

Electromotive Force of an Oxygen Concentration Cell and Magnetite Measurements in connection with the Vacuum Treatment of Molten Matte and White Metal*

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The EMF of an oxygen concentration cell in sulfide melts (matte and white metal) has been measured under a reduced pressure of around 0.5 mmHg at 1200°C by means of a solid-electrolyte cell and the results are presented as a function of the calculated partial pressure of oxygen, together with the EMF of molten slag, blister copper, and the Cu-O system. Zinc in matte affects the EMF to a great extent.

The magnetite contents in matte, white metal, and slag are semi-quantitatively determined by a magnetic method. The amount of SO₂ gas liberated during the vacuum treatment is discussed in relation to the difference of magnetite contents before and after the vacuum treatment.

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I. Introduction

In a previous paper⁽¹⁾ the experimental results of a vacuum treatment of samples of matte and white metal at 1200°C and some thermodynamic considerations have been presented in relation to the removal of volatile impurities in the copper smelting process. This paper is the continuation that follows the previous work and describes the EMF measurements of an oxygen concentration cell in sulfide melts or molten slags and the determination of magnetite contents in sulfide samples. The experiments have been carried out simultaneously with the experiments for the removal of impurities under reduced pressures.

As discussed in the previous paper the partial pressure of oxygen plays an important role in the conventional copper smelting process. The EMF in molten copper has been measured by the aid of a solid-electrolyte cell using calcia stabilized zirconia⁽²⁾⁻⁽⁷⁾. When the cell is developed to measure the EMF in various copper sulfide melts, it will serve for a better understanding of the copper smelting process as well as for the process control in field operations.

II. Experimental

1. Sample

Sulfide samples used in this study were the same as those described in the previous paper⁽¹⁾, except for a sample of white metal which was prepared by

vacuum lift refining of 4-kg white metal A containing impurities. The compositions of samples are listed in Table 1.

Table 1 Compositions of matte and white metal.

Sample	%Cu	%Fe	%S	%As	%Sb	%Bi	%Zn	%Pb
Matte A-A	45.97	22.64	23.62	0.15	0.30	0.044	2.71	1.55
Matte A-B	46.72	19.64	22.08	0.75	0.31	0.057	5.39	1.47
White metal A	72.42	5.55	16.70	0.05	0.28	0.007	0.35	0.24
White metal*	77.65	0.21	18.66	0.32	0.16	0.193	0.17	0.41

* Vacuum lift refined sample.

Slags were prepared by melting a mixture of the furnace slag and quartz powder in a quartz crucible. The melt saturated with silica was then blown by an Ar-O₂ or Ar-H₂ gas mixture in order to increase or decrease the ferric/ferrous ratio. The melt was cooled in argon gas after the EMF measurement and the contents of Fe³⁺, Fe²⁺, and SiO₂ were chemically determined. The approximate composition of slag was 42.8%-48.9% SiO₂, 35.0%-37.1% total Fe and 0.5%-1.06% Cu, and the ferric/ferrous ratios were in the range from 0.39 to 0.027.

2. Apparatus

(1) EMF measurement of an oxygen concentration cell

In the earlier stage of the experiment the tempera-

(3) W. Pluschkell and H. J. Engell: *Z. Metallk.*, **56** (1965), 450.

(4) T. C. Wilder: *Trans. Met. Soc. AIME*, **236** (1966), 1035.

(5) H. Rickert and H. Wagner: *Electrochim. Acta*, **11** (1966), 83.

(6) C. M. Diaz and F. D. Richardson: *Trans. Inst. Min. Met.*, **76** (1967), C 196.

(7) Z. Kozuka, K. Suzuki, T. Oishi, and J. Moriyama: *J. Japan Inst. Metals*, **32** (1968), 1132.

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(1) H. Kametani and C. Yamauchi: *Trans. JIM*, **14** (1973), 218.

(2) H. Kametani and C. Yamauchi: *Trans. JIM*, **13** (1972), 13.

ture of the melt in the vacuum vessel was measured with a thermocouple in an alumina-protected tube dipped in the melt (refer to Fig. 1 in the previous paper⁽¹⁾). Then a calcia stabilized zirconia tube was used in place of the alumina tube so as to permit to measure simultaneously the temperature and the EMF of sulfide melt during the vacuum treatment.

