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The Determination of the Amount of Oxygen in Molten Copper-Nickel and Copper-Silver Alloys by the EMF Method

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Using the following solid oxide-electrolyte galvanic cells, Pt/air//ZrO_2 (+CaO) O//(in Cu–Ni alloy)/Mo and Pt/air//ZrO_2 (+CaO) O//(in Cu–Ag alloy)/Mo, the electromotive forces of the cells have been measured as a function of the oxygen concentration in copper-nickel or -silver alloys at oxygen concentrations ranging from several ppm to 1000 ppm, at 1210°C for copper-nickel alloys and at 1100°C or 1200°C for copper-silver alloys respectively. The activity coefficient of oxygen has been determined from the electromotive force for the alloy systems investigated. In the case of copper-nickel, the activity coefficient of oxygen decreases with an increase in the nickel concentration and also with a decrease in the oxygen concentration. The solubility of oxygen in the copper-nickel alloy has also been measured at 1210°C by the use of the following galvanic cell, Pt/air//ZrO_2 (+CaO)//O(in Cu–Ni alloy), NiO/Mo.

The determination of the amount of oxygen in molten metals and alloys is of great importance in the metallurgical process or in controlling the quality of products. In recent years, there have been many studies concerning the direct electrochemical measurement of the oxygen content in molten iron[1–9] or copper.[10–14] These investigations have employed galvanic cells, the electrolytes in which are various solid mixed-oxides which conduct the current through the migration of oxide ion vacancies. Since the work of Kiukkola and Wagner[15] was reported, such electrolytes have been used in numerous cell studies in order to determine the thermodynamic properties of metallic oxides, the partial pressure of oxygen in various atmospheres, and the properties of oxygen dissolved in metals and alloys. The advantage of this electrochemical method is that it make possible the fast, direct, and continuous determination of oxygen.

In a previous paper,[16] the determination of the amount of oxygen in molten copper and copper-tin alloys by the EMF method using lime-stabilized zirconia as the solid electrolyte was reported by the author. In this investigation, a study of the determination of the amount of oxygen in molten copper-nickel and copper-silver alloys has been made by the same method. The main objects of this investigation are to determine the relationship between the electromotive forces of the following cells and the oxygen contents in copper-nickel and copper-silver alloys and to determine the activity coefficients of the oxygen in these alloys.

$$\mathrm{Pt/air//ZrO_2(+CaO)//O(in\ Cu\text{–}Ni\ alloy)/Mo} \qquad (1)$$

$$\mathrm{Pt/air//ZrO_2(+CaO)//O(in\ Cu\text{–}Ag\ alloy)/Mo} \qquad (2)$$

Since the transference number of oxide ion in stabilized zirconia is regarded as unity under the experimental conditions of this work,[9,17–19] the electromotive force (E) of the cell, (1) or (2), is:

$$\begin{aligned} E &= (2.303\boldsymbol{RT}/4\boldsymbol{F})\log(0.21/P_{O_2}) - E_{th} \\ &= (2.303\boldsymbol{RT}/4\boldsymbol{F})\log(0.21/a_O^2) - E_{th} \qquad (3) \end{aligned}$$

where $\boldsymbol{F}$ is the Faraday constant, where P_{O_2} and a_O are the partial pressure and the activity of oxygen in the liquid alloys with respect to a reference state of pure oxygen gas at 1 atmospheric pressure respectively, and where E_{th} is the thermoelectromotive force of the Pt–Mo thermocouple, which has been measured previously and expressed by Eq. (4),[16] where molybdenum is positive and where t is the temperature in °C:

$$E_{th}(\text{in mV}) = 406.3/t^{1/2} + 0.04352t - 29.09 \qquad (4)$$

At a given temperature, all the terms of Eq. (3) are constants except E and a_O. Thus, a_O can be determined by the measurement of the electromotive force.

The electromotive force is also related to the mole fraction of oxygen (N_O) by Eq. (5) in the oxygen concentration range over which the activity of oxygen obeys Henry's law:

$$\begin{aligned} E &= (2.303\boldsymbol{RT}/4\boldsymbol{F})\log 0.21K \\ &\quad - E_{th} - (2.303\boldsymbol{RT}/2\boldsymbol{F})\log N_O \qquad (5) \end{aligned}$$

where K is the equilibrium constant for the reaction:

$$O_2(g) = 2O\ (\text{in alloy, liq.}) \qquad (6)$$

At a given temperature, the electromotive force of the cell, (1) or (2), is a linear function of $\log N_O$.

