated, and then purified argon gas (or H_2-Ar gas mixture) was introduced at a flow rate of 200 mL/min STP. Then, the system was heated to the experimental temperature (1823 K). When the sample was melted, the shape of the sessile drop was monitored by a digital video camera for 30 to 180 min. After experiments, the sample was rapidly solidified in the furnace to protect additional reactions with atmosphere. The sample drops were analyzed after each experiment for chromium and oxygen. Chromium and oxygen contents in the samples were 10 and 30 wt pct and 0.003 to 0.055 wt pct, respectively. Sulfur content in the samples was found to be less than 10 ppmw from chemical analysis. The oxygen activity of each sample was determined from the compositions after experiments, which was considered as a value at equilibrium, as descried previously.

The surface tension of the alloys was calculated by determining the curve of best fit between the numerical solution of the Laplace equation and 41 points experimentally measured from the image contour of a sessile drop. In this calculation, the density of liquid Fe-Cr alloys was determined from Eq. [4].

$$\rho_{\text{Fe-Cr}}\,(\text{g/cm}^3) = 7.10 - 0.0033 \times [\text{wt pct Cr}] \qquad [4]$$

where the values used of density of pure liquid iron (7.10 g/cm^3) and the concentration dependence (−0.0033) were those obtained, respectively, by Jimbo and Cramb[34] at 1823 K and Mittag and Lange[19] at 1883 K, assuming that the concentration dependence would not be changed very much by the difference in temperature of 60 K.

Cr_2O_3 is formed by Reaction [5] if chromium content is higher than 2.1 wt pct in the Fe-Cr-O system.[35]

$$2\underline{\text{Cr}} + 3\underline{\text{O}} = \text{Cr}_2\text{O}_3\,(\text{s}) \qquad [5]$$

$$\log K = -\log a_{\text{Cr}}^2 - \log a_{\text{O}}^3 = 36{,}200/T - 16.1 \qquad [6]$$

The activities of chromium and oxygen were calculated from consideration of the activity coefficients of chromium (f_{Cr}) and oxygen (f_O). For the calculation of the activity coefficients, the interaction coefficients of $e_{Cr}^{Cr}(0)$, $e_O^O(-0.200)$, $e_O^{Cr}(-0.033)$, and $e_{Cr}^O(-0.119)$ were obtained from the literature.[35,36] (Although References 35 and 37 considered the second-order interaction coefficients, recent work after Itoh *et al.*[36] showed that the activity of chromium and oxygen in the liquid Fe-Cr-O system could be expressed without the second or much higher order interaction coefficients.) The oxygen contents in a liquid Fe-Cr-O alloy in equilibrium with Cr_2O_3 are 262 and 588 ppmw for the alloys containing 10 and 30 wt pct Cr, respectively. In the present work, experiments were carried out in the region where no pure Cr_2O_3 is formed. Nevertheless, it should be noted that Al_2O_3-Cr_2O_3 solid solution was formed at the interface between the alloy and the substrate. It was found that the oxygen concentration in the bulk metal was in equilibrium with the substrate.

III. RESULTS AND DISCUSSION

A. *Surface Tension of Liquid Fe-Cr Alloys*

In Figure 1, the surface tension value from the present work for the alloy containing 10 wt pct Cr, 29 ppmw O, and 7 ppmw S (1853 mN/m) in Ar-25 pct H_2 gas atmosphere is presented, together with the values reported by previous investigators.[16–23] In the present work, we were unable to decrease the oxygen content below 29 ppmw. Nevertheless, the present result shows higher value than previous results. The highest reported value of the surface tension of liquid Fe-Cr alloy at 1823 K is 1754 mN/m for Fe-16 wt pct Cr containing 30 to 40 ppmw O from Mukai *et al.*[16] This value was obtained in an atmosphere of Ar-15 pct H_2 gas mixture. Due to the strong affinity of oxygen to chromium (Cr_2O_3 (s) + 3Fe (l) = 2Cr (l) + 3FeO (l), $\Delta G^o = 44.139$ kcal/mol, at 1823 K[38]), one may expect that the adsorption of oxygen on the surface of liquid Fe-Cr alloys readily occurs. Probably, the previous lower observations have been due to oxygen (or sulfur) contamination. In order to reduce the effect of oxygen, one may increase the experimental temperature, because the chemisorption of gas species reduces with increasing temperature. Hence, an experiment at a higher temperature is more effective for the determination of accurate surface tension values without the contamination of surface-active elements.[39] However, at much higher temperatures, the reactions between liquid alloys and solid substrates may readily occur, with consequent contamination of the liquid alloy. To avoid such contamination, Nogi *et al.*[23] investigated the surface tension of liquid Fe-Cr alloys across the concentration range from 0 to 100 wt pct Cr at 2023 K, using the levitation method. In their experiment, it was found that the surface tension of pure electrolytic chromium containing 15 ppm oxygen and 180 ppm sulfur under Ar-H_2 atmosphere was lower than that of Puratronic chromium (<1 ppm oxygen and <1 ppm sulfur) by about 160 mN/m.