The oxygen concentration cell consists of (Pt. 13% Rh)+Pt O₂ (1 at.)/ZrO₂·CaO/sulfide melt/Mo. The Pt and Mo electrodes were connected with a five-figure digital voltmeter for precise reading of the EMF and in parallel with a mV meter and a recorder for continuous recording. The correction of the read values was made in the same way as described in the EMF measurements of molten copper in previous work⁽²⁾, i.e., calibrated by pure copper melts containing the known amounts of dissolved oxygen.

A zirconia tube of 5 mm ID and 50 cm length and the Mo electrode (a wire of 1 mm ϕ) were vertically set through a synthetic rubber stopper at the top of the vacuum vessel so as the lower ends located just above the charge in the crucible. After melting of the charge and just before the start of pressure reduction at 1200°C both electrodes were lowered to dip in the melt. All zirconia tubes were tested under a vacuum of about 10⁻³ mmHg for several hours prior to the experiment.

An observation of the zirconia tube after a run revealed that only an extremely thin layer of the outer surface of the tube was attacked by the sulfide melt during the immersion for about 1 hr. It seems that the zirconia tube is stable against the sulfide melt for a prolonged period of continuous measurement, whereas the Mo electrode is dissolved slowly in the sulfide melt.

The EMF measurement of silica-saturated slags was carried out at 1250°C in the quartz crucible of 3.5 cm ID with an oxygen concentration cell consisting of Pt O₂ (1 at.)/ZrO₂·CaO/molten slag/Pt. The details of the cell and the procedure are the same with those described above, except for the use of a Pt electrode (a wire of 0.5 mm ϕ) in place of the Mo electrode which is dissolved quickly in the molten slag. The temperature of the melt was separately measured using a thermocouple.

The zirconia tube was, in contrast to the high stability against sulfide melt, easily attacked by molten slag at the experimental temperature. After the measurement for 30 min about one half of the thickness (1.5 mm) of the tube became black, although no appreciable change of the EMF was found during the measurement.

(2) Magnetic method for magnetite determination

The magnetite contents in matte, white metal and slag were determined semi-quantitatively by a magnetic method developed in our laboratory, the details of which will be published elsewhere. In brief, an oscillator with a tank circuit consisting of a coil of 1.5 cm ID and 2.4 cm length and a midge variable condenser of max. 50 pF was constructed. A test

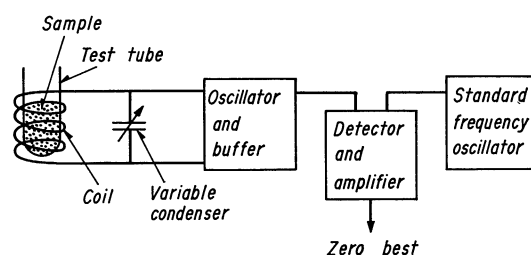


Fig. 1 Block diagram of the apparatus for magnetic measurement.

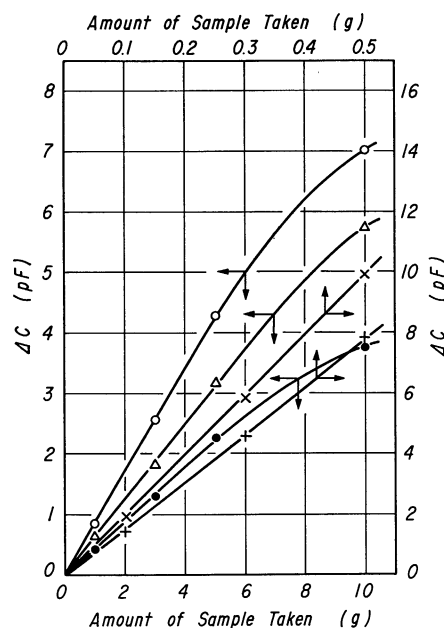


Fig. 2 Variation of ΔC (as read) with the amount of magnetic materials.

