Removal of Carbon from 25% Cr-Fe Alloy during Vacuum Arc Remelting

By Yasushi NAKAMURA,** Hidetake ISHIKAWA,*** Takamasa ONO**** and Masatoshi KUWABARA**

Synopsis

A kinetic study was made on the reaction, C + O = CO, taking place during vacuum arc remelting of 25% Cr-Fe alloy to know availability of this remelting process for the production of high-chromium ferritic stainless steel with extremely low carbon content. Electrode steel to be remelted contained about 0.015~0.05% carbon. Oxygen concentration was higher than that of carbon. The residual carbon concentration in the resulting ingot, \( C_{sp} \), was found to be determined by the three factors: the remelting rate, \( m \), the total surface area of the metal pool at the electrode tip, \( S \), and the carbon concentration in the electrode, \( C_e \). The observed results conform fairly to the following equation.

\[
(C_e/C_{sp})^{1/2} = 1 + (k/2)(pS/m)
\]

where, \( p \) is the density and \( k \) is the mass transfer coefficient. This equation was derived on the assumption that the transfer of carbon across the boundary layer in the melts is the rate-controlling step. The value of \( k \) was obtained to be 0.025cm/sec.

I. Introduction

High-chromium ferritic stainless steels with extremely low carbon (less than 0.005%) and nitrogen contents are known to exhibit excellent corrosion-and impact-resistances.\(^1\)\(^-\)\(^2\)\(^1\) It is, however, difficult to remove carbon to such a low level from liquid high-chromium steels with conventional degassing furnaces, such as DH, RH, and AOD, without a large amount of chromium loss. Thus these alloys have been commercially produced by the electron-beam continuous melting and the vacuum induction melting processes.\(^5\)\(^-\)\(^2\)\(^1\) However, considerable losses of chromium and manganese due to the evaporation and relatively high cost for the installation seem to limit their application. It is, therefore, of metallurgical interest to study the degree of carbon removal in conventional refining processes other than electron-beam melting and vacuum induction melting.

Consumable vacuum arc remelting (VAR) process is expected to give sufficiently high degree of carbon removal, because the apparent operating pressure of VAR is as low as that in a vacuum induction furnace. A number of works concerning physical and chemical phenomena occurring in VAR have been reported. The results are reviewed by Child and Oldfield\(^4\) and Wood and Beall.\(^5\) Most steels to be remelted are deoxidized before the electrode preparation. However, residual oxygen in the electrodes is further reduced during VAR due to the reaction between carbon and oxygen in the electrodes; \( C + O = CO \).\(^6\)\(^-\)\(^7\) Unfortunately, few systematic and quantitative studies have been performed on this reaction from the view point of carbon removal. Hence, the present experiment of VAR in a small unit is made to elucidate factors influencing carbon removal during VAR of 25% Cr-Fe alloy.

II. Experimental

An equipment designed by Japan Vacuum Eng. Co., Ltd. and remelting procedure were essentially similar to usual ones described in the literature.\(^4\)\(^-\)\(^5\) The experimental conditions are shown in Table 1. The 25% Cr-Fe alloy with carbon content of 0.05~0.015% and oxygen content higher than that of carbon was melted and cast in a vacuum induction furnace. The ingots thus made were forged and machine-cut to form desired shapes of the electrodes. The electrode was vertically supported by a water-cooled shaft in the furnace. During the remelting, the descending length of the shaft was measured at regular intervals and thereby the rates of the electrode consumption, \( v_e \), and the ingot growth, \( v_{ig} \), were calculated in cm/min unit. Operating pressure at the furnace head was also measured with a vacuum gauge. After remelting, the ingot was longitudinally sectioned, and samples for chemical analyses of carbon, oxygen, and chromium were taken from the center of the ingot. Total uncertainty in the measurement of carbon content was below 10% of the concentration. Distribution of carbon along the ingot axis was preliminarily examined, but no significant variation beyond experimental limits was observed.