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Experimental

An internal cell arrangement is shown in Fig. 1. About 600 g of molten Cu–Ni or Cu–Ag alloy was placed in the alumina crucible (66 mm i.d., 100 mm height), in which a stabilized zirconia in the form of a closed-end tube (500 mm long, 13 mm o.d., 8 mm i.d.) and a Pt–Pt/13% Rh thermocouple in an alumina sheath were immersed. A platinum contact wire was pressed (with a spring mechanism) against the inside bottom wall of the electrolyte tube, which was flushed continuously with a stream of air *via* an alumina tube inserted inside the electrolyte tube. The platinum contact wire acted as the reference electrode ($P_{O_2}=0.21$ atm.). A molybdenum contact wire was immersed in the alloy melt only at the times when the measurements were taken, because dissolved oxygen attacked molybdenum and eventually broke the electrical contact if the molybdenum wire was immersed continuously in the melt with a high oxygen content. A radiation shield of inconel or of alundum was placed on the alumina crucible. The whole of the cell was enclosed in an alumina outer tube which was closed gas-tight at the top with a water-cooled brass head.

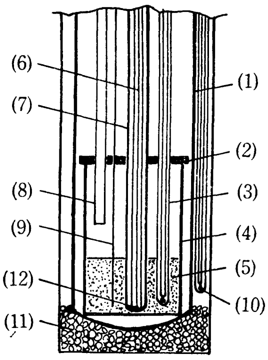

Fig. 1. Experimental cell.
(1) quartz tube, (2) inconel or alundum radiation shield, (3) Pt-Pt/13%Rh thermocouple in alumina tube, (4) alumina crucible, (5) Cu-Ni or Cu-Ag alloy melt, (6) Pt lead in alumina tube, (7) ZrO_2(+CaO) tube, (8) quartz sampling guide and addition tube, (9) Mo lead, (10) thermocouple for temperature control, (11) alumina, (12) Pt electrode

After the system had been evacuated and then filled with purified argon, the entire cell unit was heated in a resistance furnace to the desired temperature. The temperature was controlled by means of a Chino E-500 Controller using a Pt–Pt/13% Rh thermocouple with an accuracy of ±2.5°C. The cell potential was measured with a Yokogawa Electric P-1 Electrometer with an accuracy of ±0.5 mV. Oxygen was added to the melt by dropping reagent-grade copper oxide (CuO) chips through the sampling guide tube. After waiting for equilibrium, as evidenced by a steady cell potential with the time, electromotive force measurements were taken for each oxygen concentration: a sample of about 20 g was taken from the alloy melt by suction into the quartz tube (4 mm i.d.) which was guided through the sampling guide tube. The quartz tube was then immediately removed from the melt and quenched in distilled water. The sample was analyzed for oxygen by the vacuum-fusion method.

The measurements were carried out for the Cu–Ni alloy containing up to 0.22 mole fraction of nickel at 1210°C and for the Cu–Ag alloy containing up to 0.031 mole fraction of silver at 1100°C and 1200°C. The oxygen concentration was changed from several ppm to 1000 ppm.

Table 1. Chemical composition of stabilized zirconia (in wt%)

ZrO_2	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
90.98	5.93	0.67	1.59	0.46	0.20	0.14

The stabilized zirconia used was a commercial zirconia tube, ZR-11, of the Nippon Kagaku Kogyo Co., Ltd.; its chemical composition is listed in Table 1.

Results and Discussion

1) Relation between Electromotive Force and Oxygen Content. The relations between the oxygen concentrations in the alloy melts and the electromotive forces measured are shown in Fig. 2—Fig. 4, where N_O, N_{Ni}, and N_{Ag} are the mole fractions of oxygen, nickel, and silver respectively. The relations have also been expressed in the form of Eq. (7), and the values of A and B have been calculated by the least-squares method and are listed in Tables 2 and 3.

