Transfer of Oxygen and Sulfur during Direct Current Electroslag Remelting

By Makoto KATO,** Kiyoshi HASEGAWA,*** Shoichi NOMURA****
and Michio INOUYE*****

Synopsis
Behaviors of oxygen and sulfur during DC ESR were investigated to treat their transfer on wide operating scales. On oxygen transfer, a carbon steel was remelted in CaF₂-Al₂O₃ slag under the atmosphere. It was confirmed that ingots remelted as electrodes of negative polarity give higher oxygen content than those as positive. These differences would be resulted from the differences of the current density and the interfacial area between the metal and the slag. The oxygen contents in the ingots remelted in a large scale furnace could be estimated from the present results on the oxygen transfer through the molten metal/slag interface, assuming that the mass transfer coefficient of oxygen depends on the current density of the interface.

On sulfur transfer, a resulfurized carbon steel was remelted in ANF-6 and ANF-7 slags under the atmospheres of varied oxygen partial pressure. Assuming the electrochemical reactions at the reacting interfaces, the accumulating rate of sulfur in the slag pool was determined. And then the sulfur in the ingot was calculated on the mass balance of sulfur. The calculated results were compared with the experimental ones. On DCSP, the calculated results show the good agreement with the experimental ones, but not on DCRP.

1. Introduction
There remains some problems on the behaviors of oxygen and sulfur during electroslag remelting (ESR). Several investigators have studied on the behavior of oxygen during ESR and obtained the results for the individual operating conditions, but few theoretical considerations throughout any operating scale except for Plöckinger.¹

In ESR process, the slag contamination action, the ingredient transfer from slag into molten metal, is not disregarded. This is especially important in the case of the remelting in a small scale ESR furnace. Because the current density is higher than that of larger scale remelting, a fear is entertained that the contamination effect would be larger than the refining effect; especially, the oxygen content in ingot probably increases after the remelting.

In order to study the oxygen transfer during ESR on various operation scales, a carbon steel (S48C) was remelted under the atmosphere by using a laboratory DC ESR unit and the results were discussed with some data in previous work.⁵

In ordinary steel-making, the desulfurization proceeds as follows:
From metal to slag;

\[ [S] + (O^{2-}) \rightarrow [O] + (S^{2-}) \]

From slag to atmosphere;

\[ 2(S^{2-}) + 3[O_2] \rightarrow 2[SO_2] + 2(O^{2-}) \]

However, the behavior of sulfur during ESR has not been throughly clarified. For instance, Hawkins⁶ and Jauch⁷ reported that the desulfurization in a slag containing high FeO was restrained by decrease in the sulfur capacity of the slag, but it was advanced conversely in a slag of low FeO. On the contrary, the faster desulfurization was found in a slag of higher FeO⁸ and it was apparently promoted in the ESR by using the electrode buried with Fe₂O₃.⁶ As the desulfurization by evaporation is restrained when the oxygen partial pressure in the atmosphere is reduced, the desulfurization is restrained in an Ar atmosphere.⁷⁻⁹ The desulfurization ratio is 4⁻¹¹ % in the air after Hawkins,¹⁰ but there is a paper reporting the ratio of desulfurization over 80 % in a CaF₂-Al₂O₃ slag and the identification of the existence of SO₂ in the melting atmosphere. Cooper et al.,¹¹ obtained nearly equal rates of desulfurization in Ar and in the air. Thus, the desulfurization during ESR is not so clear.

It is essential to determine the reaction interface for the transfer of sulfur. The following interfaces are considered to be related to the transfer of sulfur in ESR.¹¹,¹²
1) Electrode tip/Slag
2) Molten droplet/Slag
3) Metal pool/Slag
4) Metal pool/ingot
5) Slag/Atmosphere
The sulfur contents in the metal pool are not different from those in the ingot according to Miska and Wahlster.¹³ Klyuev and Spitzberg¹⁴ show that the droplet falls down through the slag pool in a short time (0.01⁻⁰.¹ sec). Therefore, the interfaces 1), 3) and 5) are considered to be mainly related to the transfer of sulfur. Electrochemically, the direct opposite reaction should be take place at the interfaces 1) and 3), and then the desulfurizing reaction is advanced by the cathodic potential drop and restrained by the anodic one.¹⁰,¹²,¹³,¹⁵ The cathodic
reaction \((S+2e \rightarrow S^{2-})\) at the interface 1) is essential in the remelting of the straight polarity (DCSP), but the reaction at the interface 3) is essential on the reverse polarity (DCRP). The rate of desulfurization in ESR has not been determined by the electrochemical reactions at the electrode tip and the metal pool.