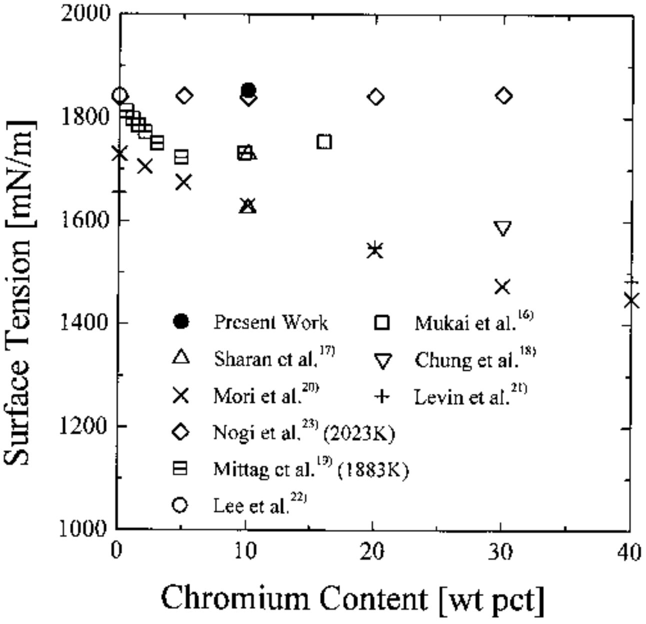

Fig. 1—Surface tension of liquid Fe-Cr alloys at 1823 K.

They also showed that sulfur in liquid Fe-Cr alloys is too difficult to remove by flowing hydrogen gas, and the surface tensions of liquid Fe-Cr alloys have almost the same values across the composition range; *i.e.*, there was no difference between the surface tension of pure liquid iron and chromium at 2023 K. Recently, Lee *et al.*[22] reported the surface tension of pure iron at 1823 K as 1842mN/m, within ±2.4 pct experimental error, using the constrained drop method, being very close to the present result for the liquid Fe-10 wt pct Cr. The highest value of the surface tension of Fe-30 wt pct Cr is 1707 mN/m, which contains 60 ppmw O. As the chromium concentration increases, the surface sites occupied by chromium having strong affinity to oxygen increase. Thus, it is considered that, with the samples of high chromium concentration, decrease in the surface tension by oxygen is inevitable. Accordingly, it is concluded that the surface tension of liquid Fe-Cr alloys has no composition dependence, but the effect of oxygen on the surface tension increases with increasing chromium content.

B. *Surface Tension of Liquid Fe-Cr-O Alloys*

The surface tension of liquid Fe-Cr-O alloys containing 10 and 30 wt pct Cr was measured with varying oxygen content at 1823 K. The results are shown in Figure 2 as a function of oxygen content. For comparison, the surface tension of liquid Fe-O from Jimbo and Cramb[30] and Fe-16 pct Cr-O from Mukai *et al.*[16] are also plotted. The surface tension markedly decreased with oxygen content, but no difference was found with chromium content. Specifically from thermodynamic considerations, however, it should be re-plotted as a function of oxygen activity. In Figure 3, the surface tension is plotted as a function of oxygen activity in the alloys. It is found that at the same oxygen activity the surface tension of liquid Fe-Cr-O alloys decreases with chromium content, which supports that oxygen shows stronger affinity to chromium than iron.

Since oxygen is a surface-active element in liquid Fe-Cr alloy,[16] the surface tension of liquid Fe-Cr-O alloys may be expressed in the form of the Belton Eq. [3] at a constant Cr content:

$$\sigma = \sigma^P - RT\Gamma_O^{sat} \ln(1 + K_O a_O) \qquad [7]$$

Here, the surface tension of liquid Fe-Cr alloys was assumed to be equal to that of pure iron, and Γ_O^{sat} and K_O were determined as follows.