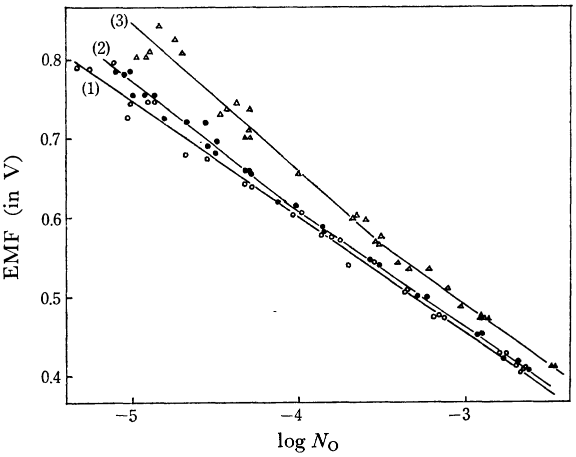

Fig. 2. Relation between the electromotive force of the cell-(1) and oxygen content at 1210°C.
(1) -○- N_{Ni}: 0.0015, (2) -●- N_{Ni}: 0.011, (3) -△- N_{Ni}: 0.10

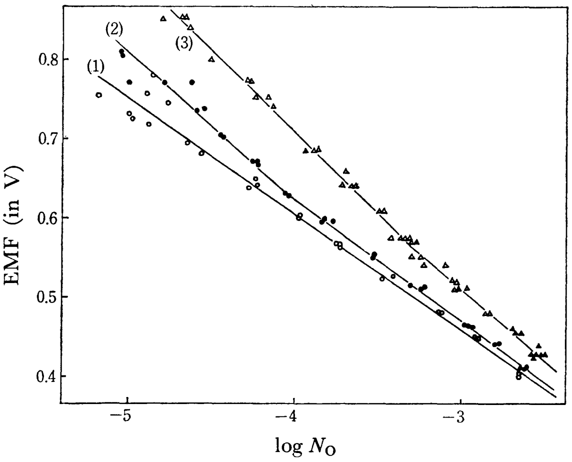

Fig. 3. Relation between the electromotive force of the cell-(1) and oxygen content at 1210°C.
(1) -○- N_{Ni}: 0.0053, (2) -●- N_{Ni}: 0.056, (3) -△- N_{Ni}: 0.22

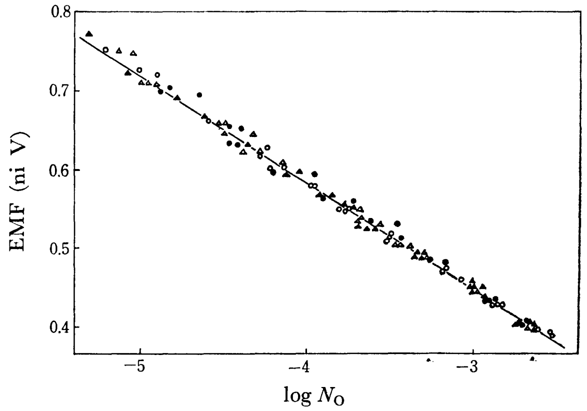

Fig. 4. Relation between the electromotive force of the cell-(2) and oxygen content at 1100°C.
-○- N_{Ag}: 0.00089, -●- N_{Ag}: 0.0029, -△- N_{Ag}: 0.0059, -▲- N_{Ag}: 0.031

Table 2. The values of A and B in Eq. (7) at 1210°C, Cu-Ni alloy

N_{Ni}	A	B
0.0015	0.012	−0.147
0.0053	0.012	−0.148
0.011	$N_O \leqq 7.7\times 10^{-5}$	
	−0.056	−0.166
	$N_O \geqq 7.7\times 10^{-5}$	
	0.022	−0.147
0.056	$N_O \leqq 8.3\times 10^{-5}$	
	−0.128	−0.187
	$N_O \geqq 8.3\times 10^{-5}$	
	0.010	−0.153
0.10	$N_O \leqq 3.0\times 10^{-4}$	
	−0.097	−0.189
	$N_O \geqq 3.0\times 10^{-4}$	
	0.029	−0.153
0.22	$N_O \leqq 5.2\times 10^{-4}$	
	−0.113	−0.206
	$N_O \geqq 5.2\times 10^{-4}$	
	−0.034	−0.182