By remelting a resulfurized carbon steel (SUM), the behavior of sulfur in ESR is investigated on the polarity of electrode, the remelting atmosphere and the slag composition.

II. Experimental

The laboratory ESR unit used (purchased by Special Refining Process Committee of the Joint Society on Iron and Steel Basic Research in ISIJ for the purpose of joint study and placed in Nagoya University) consists of a DC power source (constant-voltage type silicon rectifier, 0-50 V arbitrary settled, 2700 A max.), a mold (copper, water cooled, \(\phi\) 110 mm), an electrode feeding device (max. 1400 mm in length) and a multichannel recorder.

The chemical compositions of the consumable electrodes and the slags used for the experiment on sulfur transfer are shown in Tables 1 and 2, respectively. The remelting conditions are summarized in Tables 3 and 4.

In the experiment on oxygen transfer, round bars of S48C with 40 and 50 mm in diameter, 1400 mm in length were remelted in CaF\(_2\)-Al\(_2\)O\(_3\) (15, 30 %) slags under the atmosphere, and both the operating voltage and current were recorded during the melting. Oxygen and carbon contents in ingots remelted were determined by a coulometric method and the other elements were determined by a spectrochemical method; sulfur in steel or in slag by the combustion method; and FeO in slag by the Reinhardt-Zimmermann method.

III. Experimental Results and the Interpretation

1. Electric Power Consumption

It is generally recognized that the electric power consumed for the remelt of the unit weight of steel, namely, the specific power consumption, decreases with increase in the melting scale. Also it is well known that the DCRP remelting of a small scale has the better melting efficiency than the DCSP; however the DCSP remelting of a large scale has rather the better efficiency.\(^{16}\) Table 3 shows the power consumption which has been calculated from the average operating current and voltage. The power consumption of the DCRP remelting was less than the DCSP remelting, and the melting efficiency was better. This fact may be resulted from the high resistance layer in the slag in the vicinity of the surface of the anodic electrode at the discharge of anions. Accordingly, the Joulic heat is generated locally around the consumable electrode boundary surface, and contributes effectively to melt the electrode material.

As for sulfur transfer, round bars of SUM with 50 mm in diameter, 1400 mm in length were remelted in ANF-6 or ANF-7 slag under a controlled atmosphere. For the control of the remelting atmosphere, a shielding cap of copper cooled by water was used. After blowing the Ar or Ar-\(O_2\) (5 %) gas of 3 l/min into the mold, the electrode was remelted under the gas stream of 2 l/min. In this case, two silica tubes of \(\phi\) 5.5 mm, located 20 mm inside of the mold wall for gas blowing were raised at the same speed as the raising slag to maintain the tips of the tubes 100 mm upper from the slag surface. During the remelting, samples were sucked up into silica tubes from the slag and metal pools with a syringe. Oxygen and carbon in steel were analyzed quantitatively by the coulometric method and the other elements were determined by a spectrochemical method.

The operating current related to the melting efficiency decreases with the increasing \(Al_2O_3\) content in the slag, because \(Al_2O_3\) controls the electric conductivity of the slag, remarkably. The operating current also showed a tendency to increase with increase in the melting rate, as a result of the inter-electrode
distance shortened by increase in the descending velocity of the electrode. The DCSP remelting was apt to increase in the power consumption as compared with the DCRP, since the operating current in the DCSP was larger than that in the DCRP.

2. Oxygen Profiles in Ingots

According to the previous work, the experimental results has the satisfactory reproducibility in a small scale ESR unit. Figure 1 shows typical examples of the profiles of oxygen and the other elements in the longitudinal center section of ingots with regard to the polarity of the consumable electrode. It is found that the oxygen content in those ingots was higher than that in the electrode independent of the polarity. Therefore, the contamination by the slag during the remelting was obvious. Especially the high oxygen content was found in the DCSP remelting. The reason is that the interfacial area of the metal pool, through which the oxygen or complexed anion in the slag is discharged, is larger than that of the electrode tip in DCRP, and also the contacting time of the metal with the slag may be longer in this polarity. Furthermore, the oxygen content decreased with the increasing Al_{2}O_{3} content as reported by Kay, who explained the results from decrease in the activity of FeO with increase in the Al_{2}O_{3} content in the slag. However, this can not be simply explained by the effect of FeO, because the present results showed that there was a correlation between the concentrations of aluminum and oxygen, and also Al_{2}O_{3} inclusions were found in the ingot. The effect of the current density at the reaction interface should be significant, since the operating current decreased with the increasing Al_{2}O_{3} content.