Generally, in order to express the surface tension of liquid Fe-Cr-O alloys by Eq. [7], the term $RT\Gamma_O^{sat}$ is determined graphically from the relation of Eq. [8] where the surface is saturated with oxygen.

$$RT\Gamma_O^{sat} = -\left(\frac{d\sigma}{d \ln a_O}\right)_T \qquad [8]$$

However, in a system readily creating oxides in low oxygen partial pressure, the term $RT\Gamma_O^{sat}$ is too difficult to determine experimentally.[40] Bernard and Lupis[41] have reported that surface-active elements such as oxygen and sulfur may exist in an ionic state at the surface of a metal, and the molar excess of surface-active elements at saturation is close to the value calculated assuming these surface-active elements are close packed as in a solid compound. Since the ionic sizes of these elements ($R(O^{2-}) = 1.40$, $R(S^{2-}) = 1.84$[42]) are much larger than those of metallic ions ($R(Fe^{2+}) = 0.74$, $R(Cr^{3+}) = 0.63$[42]), the molar excess of oxygen at saturation in the surface of liquid Fe-Cr-O alloys may be a constant, independent of chromium content, and the term RTG_O^{sat} can be considered as the same value as in pure liquid iron. In the present work, the recommended value (279) from Jimbo *et al.*[43] was used.

In order to determine the adsorption coefficient, Eq. [7] is rewritten by Eq. [9].

$$\exp\left(\frac{\sigma^P - \sigma}{RT\Gamma_O^{sat}}\right) - 1 = K_O a_O \qquad [9]$$

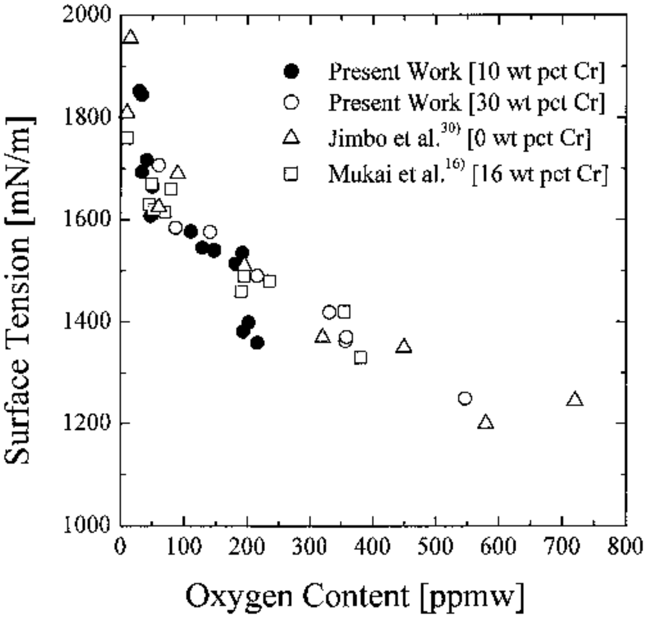

Fig. 2—Surface tension of liquid Fe-Cr-O alloys as a function of oxygen content at 1823 K.

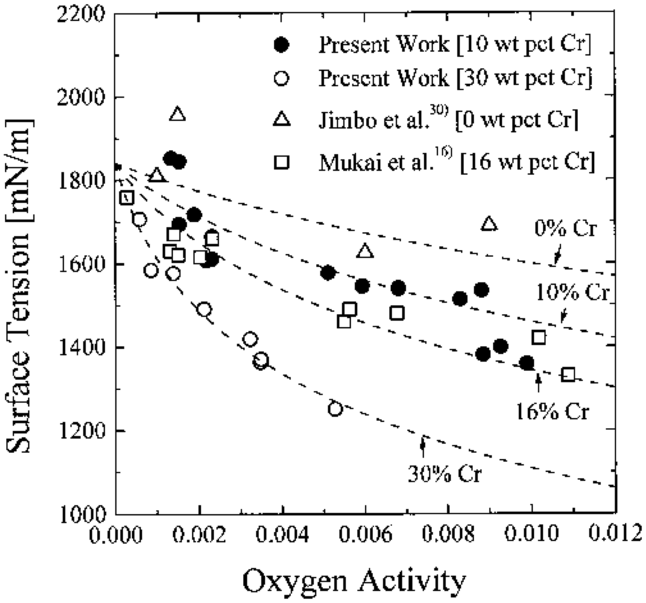

Fig. 3—Surface tension of liquid Fe-Cr-O alloys as a function of oxygen activity at 1823 K.

If we plot the left side of Eq. [9] at constant chromium content as a function of a_o, then we can obtain the oxygen adsorption coefficient K_o from the slope of the linear relationship. Figure 4 shows the left-hand side of Eq. [9] for liquid Fe-Cr-O alloys containing 0, 10, 16, and 30 wt pct Cr as a function of the oxygen activity, a_o. The oxygen adsorption coefficients were obtained by the linear fit of Eq. [9] to experimental results. In Figure 5, the adsorption coefficient is shown with respect to chromium content. As the chromium content increases, the adsorption coefficient drastically increases due to its strong affinity to oxygen. From the best fit to a polynomial equation, the oxygen adsorption coefficient can be expressed as a function of chromium content.