ΔC : the difference of capacity in pF in the presence and absence of a sample, \circ : matte from a flash smelting furnace, \bullet : matte from a blast furnace, \triangle : white metal, \times : commercial magnetite, and $+$: iron powder. Scales are shown respectively by arrows.

tube containing 5 g of a pulverized sample was placed in the coil and the decrease of oscillating frequency due to an increase of inductance in the presence of magnetite in the sample was compensated with the variable condenser with regard to the standard frequency of about 8 kc by the zero beat method. The block diagram of the apparatus is illustrated in Fig. 1.

The magnetite content is represented semi-quantitatively here as the decrement of the capacity in pF, ΔC . Although the oscillator and the detector were a hand-made set, they were capable of detecting a frequency difference of about 0.1 cps. The calibration was made using the weighed amounts of iron powder, commercial magnetite powder, and sulfide samples. It has been confirmed that the ΔC is proportional to the amount of magnetic material placed in the test tube as shown in Fig. 2.

The samples of matte, white metal and furnace slag weighing 5 g were employed, while in the case of converter slag containing a large amount of magnetite, a 0.5-g sample was used.

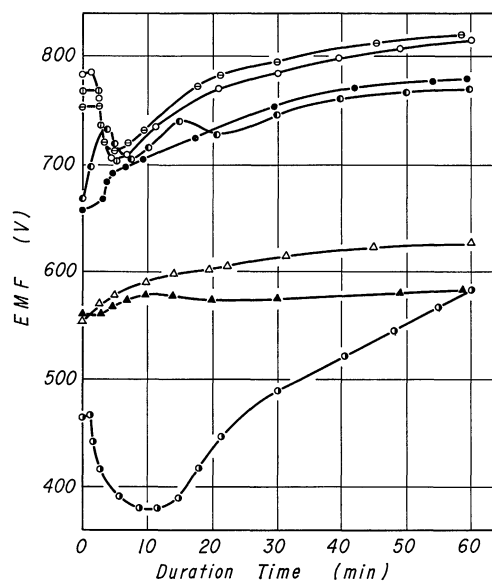


Fig. 3 Variations in EMF of sulfide melts with time under reduced pressures at 1200°C.
 Legend; ●: matte A-A, ○, ⊙: matte A-B, ⊚: matte A-B (interrupted), ● and ⊚: run A and run B, respectively (see text), △: white metal H, ▲: vacuum lift refined white metal.

The amount of SO₂ gas liberated during the vacuum treatment was derived from the weight increment of an absorber tube using 20-g of granular ascalite connected between a rotary pump and the vacuum vessel.

3. Experimental results

(1) EMF of the oxygen concentration cell

The variations of the EMF with time are summarized in Fig. 3. The EMF rised asymptotically with time under a reduced pressure, when the impurity content in the sulfide sample was low as in the case of matte A-A, white metal and refined white metal. Here a higher EMF corresponds to a lower concentration of oxygen dissolved in the melt and the dissolved oxygen is most likely to escape as SO₂ under reduced pressures.

In the case of mattes A-B and H having a high Zn content of about 5%, it was observed that the EMF decreased in the initial stage of the vacuum treatment and then gradually increased.

Since the drop of the EMF corresponds to an increase of the activity of oxygen in the melt, it is reasonable to consider that the decrease in concentration of such an active metal as Zn due to the vacuum treatment is associated with an increase of the activity coefficient of oxygen in the residual melt.

A run was then interrupted at the minimum point of the EMF and the content was analyzed. In Table 2 the composition of the interrupted sample is compared

with that of a sample treated for 1 hr. The zinc content decreased from 5.39% (see Table 1) to 1.35% during the initial drop of EMF (about 5 min) and then decreased further to 0.007% in 55 min, while the EMF increased.

In order to ascertain the above consideration, two runs using matte A-A with the addition of zinblende were made and the result is also shown in Fig. 3.

In run A, 6 g of zinblende (pure mineral, pulverized) was mixed with 100 g of the matte A-A and placed in the vacuum vessel to melt directly without agitation. The result was not satisfactory owing to a fluctuarion of the EMF which may arise from the convection in the heterogenuous melt with regard to the Zn concentration.