The behaviors of the other elements are briefly summarized as follows: Aluminum was remarkably picked up into ingot from the slag in the DCSP remelting, but little in the DCRP. The desulfurization was observed, especially in the DCRP remelting. Silicon and manganese were decreased by the oxidation as compared to the concentrations in the electrode. Nickel, chromium, copper and carbon were a little transferred in DC ESR.

2. Experiment on Sulfur Transfer

1. Sulfur Profiles in Ingots

Figure 2 shows the typical axial distributions of sulfur at the center and in the side of two ingots. As the sulfur content in the ingot is regarded as uniform when the remelting is stabilized, we discuss the behaviors of the sulfur transfer as follows: Atom of sulfur was remarkable transferred from the slag to the metal in the DCSP remelting, but little in the DCRP. The desulfurization was observed, especially in the DCRP remelting. Silicon and manganese were decreased by the oxidation as compared to the concentrations in the electrode. Nickel, chromium, copper and carbon were a little transferred in DC ESR.
on hereafter the sulfur content at the center of the ingot.

2. Influence of Oxygen Partial Pressure on the Sulfur Content in Ingot

The oxygen partial pressure in the remelting atmosphere influences remarkably on the transfer of sulfur in DC ESR. For the remelting of DCSP in ANF-6 slag, the sulfur content were uniform in the ingots, but there was a tendency of the higher amount of sulfur under the lower oxygen partial pressure. The highest rate of the desulfurization was obtained on the remelting in the air. For DCRP in ANF-6 slag, the sulfur contents in ingots increased almost linearly from the initial desulfurized level with the melting time and much less in the ingot remelted in the air. Thus, the oxygen partial pressure much influenced upon the sulfur content in ingot. However, the sulfur content in the ingot remelted in Ar gas was not so different from that in Ar-O$_2$ (5 %) gas. It was probably dependent upon the gas flow method.

Table 4 shows the rates of desulfurization defined as follows:

\[
\text{Rate of desulfurization by evaporation (\%) = } \frac{(S \text{ in raw material}) - (S \text{ in ingot}) - (S \text{ in slag})}{(|S \text{ in raw material} - (S \text{ in ingot})|)} \times 100
\]

3. Influence of Slag Composition on the Sulfur Content in Ingot

The sulfur content in the ingot remelted in ANF-6 slag was remarkably different from that in the ingot remelted in ANF-7 slag. For example, by DCSP in the air, the ingots remelted in ANF-6 slag showed the uniform contents of sulfur and were desulfurized by about 35 %; on the contrary, the ingots remelted in ANF-7 slag showed the very low sulfur contents at the start of the remelting, but recovered the sulfur contents with the melting time. On the other hand, by DCRP in the air, the ingots remelted in both slags showed very low sulfur contents and high rates of desulfurization.

4. Influence of the Electrode Polarity on the Sulfur Content in Ingots

In DCSP of ANF-6 slag in the air, the rate of desulfurization was about 18 % and the ingot showed the uniform distribution of sulfur, but in DCRP, the desulfurization was more advanced than in DCSP at the early stage of the remelting and ceased gradually until the ingot showed the same content of the raw material. The results that the electrode polarity influenced obviously on the desulfurization is probably caused by the high current density of the electrode, since we used a laboratory ESR unit, the current density of which is 4~5 times as high as that in practical ESR.

5. Sulfur and FeO Contents in Slag, and Sulfur Content in Slag Skin

On the remelting in the air, the sulfur contents in ANF-7 slag were about 5 times as higher as that in ANF-6 slag, and then the different slag compositions were obvious. Each slag contained the higher
amount of sulfur in DCRP than that in DCSP. The similar behavior of sulfur was observed in Ar gas, and the sulfur contents were higher than in the air, for both the slags.

FeO contents in ANF-6 slag depended on the oxygen partial pressure of the remelting atmosphere and was the highest in the air. As for the polarity, the remelting of DCRP gave higher FeO contents in the slag than that of DCSP.

The sulfur in the slag skin was corresponded to that in the slag by DCRP, but by DCSP it was very high above that in the slag.

IV. Discussion

1. Ratio of Oxygen Absorbed: Oxygen Transfer through the Metal Pool Boundary Surface

As mentioned above, the influence of the current density at the reaction surface must be significant in the oxygen transfer during the remelting. Now, the ratio of the oxygen absorbed, $\eta$, is defined as follows, in order to determine the rate process in ESR.

$$\eta = \frac{A+B}{C}$$

where,

- $A$: Oxygen fixed in ingot (g/min);
  $$A = [(\text{Oxygen concentration of ingot}) - (\text{Oxygen concentration of electrode material})] \times (\text{Melting rate})/100$$

- $B$: Oxygen reacted with silicon (g/min),
  $$B = [(\text{Silicon concentration of electrode material}) - (\text{Silicon concentration of ingot})] \times (\text{Melting rate})/100$$

- $C$: Oxygen reacted to the reaction boundary surface (g/min).