III. Results

The observed contents of solute elements in the resulting ingot after VAR (final solute content) are compared with those in the electrode (initial solute content). Final chromium content is found to be about 0.2% less than the initial one. Some of the observed values of initial and final contents of carbon or oxygen are shown in Table 2. The table also shows the ratio (\( J \)) of removed carbon to removed

<table>
<thead>
<tr>
<th>Mold ID x L (mm)</th>
<th>Electrode Dia. (mm)</th>
<th>Current (KA)</th>
<th>Voltage (V)</th>
<th>Pressure (g/Hg)</th>
<th>Melting rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103 x 500</td>
<td>48/50/57</td>
<td>1.2 ~ 2.5</td>
<td>24 ~ 26</td>
<td>0.2 ~ 10</td>
<td>420 ~ 1340</td>
</tr>
<tr>
<td>145 x 500</td>
<td>50/85/90</td>
<td>1.5 ~ 3.0</td>
<td>25 ~ 27</td>
<td>0.5 ~ 10</td>
<td>720 ~ 1400</td>
</tr>
</tbody>
</table>

Table 1. Experimental conditions
oxygen in mole. The observed values of $J$ for most of the present experiments are close to unity. This result indicates that carbon-monoxide is the main product of the reaction between carbon and oxygen in the alloy, $\text{C}+\text{O} \rightarrow \text{CO}$.

The relation between final carbon and oxygen contents is examined for the cases where electrodes with different oxygen contents but with the same carbon content are remelted at a specified remelting rate. The observed values of the final carbon content are found to be independent of the final oxygen content as shown in Fig. 1. Dotted curves represent the relation between carbon and oxygen contents in liquid $25\%\text{Cr-Fe}$ alloy in equilibrium with carbon-monoxide at $1600^\circ\text{C}$, which is calculated from thermodynamic data. The observed values are far from the equilibrium expected from the operating pressures measured at the furnace head. The pressure over the liquid metal pool is reported to range from $10^2$ to $20$ Torr above the operating pressure. However, the equilibrium values at such relatively higher pressures seem unlikely to give any reasonable explanation for the observed values.

As shown in Fig. 2, the observed values of the degree of carbon removal, $C_p/C_i$, where $C_p$ and $C_i$ are the final and initial carbon contents, respectively, are approximately expressed by a function of single variable, $1/\nu_p + 1/\nu$, where $\nu_p$ and $\nu$ are the rates of the ingot growth and the electrode consumption in cm/min unit, respectively. This variable is equivalent to $\rho S/m$, where $m$ is the remelting rate in g/min unit, $S$ is the total free-surface area of the metal pool at the top of the ingot and of the metal fluid layer at the tip of the electrode, and $\rho$ is the density.

**IV. Discussion**

The work of Belyanchikov et al. shows that gas evolution in the interior of the metal pool increases with increasing the remelting rate. In the present work this increase, however, is not discernible. Accordingly, the gas/melt interfaces considered are expected to be main reaction sites for carbon removal during VAR, as was pointed out by Child and Oldfield.

Carbon transport from both of the metal pool and the fluid layer to the furnace head consists of a series of consecutive steps. A theoretical consideration for each step reveals that the simultaneous transfer of carbon and oxygen across a boundary layer in the melt adjacent to the gas/melt interface is the rate-deter-

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**Table 2. Results of chemical analyses**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>V-9</th>
<th>V-14</th>
<th>V-29</th>
<th>V-33</th>
<th>V-50</th>
<th>T-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.024</td>
<td>0.025</td>
<td>0.020</td>
<td>0.038</td>
<td>0.019</td>
<td>0.013</td>
</tr>
<tr>
<td>Final</td>
<td>0.0058</td>
<td>0.0066</td>
<td>0.0047</td>
<td>0.011</td>
<td>0.0044</td>
<td>0.0026</td>
</tr>
<tr>
<td>Oxygen content (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.031</td>
<td>0.046</td>
<td>0.054</td>
<td>0.055</td>
<td>0.026</td>
<td>0.017</td>
</tr>
<tr>
<td>Final</td>
<td>0.0071</td>
<td>0.023</td>
<td>0.034</td>
<td>0.020</td>
<td>0.0065</td>
<td>0.0070</td>
</tr>
<tr>
<td>$J$</td>
<td>1.01</td>
<td>1.07</td>
<td>1.03</td>
<td>1.03</td>
<td>1.00</td>
<td>1.25</td>
</tr>
</tbody>
</table>

$J$: ratio of removed carbon to removed oxygen in mole.