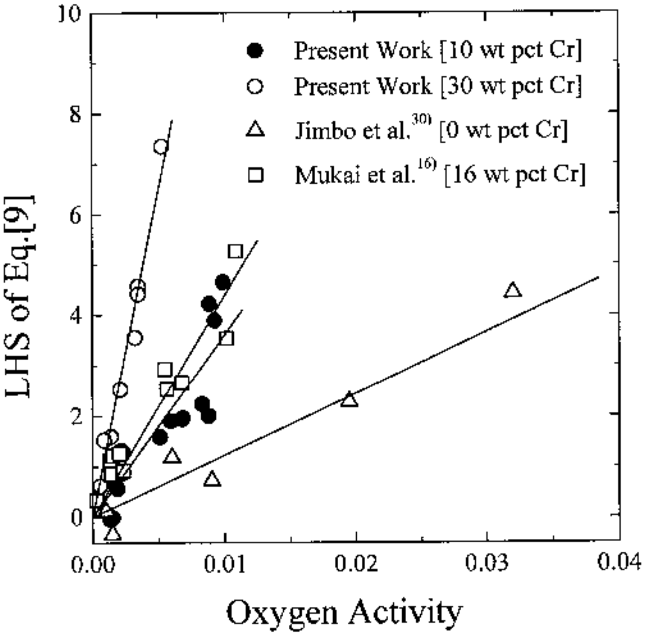

Fig. 4—Graphical determination of the oxygen adsorption coefficient for liquid Fe-Cr-O alloys ([wt pct Cr] = 0, 10, 16, and 30) at 1823 K.

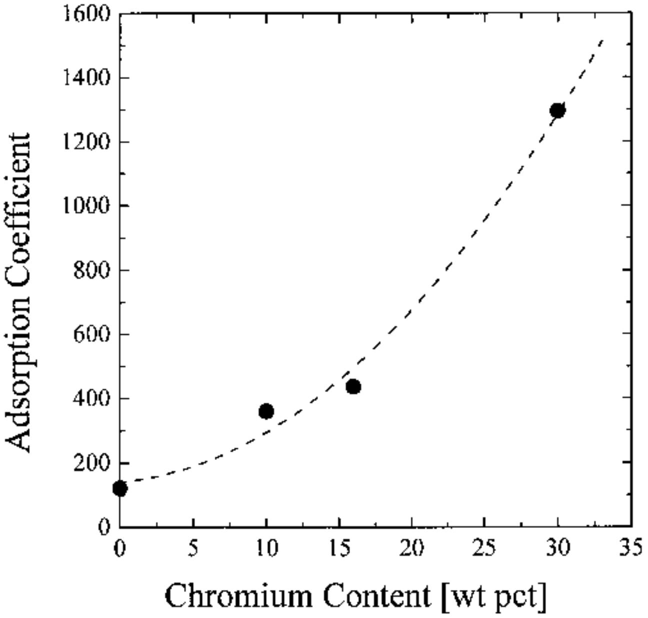

Fig. 5—The oxygen adsorption coefficient K_O at 1823 K as a function of chromium content.

$$K_O = 140 + 4.2 \times [\text{wt pct Cr}] + 1.14 \times [\text{wt pct Cr}]^2 \quad [10]$$

Based on the results described previously, the surface tension of liquid Fe-Cr-O alloy at 1823 K can be expressed as a function of oxygen activity in the alloy as

$$\sigma = 1842 - 279 \ln (1 + K_O a_O) \quad [11]$$

In Figure 3, the calculated surface tension for each alloy is given by dashed lines, which show reasonable accordance with the measurements.

C. *Comparison of the Adsorption Coefficient with Data for Kinetics of Nitrogen Dissociation on Liquid Fe-Cr-O Alloys*

The adsorption coefficient can also be obtained from the kinetic study on interfacial reactions. The interfacial reaction rates of nitrogen absorption into liquid iron or iron-based alloys can be written as[1,44]

$$N_2 \text{ (g)} = 2\underline{N} \text{ (wt pct)} \quad [12]$$

$$v = kP_{N_2} \quad [13]$$

where k (mol/cm^2 s atm) is the rate constant of the interfacial reaction. By using the ^{14}N-^{15}N isotope exchange technique, Ono *et al.*[7] and Lee and Morita[11] showed that the dissociation of adsorbed N_2 is the rate-determining step of the interfacial reaction. Accordingly, the rate constant could be expressed as Eq. [14] assuming Langmuir-type ideal adsorption.