The value $C$ could not be accurately calculated, because the electrochemical behavior of the fused slag during ESR is not yet clear. Here, it is assumed that the anions reached to the anodic boundary surface are proportional to the number of anions in the slag.

Namely, in the remelting of the CaF$_2$ A1$_2$O$_3$ slag, the value $C$ is estimated on the assumptions that A1$_2$O$_3$ is dissociated in the slag and the aluminate anions discharge at the anodic surface as follows*:

$$\text{A1}_2\text{O}_3 \rightarrow \text{Al}^{3+} + \text{AlO}_2^{2-}$$
$$\text{AlO}_2^{2-} - 3e \rightarrow (1/2)\text{Al}_2\text{O}_3 + (3/2)\cdot \text{O}$$

$$C = 16 \times 60 \times (3/2) \cdot N_{\text{AlO}_2} \cdot I / 100 \times 96 500$$

where, $I$: the operating current expressed in ampere.

The results show that $\eta$ was 0.003 to 0.006 independent of the amount of A1$_2$O$_3$. In this work, as the current density at the anodic boundary surface was high enough and then the operating voltage dropped locally in this anodic layer, it is possible that the sufficient amount of oxygen was supplied to the molten metal surface from the fused slag. Therefore, the rate determining steps of the oxygen transfer in ESR is the mass transfer in the molten metal.

For the oxygen transfer from the slag during ESR, the interfaces of a) electrode tip/slag, b) metal droplet/slag, and c) metal pool/slag were taken into account. Here, the transfer through the interface b) could be neglected, because the falling time of the droplet through the slag was extremely short (0.02-0.1 sec).* Therefore, the transfer through both the interfaces of a) and c) should be considered. In DCSP remelting, oxygen is picked up through the interface c) but not removed through a) because of the low oxygen content of the electrode material. In DCRP remelting, oxygen is picked up through the interface a) and removed through the interface c). Further consideration of these transfer of oxygen are discussed in next section.

2. Mass Transfer Coefficient of Oxygen across the Metal Pool/Slag Interface

The ratio of oxygen absorbed from the fused slag in DCSP remelting could be controlled by the diffusion in the boundary layer of the metal pool as described in Section IV. 1. 1. The rate equation in this case is as follows:

$$\frac{dC}{dt} = (F/V) \cdot k_s \cdot (C^* - C) \quad \text{......(1)}$$

where, $C$: oxygen concentration (%)
$F$: interfacial area (cm$^2$)
$V$: volume of molten metal (cm$^3$)
$C^*$: saturated interfacial oxygen concentration (%)
$k_s$: oxygen transfer coefficient (cm/sec).

This equation may be integrated by using the following boundary conditions:

$$\text{at } t = 0, \quad C = C_0$$
$$\text{at } t = t, \quad C = C_t$$

into

$$\ln (C^* - C_0)/(C^* - C_t) = (F/V) \cdot k_s \cdot t \quad \text{......(2)}$$

By representing the melting rate as $w$, the volume $V$ is given by $wt/p$, where $p$ is the density of metal. Then Eq. (2) becomes Eq. (3).

$$\log (C^* - C_0)/(C^* - C_t) = (p \cdot F \cdot k_s)/2.3w \quad \text{......(3)}$$

Now, by the substitution of $C^* = 0.22\%$ and $C_0 = 0\%$ in Eq. (3), the mass transfer coefficient of oxygen is calculated as shown in Table 5. Figure 3 shows the relationship between those values and the current density at the surface of metal pool, $J_{p\text{ool}}$, which is approximated with (the average operating current)/(2$\pi$R$^2$), namely, the average current density of mold, $J_p (A/mm^2)$, where $D$ is the diameter of the mold. A

* Although the various dissociation reactions of A1$_2$O$_3$ are probable in fused slag, the simultaneous increase of [Al] and [O] in the ingot by DCSP remelting as shown in Fig. 1 could be understood by applying this formula. That is, in DCSP remelting, as the aluminate anion discharges at the anodic metal pool surface, oxygen is provided sufficiently to molten metal and A1$_2$O$_3$ produced by the above discharge is fixed in the ingot as inclusions. However, it is difficult to estimate the number of cation discharged at the cathodic surface of the molten droplet, and the mass of metal returned to the slag through the metal pool surface. What is the actual dissociation reaction of A1$_2$O$_3$ in the slag, is not discussed any longer here.
A linear relationship was clearly observed and was represented as Eq. (4).

\[ \log k_s = 1.8335 \cdot \log J_D - 1.8123 \] ............(4)

Here, it is assumed that the following conditions should be satisfied.
1. Silicon is oxidized at the interface.
2. Carbon is not oxidized.
3. On the metal pool surface, oxygen is saturated, and its value is 0.22 %.
4. Interfacial area does not change even if SiO\(_2\) or Al\(_2\)O\(_3\) are produced on the boundary surface.
5. The boundary surface is not disturbed by the falling droplet.