Then the same mixture of matte and zinblende was premelted and the homogenized product was remelted in the vacuum vessel in run B. In this case the behavior of the EMF was quite analogous to mattes A-B and H, that is, a minimum of the EMF was found. However, the EMF curve lies in a very low area. The reason of the abnormally low EMF is not clear, but this fact suggests difficulties in preparing the sulfide melt in the "normal" state using a small-sized apparatus in a laboratory.

In Fig. 4 the variation of the EMF of slag saturated with silica at 1250°C is shown as a function of the log of the ferric/ferrous ratio chemically determined after solidification. The region of the ferric/ferrous ratio is restricted by the lower and upper limits given by

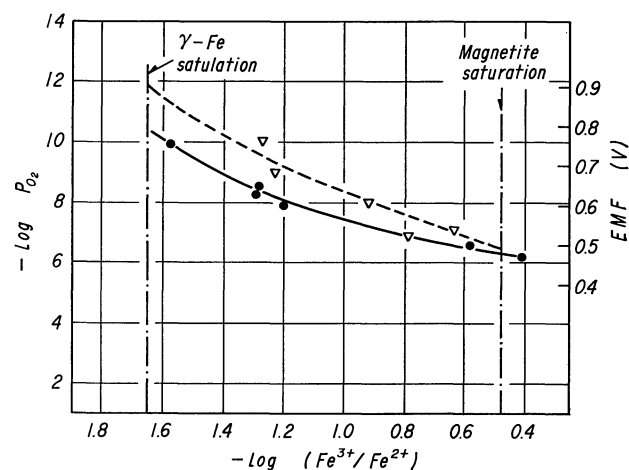


Fig. 4 Variation in EMF of silica saturated slag with the ferric/ferrous ratio referring to the partial pressure of oxygen.
 $-\log P_{O_2}$ vs. $-\log (Fe^{3+}/Fe^{2+})$; ▽: Michal and Schuhmann (1200°C)⁽⁹⁾, broken line: Turkdogan and Bills (1250°C)⁽¹⁰⁾. Oxygen potential vs. $-\log (Fe^{3+}/Fe^{2+})$; ●: present work (1250°C).

Table 2 Compositions of a sample interrupted at 5 min and a sample treated for 1 hr.

Sample (matte A-B)	%Cu	%Fe	%S	%As	%Sb	%Bi	%Zn	%Pb
Interrupted at 5 min	52.58	20.08	22.87	0.21	0.09	0.023	1.35	0.07
Treated for 1 hr	53.52	20.56	23.66	0.05	0.02	0.003	0.007	tr

isotherms in the $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system⁽⁸⁾. The melt is in equilibrium with solid $\gamma\text{-Fe}$ at the lower limit at about $(\text{Fe}^{3+}/\text{Fe}^{2+})=0.023$, while the melt is, under a high oxygen partial pressure, saturated with magnetite at the upper limit at about $(\text{Fe}^{3+}/\text{Fe}^{2+})=0.33$.

(2) Magnetite content

The measured values, ΔC , of magnetite contents of the sulfide samples were in the pF range from 2.5 to 6.0 for mattes and from 4.0 to 9.0 for white metals, and no apparent relation between their values and the composition was found. Therefore, the ratio of the read value to the iron content is plotted against the iron content in a log-log diagram, as in Fig. 5. The distribution of points is represented by a straight line, which will be discussed later.

The change of ΔC before and after the vacuum treat-

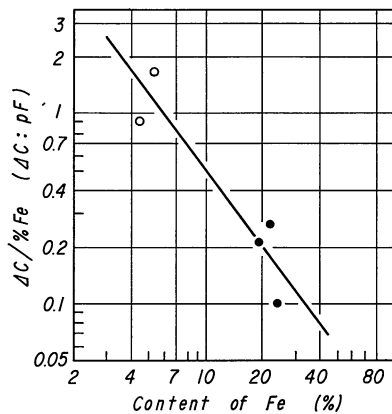


Fig. 5 Relation between the magnetite content (in $\Delta C/\% \text{Fe}$) and the iron content in matte and white metal.