Table 3. The values of A and B in Eq. (7) at 1100°C and 1200°C, Cu-Ag alloy

N_{Ag}	1100°C		1200°C	
	A	B	A	B
0.00089	0.040	−0.136	0.010	−0.146
0.0029	0.041	−0.136	0.010	−0.146
0.0059	0.041	−0.136	0.007	−0.146
0.031	0.039	−0.136	0.010	−0.146

$$E = A + B \log N_O \qquad (7)$$

As is shown in the results, in the cases of both Cu–Ag and Cu–Ni alloys containing not more than 0.0053 mole fraction of nickel, the relation between the electromotive force and log N_O is shown by a straight line over the oxygen concentration range investigated. On the other hand, in the case of the Cu–Ni alloy containing 0.011 mole fraction of nickel or more, the relation is divided into two regions, lower and higher concentration regions of oxygen, and is shown by a straight line in each region. In the latter case, the majority of the B values in Eq. (7) exhibit deviations from the Nernstian slope (−0.147 at 1210°C). These deviations are due to the lowering of the activity coefficient of oxygen with a decrease in the oxygen concentration as will be discussed later. Phenomena similar to those discussed above were also observed in the Cu–Sn alloy system.16)

In any case, we can use the relations shown in Fig. 2—Fig. 4 as calibration curves for the determination of the amount of oxygen in molten Cu–Ni and Cu–Ag alloys.

2) Activity of Oxygen. The activity coefficient of oxygen (γ_O), as defined by Eq. (8), has been determined. From Eqs. (8) and (3), we obtain Eq. (9). By substituting E and E_{th}, which have been already given by Eqs. (7) and (4) respectively, into Eq. (9), we can obtain the activity coefficient of oxygen as a function of the mole fraction of oxygen at each temperature

$$a_O = \gamma_O \cdot N_O \qquad (8)$$

$$\log \gamma_O = (1/2) \log (0.21/N_O{}^2) - 2\boldsymbol{F}(E+E_{th})/2.303\boldsymbol{RT} \qquad (9)$$

and at each concentration of nickel or silver. The activity coefficient of oxygen thus obtained has been expressed in the form of Eq. (10); the values of A and B in Eq. (10) are listed in Tables 4 and 5. From the results listed in those tables, it can be seen that: (1) in cases of both Cu–Ag and Cu–Ni alloys containing not more than 0.0053 mole fraction of nickel, the activity coefficient of oxygen is independent of the oxygen concentration and the activity of oxygen follows Henry's law. (2) in the Cu–Ni alloy containing 0.011 mole fraction of nickel, the decrease in the activity coefficient of oxygen with a decrease in the oxygen concentration is seen in the lower oxygen concentration region, while in the higher oxygen concentration region, the activity of oxygen follows Henry's law. (3) in Cu–Ni alloys containing 0.056, 0.10, and 0.22 mole fractions of nickel, the activity coefficient of oxygen decreases with a decrease in the oxygen concentration and the activity of oxygen no longer follows Henry's law over the whole oxygen concentration region investigated. Similar phenomena in the activity coefficient of oxygen were also observed in the Cu–Sn–O system.16) It is worth noting that the lowering of the activity coefficient of oxygen with a decrease in the oxygen concentration was observed in copper alloy with nickel or tin, but not in the case of copper16) or copper-silver alloy. The origin of these phenomena is not obvious. However, in view of the fact that the affinity of nickel or tin for oxygen is stronger than that of copper or silver, it probably depends on the affinity of the atoms of alloying elements for oxygen atoms, or it may be due to the formation of the molecular species or the dipoles between oxygen atoms and the atoms of the alloying elements, the oxygen atoms in which may be bonded more tightly to nickel or tin atoms as the concentration of oxygen decreases. Kozuka *et al.*14) have noted that phenomena similar to those described above which were also observed by them in the Cu–O system are probably