### 3. Oxygen Transfer during DCRP ESR

#### (1) Estimation of the Oxygen Content in Molten Electrode Tip

In DCRP remelting, oxygen transfers from the slag to iron melt of the electrode tip, and then it does reversely from the metal pool to the slag. Now, it is assumed that the relationship between the mass transfer coefficient of oxygen and the current density which has been obtained in DCSP remelting is also valid in DCRP. Then, the oxygen content in the molten electrode tip \( (C_e) \) becomes the function of the oxygen content in the metal pool \( (C_i) \). That is,

\[ C_e - C_i = (F/V) \cdot k_s \cdot C_i \] ........................(5)

From Eq. (5), \( C_e/C_i \) was calculated and is shown in Fig. 4 with the mold diameter. When the mold diameter is larger than 200 mm, it is suggested that the deoxidation through the interface between the fused slag and the metal pool is not practically impossible. That is to say, the oxygen content in the molten electrode tip is nearly the same as in the ingot.

#### (2) Oxygen Transfer Coefficient on Molten Electrode Tip

Figure 5 shows the relationships between the mass transfer coefficient of oxygen and the current density at the molten electrode tip surface which are obtained by using \( C_e \) in Section IV. 1. 3. (1) in the same way as in DCSP. However, as shown in the previous work of the model experiment,\(^{21}\) those results are not reliable, because it is not possible that the mass transfer coefficient of oxygen on the molten electrode tip is smaller than that on the metal pool. In other words, as the electric current concentrates on the droplet formed on the electrode tip, the relationship

---

### Table 5. Mass transfer coefficient of oxygen in DCSP with data used.

<table>
<thead>
<tr>
<th>No.</th>
<th>Steel</th>
<th>Area of metal pool, ( F_p ) (cm(^2))</th>
<th>Current density at metal pool, ( J_D ) (A/mm(^2))</th>
<th>Average melting rate (g/min)</th>
<th>[ \text{O}_{\text{logot}} ] %</th>
<th>[ \text{O}_{\text{loex}} ] %</th>
<th>Oxygen removed %</th>
<th>( k_s ) (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>Pure iron</td>
<td>3.80</td>
<td>1.05</td>
<td>78</td>
<td>0.0713</td>
<td>0.0091</td>
<td>0.0622</td>
<td>0.0152</td>
</tr>
<tr>
<td>73</td>
<td>S55C</td>
<td>3.80</td>
<td>0.658</td>
<td>78</td>
<td>0.0569</td>
<td>0.0086</td>
<td>0.0393</td>
<td>0.0075</td>
</tr>
<tr>
<td>91</td>
<td>SK3</td>
<td>3.80</td>
<td>0.658</td>
<td>84</td>
<td>0.0561</td>
<td>0.0044</td>
<td>0.0317</td>
<td>0.0076</td>
</tr>
<tr>
<td>1</td>
<td>S48C</td>
<td>95.0</td>
<td>0.17</td>
<td>175</td>
<td>0.0315</td>
<td>0.0042</td>
<td>0.0273</td>
<td>0.00054</td>
</tr>
<tr>
<td>10</td>
<td>S48C</td>
<td>95.0</td>
<td>0.21</td>
<td>246</td>
<td>0.0312</td>
<td>0.0042</td>
<td>0.0270</td>
<td>0.00076</td>
</tr>
<tr>
<td>2</td>
<td>S48C</td>
<td>95.0</td>
<td>0.20</td>
<td>227</td>
<td>0.0336</td>
<td>0.0042</td>
<td>0.0294</td>
<td>0.00084</td>
</tr>
<tr>
<td>6</td>
<td>S48C</td>
<td>95.0</td>
<td>0.25</td>
<td>290</td>
<td>0.0375</td>
<td>0.0042</td>
<td>0.0333</td>
<td>0.0011</td>
</tr>
</tbody>
</table>
between \( k_{sp} \) and the current density which is obtained from the electrode cross-sectional area may be nonsense.