$$k = k^\circ(1 - \theta_O)^2 = \frac{k^\circ}{(1 + K_O a_O)^2} \quad [14]$$

where k^o is the rate constant on the pure liquid iron surface (or iron-based alloy free of oxygen). Equation [14] can be rewritten as Eq. [15]:

$$\frac{1}{\sqrt{k}} = \frac{1}{\sqrt{k^\circ}} + \frac{K_O}{\sqrt{k^\circ}} a_O \quad [15]$$

If the value of $1/k^{1/2}$ is plotted as a function of a_O, then from the intercept with a vertical axis and the slope of a regression line, the values of k^o and K_O can be obtained.

Choh *et al.*[45] and Yamamoto[46] measured the rate of nitrogen desorption from Fe-20 wt pct Cr-O alloys at 1873 K using the sampling technique under reduced pressure. From their results, we can compute the rate constant of nitrogen absorption using the equilibrium constant of Reaction [12][35] and the activity coefficient of nitrogen (f_N[47]). In Figure 6, $1/k^{1/2}$ for Fe-20 wt pct Cr is plotted against oxygen activity. From the intercept and the slope of the straight line described in Figure 6, the values for k^o and K_O are determined as 4.96×10^{-5} (mol/cm^2 s atm) and 513, respectively. The value for K_O is slightly lower than that (677) obtained from Eq. [10]. As described earlier, oxygen adsorption decreases with increasing temperature, so that the slight decrease in the adsorption coefficient with increasing temperature by 50 K is considered reasonable. (Following

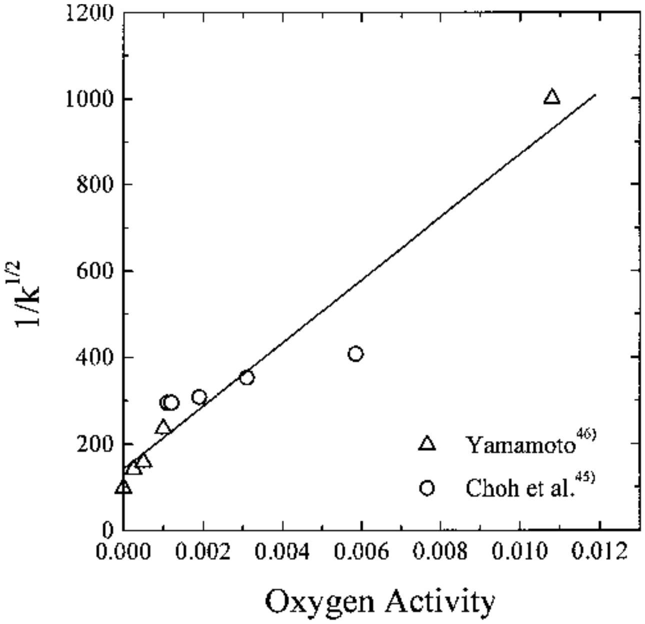

Fig. 6—Graphical determination of the oxygen adsorption coefficient for liquid Fe-20 wt pct Cr-O alloys at 1873 K.

Ono *et al.*[48], the adsorption coefficient at 1973 K was evaluated as 100 for the liquid Fe-20 wt pct Cr alloys.)

IV. CONCLUSIONS

In order to understand the processing of stainless steels containing oxygen, the surface tension of liquid Fe-Cr-O alloy was investigated using the sessile drop method, yielding the following results.

1. The surface tension of liquid Fe-Cr-O alloys ([wt pct Cr] $<$ 30) at 1823 K is given as follows: $\sigma = 1842 - 279 \ln (1 + K_O a_O)$, where $K_O = 140 + 4.2 \times$ [wt pct Cr] $+ 1.14 \times$ [wt pct Cr]^2.
2. The rate constant of nitrogen dissociation on the liquid Fe-20 wt pct Cr-O alloys can be predicted reasonably well using the oxygen adsorption coefficient obtained in the present work.

APPENDIX

Some measurements of the surface tension of liquid Fe-Cr-O alloys have been made in a dynamic reactive system by flowing 25 pct H_2-Ar gas mixture. Thus, oxygen in alloys was removed by hydrogen during the experiments. In order to determine the oxygen activity at the surface, the kinetic of Reaction [A1] has been studied:

$$H_2 + \underline{O} = H_2O \qquad [A1]$$

From the changes in the oxygen concentration of alloys before and after experiments, we can roughly estimate the total reaction rates. For example, oxygen concentration of Fe-10 wt pct Cr-O alloy decreased from 54 to 41 ppmw after 77 minutes by hydrogen deoxidation, suggesting that about 200 minutes would be required for its reduction to half. Three possible rate-determining steps are possible in hydrogen deoxidation:

(1) mass transfer of hydrogen gas to the surface of liquid alloys,
(2) chemical reaction between hydrogen gas and oxygen at the surface of liquid alloys, and
(3) mass transfer of oxygen in the liquid alloys.