$$\log \gamma_O = A + B \log N_O \qquad (10)$$

TABLE 4. THE VALUES OF A AND B IN EQ. (10) AT 1210°C, Cu-Ni ALLOY

N_{Ni}	A	B
0.0015	−0.660	0
0.0053	−0.660	0
0.011	$N_O \leqq 7.7\times10^{-5}$	
	−0.197	0.129
	$N_O \geqq 7.7\times10^{-5}$	
	−0.728	0
0.056	$N_O \leqq 8.3\times10^{-5}$	
	0.293	0.272
	$N_O \geqq 8.3\times10^{-5}$	
	−0.646	0.041
0.10	$N_O \leqq 3.0\times10^{-4}$	
	0.082	0.286
	$N_O \geqq 3.0\times10^{-4}$	
	−0.775	0.041
0.22	$N_O \leqq 5.2\times10^{-4}$	
	0.191	0.401
	$N_O \geqq 5.2\times10^{-4}$	
	−0.347	0.238

TABLE 5. THE VALUES OF A AND B IN EQ. (10) AT 1100°C AND 1200°C, Cu-Ag ALLOY

N_{Ag}	1100°C		1200°C	
	A	B	A	B
0	−0.863	0	−0.654	0
0.00089	−0.863	0	−0.649	0
0.0029	−0.870	0	−0.649	0
0.0059	−0.874	0	−0.672	0
0.031	−0.865	0	−0.649	0

due to impurities in the copper. If this is so, it is probably that the impurities are elements which have a strong affinity for oxygen.

On the other hand, as is shown in Tables 4 and 5, the activity coefficient of oxygen in the Cu-Ni alloy is also affected by the addition of nickel and decreases with an increase in the nickel concentration. This decrease in the activity coefficient of oxygen, as expressed by Eq. (11) in both the nickel concentration range of not more than 0.011 mole fraction and the oxygen concentration range over which the activity coefficient of oxygen is independent of the oxygen concentration, is due to the interaction between oxygen and nickel atoms. The usual way of expressing this

$$\log \gamma_O = -8.06N_{Ni} - 0.636 \qquad (11)$$

interaction is in terms of the interaction coefficient, $\varepsilon_O^{(Ni)}$, derived by Wagner.[20] The value of $\varepsilon_O^{(Ni)}$ obtained from the present work, −8.06, that is, the slope of function (11), is in near agreement with the value determined by Oishi *et al.*, −7.00.[21]

3) Solubility of Oxygen. The solubility of oxygen in Cu–Ni melts containing 0.056, 0.10, and 0.22 mole fractions of nickel has been measured at 1210°C. By substituting E_s, which is the electromotive force of Cell (12) measured at 1210°C in a fixed mole fraction of nickel under the equilibrium conditions of Reaction (13), into E in Eq. (7), we can obtain the solubility (in mole fraction) of oxygen in the Cu–Ni melt. The solubilities thus obtained are listed in Table 6.

$$\text{Pt/air//ZrO}_2\text{(+CaO)//O(in Cu-Ni, liq.), NiO/Mo} \qquad (12)$$

$$\text{Ni(in Cu-Ni, liq.)} + \text{O(in Cu-Ni, liq.)} = \text{NiO(s)} \qquad (13)$$

The experiments were carried out as follows: after assembling the cell as has been described above, the cell system was evacuated, filled with purified argon, and then heated to 1210°C. Oxygen was added to the Cu–Ni melt until the oxygen concentration near the solubility of oxygen was reached, and then nickel oxide (NiO) powder was added to the melt. After the equilibrium has been reached, the potential (E_s) was measured, at the same time, a sample for oxygen analysis was taken. The oxygen content of the sample taken, that is, the solubility of oxygen, was determined by the vacuum-fusion method; these values are listed in Table 6 and compared with those calculated from E_s and Eq. (7).

The solubility of oxygen, as calculated from E_s and Eq. (7), is in good agreement with that determined by the analysis of oxygen; the solubility of oxygen decreases with an increase in the nickel concentration in the nickel concentration range investigated.

TABLE 6. SOLUBILITY OF OXYGEN IN Cu-Ni ALLOY AT 1210°C

N_{Ni}	Solubility (mole fraction)	
	Calculated[a]	Analyzed[b]
0.056	0.00482	0.00478
0.10	0.00392	0.00387
0.17	—	0.00300
0.22	0.00291	0.00284

a) Calculated from E_s and Eq. (7).
b) Analyzed by vacuum-fusion method.

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