The relationship between the weight of the droplet formed at the electrode tip and the melting rate in DCRP remelting is shown in Fig. 6. As the range of the melting rate is defined by the mold diameter, the weight of the falling droplet is also determined. On the assumptions that the pendant droplet on the electrode tip is a sphere and the reaction takes place only on the surface of this droplet, the mass transfer coefficient of oxygen \( k_{sp} \) can be calculated from the interfacial area, if the spherical surface area and the frequency of the droplet removal are determined every second.

Table 6 shows the results of the calculation. Although the mass transfer coefficient of oxygen \( k_{sp} \) may depend on the melting rate, the oxygen content in the ingot in DCRP remelting can be estimated if \( k_{sp} \) is assumed to be constant.

4. Comparison of Oxygen Content in Ingot by DCSP and DCRP Remeltings

Although the relationship between the oxygen content and the mold size in DCRP is not yet clear, relationships in DCSP and DCRP are summarized in Fig. 7, based on the above discussion. Those results suggest that the DCRP remelting is rather desirable in respect to the oxygen contamination than the DCSP remelting in molds less than 100 mm in diameter. However, the DCSP remelting becomes favorable in larger molds like as the industrial scale. This conclusion has been already shown in Plockinger’s report where the same experimental results are summarized. Here, some theoretical considerations are suggested.

2. On Sulfur Transfer

1. Sulfur Transfer in DC ESR

Photograph 1 shows the sulfur prints of the vertical
sections of the electrode tips. The desulfurized layer on DCSP and the sulfurized layer on DCRP are clearly observed, respectively. Therefore, the desulfurization in a small scale ESR furnace as this experiment is mainly determined by the following electrochemical reactions:

at the cathode

\[ [S] + 2e^- \rightarrow (S^{2-}) \] .............................................(6)

at the anode

\[ (S^{2-}) \rightarrow [S] + 2e \] .............................................(7)

from slag to atmosphere

\[ (S^{2-}) + \frac{3}{2} [O_2] \rightarrow [SO_2] + (O^{2-}) \] ..........(8)

As for DCSP, sulfur in the electrode dissolves into the slag by the cathodic reaction (6). A part of sulfur dissolved in the slag is absorbed by the melt of the electrode tip and some part is removed to the atmosphere by the reaction (8) at the interface (5). Thus, the residue of sulfur stores up in the slag pool.

On DCRP, sulfur in the metal pool dissolves into the slag pool. A part of sulfur in the slag pool is absorbed by the melt of the electrode tip and some part is removed to the atmosphere. The residue accumulates in the slag pool.

Namely, the sulfur content in the slag pool is defined as a result of the competition of each rates of the sulfur transfers from the metal to slag, from the slag to metal, and from the slag to atmosphere, respectively. We discuss the sulfur transfer during ESR with the sulfur contents in the slag pool which are easily given by the analysis of the samples sucked from the slag pool.

2. Sulfur Transfer in DCSP ESR

(1) Accumulating Rate of Sulfur in Slag Pool

The accumulating rate of sulfur in the slag pool may be described by Eq. (11).

\[ V = V_o - a \cdot t \] ..................................................(9)

\[ -d(S)/dt = (F_o/V) \cdot k_{ma} \cdot [S] \] ................................(10)

\[ d(S)/dt = (1/V) \cdot [(F_o + F_w) \cdot k_{ma} \cdot [S] - (a + \beta) \cdot (S)] \] ..................................(11)

where, \( V \): the volume of slag (cm\(^3\))
\( V_o \): the initial volume of slag (cm\(^3\))
\( a \): the forming rate of the slag skin (cm\(^3\)/sec)
\( (S) \): the sulfur content in slag pool (%)
\( [S] \): the sulfur content in electrode tip (%)
\( F_o \): the interfacial area between the electrode tip and slag (cm\(^2\))
\( F_w \): the forming area of slag skin (assuming \( F_w/8 \), \( F_w \): the interfacial area between the slag and the wall of mold (cm\(^2\)))
\( F_o \): the interfacial area between the slag and the atmosphere (cm\(^2\))
\( P_{O_2} \): oxygen partial pressure (atm)
\( k_{ma}, k_{sm}, k_{sg} \): mass transfer coefficient of sulfur from metal to slag, from slag to metal, and from slag to atmosphere (cm/sec), respectively

\[ a = (F_o + F_w) \cdot k_{ma} \cdot [S] \]
\[ \beta = (F_o + F_w) \cdot k_{ma} + F_g \cdot k_{sg} \cdot P_{O_2} \]

Under the conditions, \((S)=0\) at \( t=0 \) and \((S)=(S)\) at \( t=t \), we can integrate Eq. (11) and then the sulfur content in slag pool is given by the following equation.