Legend; ●: matte, ○: white metal

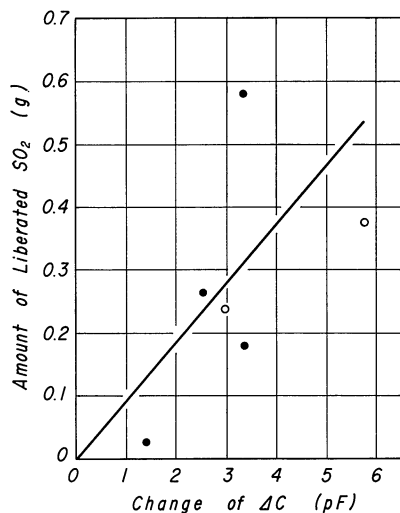


Fig. 6 Relation between the amount of SO_2 liberated during the vacuum treatment and the change in magnetite content (in ΔC) before and after the vacuum treatment.

Legend; ●: matte, ○: white metal

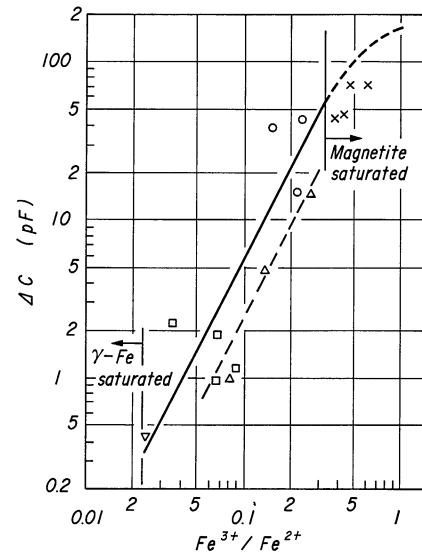


Fig. 7 Relation between the magnetite content (in ΔC) and the ferric/ferrous ratio in various slags.

Legend; ×: solid deposit in flash smelting furnace (Beko), ○: converter slag, □: slag from flash smelting furnace, ▽: slag from slag cleaning furnace, △: silica saturated slag.

ment is of interest in relation to the reduction of magnetite under reduced pressure to liberate SO_2 gas, hence to the capacity of a vacuum pump installation, so that the change examined is shown in Fig. 6. It is seen that the total amount of SO_2 gas liberated tends to increase with an increase of the change of ΔC . In a few exceptions the ΔC values increased after the vacuum treatment.

The relation between ΔC and the ferric/ferrous ratio of various slags is shown in Fig. 7, though the relation is not directly concerned with the vacuum treatment of sulfides.

The straight line in Fig. 7 represents the dependence of ΔC on the square of the ferric/ferrous ratio in slag in the range from 0.02 to 0.4, over which the slag is nearly saturated with magnetite and the line bends as shown by a broken curve.

III. Discussion

1. EMF in various melts in the copper smelting process

At the present time thermodynamic data on the correlation between the EMF and dissolved oxygen in the sulfide melts are not available. However, the copper smelting process under a reduced pressure can be thermodynamically represented as a function of oxygen partial pressure, when the reduced pressure is taken to be equal to the partial pressure of SO_2 , as described in a previous paper⁽¹⁾. The measured values of the EMF for the various melts in connection with the copper smelting process are, therefore, illustrated in Fig. 8 as a function of the oxygen partial pressure. The oxygen partial pressure is calculated assuming that the melt is in equilibrium with the gas phase and that the pressure of gas phase is equal to the partial

(8) E. F. Osborn and A. Muan: *Phase Diagrams for Ceramists*, the Amer. Ceram. Soc., (1964), p. 60.