If one of the reaction steps is determined, we may consider that other steps are almost in equilibrium state. Hereafter, the rate for each step will be evaluated and compared with the overall reaction rate.

A. *Mass Transfer of Hydrogen Gas*

If the gas-phase mass transfer is the rate-determining step, the pressure of hydrogen at the gas-metal interface is essentially zero. Thus, the rate of H_2 transfer in the gas phase is given by

$$H_2^g \rightarrow H_2^i \qquad [A2]$$

$$J_{H_2} = \frac{k_g}{RT} p_{H_2}^g \qquad [A3]$$

where H_2^g and H_2^i are the H_2 in the gas phase and at the gas-metal interface, respectively, and J_{H_2} is the flux of hydrogen in the gas phase ($= -J_o = -J_{H_2O}$), and k_g is the gas-phase mass-transfer coefficient. The Ranz Marshall equation can be used to estimate the value of k_g:[49]

$$\mathrm{Sh} = \frac{k_g d}{D_{H_2Ar}} = 2.0 + 0.6\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3} \qquad [A4]$$

where d is the diameter of the reaction chamber, Sh is the Sherwood number, Re is the Reynolds number ($= \rho_g u d/\mu_{H_2Ar} = 1.708$ at 1823 K, where ρ_g is the density of the gas phase, u is the gas velocity, and μ_{H_2Ar} is the viscosity of the gas mixture), and Sc is the Schmidt number ($= \mu_{H_2Ar}/D_{H_2Ar}\rho_g = = 0.2321$ at 1823 K). If we assume that the gas phase behaves ideally, the relative diffusivity, D_{H2Ar}, can be estimated by

$$D_{H_2Ar} = 0.00186 \frac{\sqrt{T^3(M_{H_2}^{-1} + M_{Ar}^{-1})}}{p\sigma^2_{H_2Ar}\Omega_{D,H_2Ar}} \qquad [A5]^{[49]}$$

where p is the total pressure ($= 1$ atm); M_{H_2} and M_{Ar} are the molar weights of H_2 and Ar, respectively; σ_{H_2Ar} is the collision diameter (3.167 Å[49]); and Ω_{D,H_2Ar} is a dimensionless function of the temperature and of the intermolecular potential field for one molecule of H_2 and one of Ar (0.6371 at 1823 K[49]). The value of D_{H_2Ar} at 1823 K is 16.34 $cm^2 s^{-1}$, and the corresponding gas mass-transfer coefficient is 10.14 cm/s. The rate equation is given by

$$-\frac{d[\text{ wt pct O}]}{dt} = 1600 \frac{A}{\rho_{\text{Fe-Cr}} V} \frac{k_g}{RT} p_{H_2}^g \qquad [A6]$$

where [wt pct O] is the oxygen concentration in the liquid alloys. If we simply assume that the metal drop is a hemisphere, then the ratio between the surface area (A) and the volume (V) is given by $3/r$, where r is the radius of the metal drop. The oxygen concentration, then, is given as a function of time (t, seconds).

$$[\text{wt pct O}](t = 0) - [\text{wt pct O}](t = t) \approx 0.0232t \qquad [A7]$$

For a sample containing 200 ppmw O initially, it will take only 0.43 seconds to reduce oxygen content to 100 ppmw. This indicates that the mass transfer of hydrogen gas is very fast. Accordingly, it cannot be a rate-determining step.

B. *Mass Transfer of Oxygen in the Alloys*

The flux of oxygen in the liquid alloys (J_o) would be the rate of Reaction [A1] if this were the slow step:

$$J_O = -\frac{k_m \rho_{\text{Fe-Cr}}}{M_O 100}[\text{wt pct O}] \qquad [\text{A8}]$$

where M_O is the molar weight of oxygen. If we simply assume that the metal drop is a hemisphere, the rate for liquid-phase mass-transfer control is given by

$$\frac{d[\text{wt pct O}]}{dt} = -\frac{3}{r}k_m[\text{wt pct O}] \qquad [\text{A9}]$$