\[ (S) = \frac{a}{\beta} \cdot [1 - (1 - a \cdot t/V_o)^{\rho \alpha}] \] .............................................(12)

(2) Sulfur Content in Ingot

On the assumption that there are no difference in the sulfur contents between the metal pool and the solidified ingot, the mass balance at the time \( t \) is expressed as following:

\[ [S]_{e} \cdot \frac{wt}{100} \cdot \frac{1}{t} \int_{0}^{t} [S] \cdot dt = \frac{(S)}{100} \cdot \rho \cdot V + \frac{\rho \alpha t}{100} \int_{0}^{t} (S)_{ma} \cdot dt + \frac{\rho \alpha}{100} \int_{0}^{t} (S)_{ma} \cdot dt \]

\[ = \frac{(S)}{100} \cdot \rho \cdot (V_o - at) + \frac{\rho \alpha}{100} \int_{0}^{t} (S)_{ma} \cdot dt \]

\[ + \frac{\rho \alpha}{100} \int_{0}^{t} (S) \cdot dt \] .............................................(13)

where, \( \rho \): the density of slag (g/cm\(^3\))
\( (S)_{ma} \): the sulfur content in slag skin (%)
\( (S) \): the sulfur content in ingot (%).

By differentiation of the above equation with \( t \), the sulfur content in the ingot is given by the following equation.

\[ [S] = [S]_e - (\rho/w) \cdot [\alpha + (\alpha + (S)_{ma})] + (S) \cdot [(F_o + F_w) \cdot P_{O_2}^2 / (a + \beta)] \] .............................................(14)

(3) Determination of the Mass Transfer Coefficient of Sulfur

As \( P_{O_2}=0 \) in pure Ar gas, when \( d(S)/dt=0 \), the following relationship is obtained.

\[ k_{ma} = [(F_o + F_w) \cdot (S)/(F_o \cdot [S]_e)] \cdot k_{sm} \] .............................................(15)

where, \( (S) \): the equilibrium concentration of sulfur in slag (%).
By the relationships (9) and (15), Eq. (11) is integrated into Eq. (16).

\[
\ln\left(\frac{[S]'}{[S]''}\right) = \left[\frac{(F_D + F_w')\cdot k_{sm}}{\rho}\right] \cdot \ln \left[\frac{V_0}{(V_0 - at)}\right] \quad (16)
\]

Applying the above relationship to the result of No. 62 (Ar, DCSP, ANF-6), the value of \([S]''\) was determined as 0.208%. With the present experimental conditions to Eq. (16), the values of mass transfer coefficient of sulfur in ANF-6 slag have been obtained as follows: \(k_{sm} = 5.31 \times 10^{-4} \text{ cm/sec}\), \(k_{sm} = 6.17 \times 10^{-3} \text{ cm/sec}\). After the calculation on these values by the try and error method, we adopted the value \(1.0 \times 10^{-2} \text{ cm/sec}\) for \(k_{sm}\).

(4) Comparison of Experimental Data with Calculated Results

The results calculated by Eqs. (12) and (14) are compared with the experimental data in Fig. 8. The sulfur content in the slag pool shows a good agreement with each other, but the one in the ingot did not agree, especially in the high \(P_{O_2}\) atmosphere. Therefore, we corrected Eq. (14) with the desulfurization related to (FeO) and \(P_{O_2}\) as Eq. (14').

\[
[S] = [S]_e - \left[\frac{(\rho/\alpha)\cdot (\rho + \alpha)\cdot [F_D \cdot k_{sg}\cdot P_{O_2}^{1/2}]}{(F_D + F_w')\cdot k_{sm}\cdot [S]_e}\right] \quad (14')
\]

By the constant \(k = 0.0123\), the calculated results showed the good agreement with the experimental data as shown in Fig. 8.

In ANF-7 slag, the mass transfer coefficient of sulfur could not be determined experimentally, for the melting was unstable in Ar gas. The calculation from the values determined in ANF-6 slag was unsuccessful as worried. As ANF-7 slag has the high sulfur capacity and gives the low rate of the desulfurization by the evaporation, Eq. (11) may be reformed as Eq. (11').

\[
\frac{d([S]')}{dt} = \left[\frac{1}{V}\right] \cdot \left[\alpha' - \beta'([S])\right] \quad (11')
\]

where, \(\alpha' \equiv \frac{F_D \cdot k_{nas}\cdot [S]_e}{[S]_e}\)

\(\beta' \equiv \left[\frac{(F_D + F_w')\cdot k_{sm} + F_D \cdot k_{nas}\cdot [S]_e}{[S]_e}\right] / ([S])\)

An example of results calculated through Eq. (11') with \(k_{nas} = 5.0 \times 10^{-2} \text{ cm/sec}\), \(k_{sm} = 5.31 \times 10^{-4} \text{ cm/sec}\) and \([S]' = 0.2\%\) is shown in Fig. 9. The calculated result shows a fair agreement with the experimental.