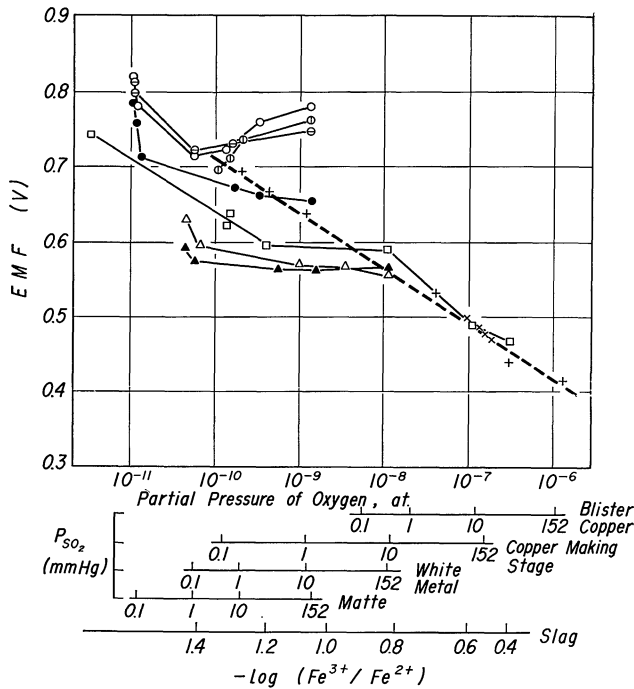


Fig. 8 EMF of various melts during the copper smelting process (1200°C).

Legend; ●: matte A-A, ○: and ⊖: matte A-B, ⊕: matte A-B (interrupted), △: white metal H, ▲: vacuum lift refined white metal, □: slag saturated with silica (1250°C), ×: data from vacuum lift refining of molten copper⁽²⁾, +: data from the Cu-O system⁽³⁾.

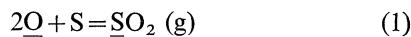
Abscissa; equilibria in the blister copper-SO₂ (%S = %O), Cu₂S-SO₂, white metal-SO₂ ($a_{\text{FeS}}=0.05$, $a_{\text{FeO}}=0.4$), matte-SO₂ ($a_{\text{FeS}}=a_{\text{Cu}_2\text{S}}=0.5$, $a_{\text{FeO}}=0.4$), and slag (silica saturated) systems are arranged according to the oxygen partial pressure (see text).

pressure of SO₂.

The abscissa of Fig. 8 consists of separate scales for different equilibria as follows.

The Cu-O system: A direct correlation between the EMF and the oxygen partial pressure can be obtained in this simple system. Data in Fig. 8 are taken from the previous literature⁽²⁾⁽³⁾.

The blister copper-SO₂ system: Dissolved oxygen, $\underline{\text{O}}$, and sulphur, $\underline{\text{S}}$, in molten copper react to liberate SO₂ as represented by

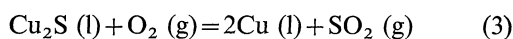


and



Data in Fig. 8 are taken from the result obtained by vacuum lift refining of molten copper⁽²⁾.

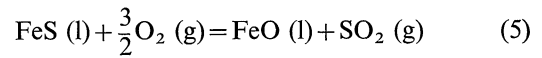
The Cu₂S-SO₂ system (the copper making stage): Cuprous sulfide is oxidized into metallic copper at an oxygen partial pressure which depends on the SO₂ partial pressure as represented by.



$$K_4 = \frac{a_{\text{Cu}}^2 \cdot P_{\text{SO}_2}}{a_{\text{Cu}_2\text{S}} \cdot P_{\text{O}_2}} = 8.15 \times 10^5 \text{ at } 1200^\circ\text{C}. \quad (4)$$

Here K is the equilibrium constant. The oxygen partial pressure is then calculated assuming $a_{\text{Cu}_2\text{S}} = a_{\text{Cu}} = 1$ and the pressure of SO₂ = 0.2.

The white metal-SO₂ system: In the presence of FeS in the melt the oxidation is represented by



$$K_6 = \frac{a_{\text{FeO}} \cdot P_{\text{SO}_2}}{a_{\text{FeS}} \cdot P_{\text{O}_2}^{3/2}} = 1.54 \times 10^{12} \text{ at } 1200^\circ\text{C}. \quad (6)$$

White metals used in this study contained more or less FeS. Therefore, a_{FeS} (= mole fraction) = 0.05 and $a_{\text{FeO}} = 0.4$ were assumed here. Comparison of the white metal-SO₂ system with the Cu₂S-SO₂ system in Fig. 8 revealed that the iron content greatly affected the oxygen partial pressure.