The hydrodynamics of a sessile drop are such that Re and Sc are very small and Sh can be assumed to be 2. Then, the mass-transfer coefficient of oxygen in the metal is

$$k_m = \frac{D_O}{r} \qquad [\text{A10}]$$

Since the relative diffusivity of oxygen in liquid Fe-Cr alloys is not reported, we use the value for pure liquid iron ($D_O = 1.4 \times 10^{-4}$ cm^2 s^{-1}[50]). The oxygen concentration is given by

$$[\text{wt pct O}](t = t) = [\text{wt pct O}](t = 0) \times 10^{-3k_m t} \qquad [\text{A11}]$$

From Eq. [A11], it takes about 3 minutes to reach half of the initial concentration. Hence, we may consider that the mass transfer in the alloys would not be a rate-determining step, and the oxygen concentration in the metal is uniform. This was also confirmed by the chemical equilibria between alloy samples and substrates. Electron probe microanalysis (EPMA) of an Al_2O_3-Cr_2O_3 solid solution at the interface proved the Cr_2O_3 content was almost identical to that estimated from the alloy composition using the literature value[51] in the derivation of the activity of Cr_2O_3. For example, the mole fraction of Cr_2O_3 at the interface was found to be 0.03 by EPMA for the sample containing 10 wt pct Cr and 47 ppmw O, which is very close to the value obtained from the chemical equilibrium of Reaction [5], 0.02. Since the oxygen concentration in the bulk alloy was in equilibrium with the substrate, the mass transfer of oxygen in the alloy is not considered to be a rate-determining step.

The chemical reaction rate is unknown. However, based on the results described previously, the chemical reaction between hydrogen gas and oxygen at the surface of liquid alloys is considered as a possible rate-determining step.