2. Sulfur Transfer in DCRP ESR

When the reactions (6) to (8) occur at the surface of the metal pool, the tip of electrode and the surface of the slag pool respectively, the accumulating rate of sulfur in the slag pool may be described approximately as following.

\[
\frac{d([S]_m)}{dt} = \left(\frac{1}{V}\right) \cdot \left[F_D \cdot k_{nas}\cdot [S]_m \right]
\]

\[
\left\{ -([S]_m - \beta''([S])\right\} \quad (17)
\]

where, \([S]_m = ([S]_e + (F_D/V_0)\cdot k_{sm}\cdot [S]_e)\) (: the sulfur content in metal pool)

\[
M = F_D \cdot k_{nas}
\]

\[
\beta'' = F_D \cdot k_{sm} + F_D \cdot k_{sg}\cdot P_{O_2}^{1/2}
\]

\[
-(1/V) \cdot (F_D + F_w) \cdot $k_{nas}$ \cdot F_D \cdot k_{sm}
\]

By the integration of the above equation, the sulfur content in the slag pool is expressed by the following equation.

\[
[S] = (M\cdot[S]_e\cdot\beta'') \cdot \left[1 - (1 - at/V_0)\cdot\beta''\right] \quad (18)
\]

Namely, the sulfur content in the ingot can be expressed as the following equation which is obtained through the mass balance of sulfur.

\[
[S] = [S]_e - \left(\frac{\rho/\alpha\cdot [M\cdot[S]_e + \alpha\cdot ([S]_e)}{[S]_e}\right)
\]

\[
-([S]_e - \beta''\cdot F_D\cdot k_{sg}\cdot P_{O_2}^{1/2})\right\} \quad (19)
\]

We could not determine the values of \(k_{nas}\) and \(k_{sm}\) for this case, because the sampling from the slag pool under pure Ar gas was not carried out. The results calculated by the mass transfer coefficient of sulfur
determined for DCSP in ANF-6 slag were compared with the experimental data, but the agreement was not good. As for DCRP, we should accumulate the further data in future.

V. Conclusions

Some knowledge on the transfers of oxygen and sulfur during ESR were obtained from the experimental results for a small direct current ESR unit of a laboratory scale.

In DCSP remelting, the oxygen transfer through the interface between the metal pool and the slag is considered to be the rate determining step, and the mass transfer coefficient shows a linear relationship with the current density at the metal pool surface. On the contrary, in DCRP remelting, the oxygen transfer through the molten electrode tip/slag interface should be significant; however, this mechanism is not yet clear. This study has suggested a simple model about the droplet formed at the electrode tip.

The oxygen content in the ingot in the large industrial ESR operation was estimated from the present results in consideration of the relationship between the current density and the mold diameter. Generally, oxygen contaminated is decreased with the increasing mold diameter, even in the DC ESR process. The DCSP remelting is more favorable than the DCRP remelting in the larger ESR. On the assumption of the electrochemical reaction at the reacting interfaces, the accumulating rate of sulfur in the slag pool was determined. And then sulfur in the ingot was calculated through the mass balance of sulfur. These results were compared with the experimental data. For DCSP, the calculated results show the good agreement with the experimental one, but not for DCRP. For judgement of application of this model for sulfur transfer, we should further discuss on the detailed data of (S), (S)₄, (FeO), etc.

Acknowledgements

The authors wish to express their gratitude to the late Professor Dr. Yasushi Kojima in Nagoya University under whom this work is conducted. The helpful discussions by the members of Special Refining Process Committee of the Joint Society on Iron and Steel Basic Research in ISIJ is gratefully acknowledged. The authors are also indebted to ISIJ for the financial support to their work and to Daido Steel Co., Ltd. and Aichi Steel Works Ltd. for the supply of the electrode materials.

REFERENCES

1) E. Plockinger: *JISI*, 211 (1973), 533.
4) R. J. Jauch: *Stahl u. Eisen*, 95 (1975), 408.
16) For example; M. Inouye, Y. Kojima and M. Kato: *Tetsu-to-Hagane*, 61 (1975), 139.
22) Y. Kojima, M. Kato, T. Toyoda and M. Inouye: *Denki-Seiko (Electric Furnace Steel)*, 45 (1975), 211.