The matte-SO₂ system: The oxidation is also represented by eqs. (5) and (6), but a high content of FeS, $\text{FeS} = \text{Cu}_2\text{S} = 0.5$ mol fraction, and $a_{\text{FeO}} = 0.4$ are assumed.

The slag system (silica saturated): The ferric/ferrous ratio in a slag is in equilibrium with the oxygen partial pressure as shown by the broken curve⁽¹⁰⁾ in Fig. 4.

All points in Fig. 8 are scattered in the vicinity of a broken straight line representing the correlation between the EMF and the oxygen partial pressure for the Cu-O system⁽²⁾⁽³⁾ and the blister copper-SO₂ system⁽²⁾. This fact is a natural consequence, since these systems are to be mutually in equilibrium with regard to the oxygen partial pressure.

The upward deviation from the broken line may be due to the presence of active impurities, by which the activity coefficient of oxygen dissolved in the sulfide melt is depressed and the EMF is increased. Some evidences are already described in Section 3. The downward deviation might be attributed to the calculation of oxygen partial pressure under very simple assumptions. The curve of the slag system may be almost superimposed on the broken straight line, if a solid line in Fig. 4 is used in place of the broken line. An experimental error is also considered that under a static condition only the surface of melt is in equilibrium with the gas phase.

2. Dissolved oxygen in sulfide melts and magnetite content

It is known that oxygen in matte and white metal exists as (i) suspended particles of slag which consists of various oxides, FeO, Fe₃O₄, SiO₂, CaO, etc. and (ii) chemically dissolved oxygen which may be represented as FeO and Fe₃O₄.

The oxygen content in matte is determined by various methods including the determination from the balance of the values in complete analysis, dissolution in a nitric acid mixture⁽¹¹⁾, leaching with a

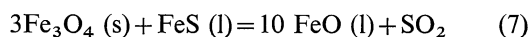
(9) E. J. Michal and R. Schuhmann, Jr.: Trans. AIME, **194** (1952), 723.

(10) E. T. Turkdogan and P. M. Bills: J. Iron Steel Inst., **186** (1957), 329.

(11) E. C. Ellwood and T. A. Henderson: Bull. Inst. Min. Met., **62** (1952), 55.

AgNO₃ solution⁽¹²⁾, leaching with a SnCl₂ solution⁽¹³⁾, and reduction with H₂ at elevated temperatures⁽¹⁴⁾. It has been reported that the oxygen content in matte is around 2% and decreases as the copper grade increases^{(14)–(19)}, and that mattes obtained from flash smelting and reverberatory furnaces contain a larger amount of magnetite than that from a blast furnace.

Magnetite in matte is reduced by FeS to liberate SO₂ gas as represented by⁽²⁰⁾



$$K_8 = \frac{a_{\text{FeO}}^{10} P_{\text{SO}_2}}{a_{\text{Fe}_3\text{O}_4}^3 a_{\text{FeS}}} = 1.1 \times 10^{-4} \quad \text{at } 1200^\circ\text{C}. \quad (8)$$

Here K_8 is the equilibrium constant. When a_{FeO} and P_{SO_2} are assumed to be 0.4 and 0.2 at., respectively, we have

$$\frac{a_{\text{Fe}_3\text{O}_4}}{a_{\text{FeS}}} = 5.8 \times 10^{-1} a_{\text{FeS}}^{-4/3}. \quad (9)$$

The left-hand side of eq. (9) corresponds to the ratio of ΔC to the iron content in matte, and the ratio is approximately proportional to a $-4/3$ power of the iron content as shown by an inclined straight line in Fig. 5.

Little is known about the magnetic property of matte and white metal, although some characteristics are made known by the physical method as compared with chemical methods. In a detailed study the rate of solidification of the sulfide melt should be taken into account⁽²¹⁾. Mazanek et al.⁽²²⁾ carried out the measurement of magnetization with a magnetic balance to estimate the sintering properties.