REFERENCES

1. R.J. Fruehan and L.J. Martonik: *Metall. Trans. B*, 1980, vol. 11B, pp. 615-21.
2. S. Ban-ya, F. Ishii, Y. Iguchi, and T. Nagasaka: *Metall. Trans. B*, 1988, vol. 19B, pp. 233-42.
3. M. Byrne and G.R. Belton: *Metall. Trans. B*, 1983, vol. 14B, pp. 441-49.
4. P.C. Glaws and R.J. Fruehan: *Metall. Trans. B*, 1985, vol. 16B, pp. 551-59.
5. P.C. Glaws and R.J. Fruehan: *Metall. Trans. B*, 1986, vol. 17B, pp. 317-22.
6. K. Harashima, S. Mizoguchi, M. Matsuo, and A. Kiyose: *Iron Steel Inst. Jpn. Int.*, 1992, vol. 32, pp. 111-19.
7. H. Ono, H. Fukagawa, K. Morita, and N. Sano: *Metall. Mater. Trans. B*, 1996, vol. 27B, pp. 848-53.
8. H. Ono, K. Iuchi, K. Morita, and N. Sano: *Iron Steel Inst. Jpn. Int.*, 1996, vol. 36, pp. 1245-49.
9. J. Zhu and K. Mukai: *Iron Steel Inst. Jpn. Int.*, 1998, vol. 38, pp. 220-28.
10. K. Morita, T. Hirosumi, and N. Sano: *Metall. Mater. Trans. B*, 2000, vol. 31B, pp. 899-904.
11. J. Lee and K. Morita: *Iron Steel Inst. Jpn. Int.*, 2003, vol. 43, pp. 14-19.
12. T. Nagasaka, R.J. Fruehan, and A.W. Cramb: *ISSTech 2003 Conf. Proc.*, “Ironmaking Process Technology/Wolf Symposium,” Iron and Steel Society, Warrendale, PA, 2003, pp. 979-92.
13. G.R. Belton: *Metall. Trans. B*, 1976, vol. 7B, pp. 35-42.
14. K. Mukai and W. Lin: *Tetsu-to-Hagané*, 1994, vol. 80, pp. 527-32.
15. K. Mukai and W. Lin: *Tetsu-to-Hagané*, 1994, vol. 80, pp. 533-38.
16. K. Mukai, Z. Li, and M. Zeze: *Mater. Trans. JIM*, 2002, vol. 43 (7), pp. 1724-31.
17. A. Sharan, T. Nagasaka, and A.W. Cramb: *Metall. Mater. Trans. B*, 1994, vol. 25B, pp. 626-28.
18. Y. Chung and A.W. Cramb: *Steel Res.*, 1999, vol. 70 (8–9), pp. 325-29.
19. U. Mittag and K. Lange: *Arch. Eisenhuttenwes*. 1976, vol. 47, pp. 65-69.
20. K. Mori, M. Kishimoto, T. Shimose, and Y. Kawai: *J. Jpn. Inst. Met.*, 1975, vol. 39, pp. 1301-07.
21. E.S. Levin and G.D. Ayushina: *Russ. J. Phys. Chem.*, 1971, vol. 45, p. 792.
22. J. Lee, A. Kiyose, S. Nakatsuka, M. Nakamoto, and T. Tanaka: *Iron Steel Inst. Jpn. Int.*, 2004, vol. 44, pp. 1793-99.
23. K. Nogi, W.B. Chung, A. McLean, and W.A. Miller: *Mater. Trans. JIM*, 1991, vol. 32 (2), pp. 164-68.
24. F.A. Halden and W.D. Kingery: *J. Phys. Chem.*, 1955, vol. 59, pp. 557-59.
25. P. Kozakevitch and G. Urbain: *Mem. Sci. Rev. Metall.*, 1961, vol. 58 (7), pp. 517-34.
26. K. Ogino, S. Hara, T. Miwa, and S. Kimoto: *Tetsu-to-Hagané*, 1979, vol. 65, (14), pp. 2012-21.
27. B.J. Keene, K.C. Mills, J.W. Bryant, and E.D. Hondros: *Can. Metall. Q.*, 1982, vol. 21 (4), pp. 393-403.
28. A. Kasama, A. McLean, W.A. Miller, Z. Morita, and M.J. Ward: *Can. Metall. Q.*, 1982, vol. 22 (1), pp. 9-17.
29. K. Ogino, K. Nogi, and C. Hosoi: *Tetsu-to-Hagané*, 1983, vol. 69 (16), pp. 1989-94.
30. I. Jimbo and A.W. Cramb: *Iron Steel Inst. Jpn. Int.*, 1992, vol. 32 (1), pp. 26-35.
31. J. Zhu and K. Mukai: *Iron Steel Inst. Jpn. Int.*, 1998, vol. 38 (10), pp. 1039-44.
32. J. Lee and K. Morita: *Iron Steel Inst. Jpn. Int.*, 2002, vol. 42, pp. 588-94.
33. J. Lee and K. Morita: *Steel Res.*, 2002, vol.73, pp. 367-72.
34. I. Jimbo and A.W. Cramb: *Metall. Trans. B*, 1993, vol. 24B, pp. 5-10.
35. *Steelmaking Data Sourcebook*, The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Gordon and Breach Science Publishers, New York, NY, 1988, pp. 255-62.
36. T. Itoh, T. Nagasaka, and M. Hino: *Iron Steel Inst. Jpn. Int.*, 2000, vol. 40, pp. 1051-58.
37. S. Dimitrov, H. Wenz, K. Koch, and D. Janke: *Steel Res.*, 1995, vol. 66, pp. 39-44.
38. E.T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, Inc., New York, NY, 1980.
39. F.C. Tompkins: *Chemisorption of Gases on Metals*, Academic Press, London, 1978, p. 11.
40. J. Lee, T. Tanaka, M. Yamamoto, and S. Hara: *Mater. Trans.*, 2004, vol. 45, pp. 625-29.
41. G. Bernard and C.H.P. Lupis: *Metall. Trans.*, 1971, vol. 2, pp. 2991-98.
42. L.H. Van Vlack: *Elements of Materials Science and Engineering*, 6th ed., Addison-Wesley Publishing Company, Reading, MA, 1989, pp. 554-55.
43. I. Jimbo, A. Sharan, and A.W. Cramb: *Trans. ISS*, 1994, vol. 21, pp. 48-55.
44. A. Obeahs, F. Tsukihashi, and N. Sano: *Trans. Iron Steel Inst. Jpn.*, 1987, vol. 33 (11), pp. 1131-35.
45. T. Choh, T. Takebe, and M. Inouye: *Tetsu-to-Hagané*, 1981, vol. 67, p. 2665.
46. K. Yamamoto: Master’s Thesis, The University of Tokyo, Tokyo, 1993.
47. F. Ishii, Y. Iguchi, and S. Ban-ya: *Trans. Iron Steel Inst. Jpn.*, 1986, vol. 26, pp. 128-32.
48. H. Ono, K. Iuchi, K. Morita, and N. Sano: *Iron Steel Inst. Int.*, 1996, vol. 36, pp. 1245-49.
49. R.B. Bird, W.E. Stewart, and E.N. Lightfoot: *Transport Phenomena*, John Wiley & Sons, New York, NY, 1960, pp. 511, 647, and 746.
50. T. Iida and R.I.L. Guthrie: *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, United Kingdom, 1993, p. 221.
51. H. Tang, T. Tsai, and A. Muan: *J. Am. Ceram. Soc.*, 1992, vol. 75, pp. 1412-15.