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**Fig. 1.** Plot of the observed carbon- vs. oxygen-content after VAR. Dotted lines show the theoretical relation between oxygen and carbon contents in liquid $25\%\text{Cr-Fe}$ alloy in equilibrium with CO atmosphere. Pressures of CO are shown in the figure.

**Fig. 2.** Relation between the degree of the carbon removal, $(C_p/C_i)$, and $(\rho S/m)$.
each other. The consideration of material balance for continuous remelting system in a steady state, thus, yields the following equation.

\[ \frac{m(C_d - C_a)}{\rho k S_d C_d} = \frac{(12/16)\phi_s}{\Phi_s} \quad \text{(1)} \]
\[ \frac{m(C_a - C_p)}{\rho k S_a C_p} = \frac{(12/16)\phi_p}{\Phi_p} \quad \text{(2)} \]

where, \( k \) is the mass transfer coefficient for carbon, \( C_d \) is the carbon concentration in metal droplets detached from the electrode tip, \( S_p \) and \( S_a \) are the free surface areas of the metal pool and the fluid layer, respectively, and \( \Phi_s \) and \( \Phi_p \) are the rates of mass transfer for oxygen in the fluid layer and the metal pool, respectively. Elimination of \( C_d \) from these equations and substitution\(^*\) of \( \frac{(S_a + S_p)}{2} \) for \( \frac{(S_a S_p)}{2} \) may yield:

\[ \left( \frac{C_i}{C_p} \right)^{1/2} \approx 1 + \left( k/2 \right) (\rho S/m) \quad \text{(3)} \]

where, \( S = S_a + S_p \).

A plot of the observed values of \( \left( \frac{C_i}{C_p} \right)^{1/2} \) against those of \( (\rho S/m) \) is shown in Fig. 2. The observed values may be fairly fitted by a straight line. The value of the gradient of the line is 0.74 cm/min, from which the value of \( k \) can be calculated to be 0.025 cm/sec. The values of the mass transfer coefficient for carbon have been reported to be 0.035\(^{13}\) and 0.032\(^{24}\) for liquid pure iron, and 0.015\(^{15}\) for liquid stainless steel from the experiments on gas/melt reactions. The present result is fully close to those reported. It seems, therefore, likely that the semiquantitative equation derived above is reasonable.

Estimation of the degree of carbon removal in a large VAR unit will be made with the aid of Eq. (3). Baarclough\(^{16}\) reported that the values of the remelting rate and the ingot diameter are 5.9\( \sim \)13 kg/min and 41\( \sim \)69 cm, respectively, when the electric current is 10\( \sim \)20 kA. Thus, the value of \( (\rho S/m) \) is evaluated to be 2.2\( \sim \)2.8 min/cm, assuming that \( S_i \) is equal to \( S_a/3 \). In this case, the relation given by Eq. (3) shows that carbon can be reduced by 85\( \sim \)90% of the initial content from the 25\%Cr–Fe alloy during VAR. Accordingly, carbon content in the electrodes to be remelted should be controlled in the range of 0.03–0.05% in order to achieve the final carbon level of less than 50 ppm in VAR processing. Such level of carbon content in the electrodes is easily obtained by using conventional degassing furnaces. In addition, it is noted that the loss of chromium during VAR is sufficiently small in comparison with an electron-beam continuous refining process.\(^5,17\)

As the result of the present consideration, VAR would be practically used as an effective method for producing high-chromium ferritic steels with extremely low carbon content.

REFERENCES


\* This substitution will give less than 5% uncertainty for \( \left( \frac{C_i}{C_p} \right) \) under the present experimental conditions.