Equation (7) is also valid for an estimation of the amount of SO₂ gas liberated from the melt under reduced pressures. When FeO in matte or white metal can be ignored, two oxygen atoms in twelve atoms constituting magnetite are liberated as a SO₂ molecule. Hence one-sixth of the total oxygen, say 2%, in matte is liberated as SO₂, i.e. about 0.7% of the weight of matte used.

By a direct estimation of magnetite in matte and white metal, the amount of SO₂ gas liberated can be calculated from the change in magnetite content

(12) C. G. Maier and G. D. Van Ardale: *Eng. Min. J.*, **107** (1919), 815.

(13) J. Kinnunen: *Chem. Analyst*: **40** (1950), 89.

(14) A. Yazawa: *Bull. Res. Inst. Min. Dress. Met. Tohoku Univ. Japan*, **13** (1957), 167.

(15) H. W. Mossman: *J. Metals*, **8** (1956), 1182.

(16) N. Korakas: *Bull. Inst. Min. Met.*, **72** (1962), 35.

(17) F. Johansen and H. Knahl: *Erzmetall*, **16** (1963), 611.

(18) U. Kuxmann and F. Y. Bor: *Erzmetall*, **18** (1965), 441.

(19) P. Spira and N. J. Themelis: *J. Metals*, **21** (1969), 35.

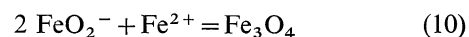
(20) M. Kameda and A. Yazawa: *Bull. Res. Inst. Min. Dress. Met. Tohoku Univ. Japan*, **11** (1955), 121.

(21) K. N. Subramanian and N. J. Themelis: *J. Metals*, **24** (1972), 33.

(22) E. Mazanek, S. Jasienska and Z. Obuszko: *J. Metals*, **21** (1969), 23.

regardless of the wüstite content in sulfide samples. The straight line in Fig. 6 shows such a relation between the amount of SO₂ gas and the change in magnetite content. The points obtained here represent the relation as a whole.

It seems that a trivalent iron in molten slag attracts oxygen anions to form an anion FeO₂⁻. Thus, the formation of Fe₃O₄ in molten slag is represented by



$$K_{11} = \frac{a_{\text{Fe}_3\text{O}_4}}{a_{\text{FeO}_2^-}^2 \cdot a_{\text{Fe}^{2+}}}, \quad (11)$$

where K_{11} is a temperature-dependent constant. When the FeO₂⁻ concentration is low and the Fe²⁺ concentration is nearly constant, we have

$$\left(\frac{a_{\text{FeO}_2^-}}{a_{\text{Fe}^{2+}}} \right)^2 \propto a_{\text{Fe}_3\text{O}_4}. \quad (12)$$

Thus, the magnetite content in slag is approximately proportional to the square of ferric/ferrous ratio. This correlation is shown by an inclined straight line in Fig. 7.

The measurement of the EMF in sulfide melts would be applied more widely to thermodynamic and kinetic researches in connection with the copper smelting process. The magnetic method for the determination of magnetite contents would also be valid for the estimation of the ferric/ferrous ratio, i.e. the partial pressure of oxygen in the gas phase being in contact with the melt, in a few minutes.

IV. Conclusion

During a vacuum treatment of matte and white metal, the EMF of the sulfide melts was measured with a solid-electrolyte (ZrO₂·CaO) cell under a reduced pressure of around 0.5 mmHg at 1200°C. The EMF rised with the time of the vacuum treatment, when the impurity content of a sulfide sample was low. When the content of zinc or such an active metal in matte is high, a drop of the EMF took place in the early stage of the vacuum treatment.

The EMF drop which corresponds to an increase of the activity of oxygen in the sulfide melt seems to be attributable to an increase of the activity coefficient of oxygen due to a decreased concentration of zinc by the treatment.

The measured EMF in sulfide melts are presented as a function of partial pressure of oxygen (calculated value), together with the EMF in molten slag, molten blister copper, and the Cu–O system.

Magnetite contents of matte, white metal, and slag were also semi-quantitatively determined by a magnetic method. An examination revealed that the amount of SO₂ gas liberated during the vacuum treatment is dependent on the change of magnetite content before and after the vacuum treatment.