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Effect of Chromium-Sulphur Interactions on the Rate of Decarburization by CO$_2$-Ar Gas Mixtures

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This study provides a comprehensive evaluation of the influence of chromium on the decarburization kinetics for systems involving CO$_2$ as the oxidant in the presence of the surface active element sulphur. The increase in decarburization rate of iron-chromium droplets, compared to chromium-free droplets containing the same amount of sulphur, can be accounted for by the solute interaction effects between chromium and sulphur in the liquid phase that resulted in a decrease of surface site occupation by sulphur.

Background

Since the advent of the Argon Oxygen Decarburization (AOD) process, many investigations were undertaken to study and improve the various process routes for stainless steelmaking. The processes are often developed based on manipulation of temperature, gas dilution and pressure in which the latter is the basis for the Vacuum Oxygen Decarburization (VOD) process. It has been recently demonstrated$^{[1]}$ that using CO$_2$ in steel decarburization is a promising approach for the retention of valuable alloying elements. In principle, CO$_2$ decarburization is similar to both the dilution (AOD) and vacuum (VOD) processes in that it lowers the oxygen potential in the steel bath, thus giving preference to the oxidation of carbon rather than chromium.

One of the earliest investigations studying the kinetics of CO$_2$ decarburization was by Baker et al.$^{[2]}$. Iron-carbon droplets with 0 to 5.5 wt pct C were levitated in an inert atmosphere, then subjected to constant flow of CO$_2$-CO/He mixtures containing up to 100 pct CO$_2$. The rate of decarburization at 1933K was found to be independent of carbon content in the melt and the rate
varied considerably with oxidant partial pressure in the gas phase. It was therefore concluded that decarburization by CO₂ is controlled wholly by diffusion in the gas phase at high carbon concentrations.

In their investigation involving elevated pressure of 40 atm., El-Kaddah and Robertson[3] demonstrated that both decarburization and carburization of Fe-C liquid alloys by CO₂-CO gas mixtures can be achieved. The kinetics of decarburization, for 1 g droplets containing 5 and 5.5 wt pct C, was found to obey a model developed for convective mass transfer in the gas phase. Their assessment of the carburization results, on the other hand, revealed that liquid phase resistance is significant at the reaction temperature of 1923K. For the gas composition studied, 1.1 or 2.15 pct CO₂, the carburization rate was controlled by mixed transport of gas and liquid phase diffusion.

Lee and Rao[4,5] carried out decarburization of levitated Fe-C-S droplets in a flowing CO-CO₂ gas stream at 1973K. The rate decreases significantly with increase in sulphur concentrations in the melt. Sulphur, being surface active, was responsible for blocking available sites for CO₂ dissociation. However, it was found that for gas streams containing 10 pct CO₂ and flowing at 1 L/min, the retarding effect of sulphur diminishes as sulphur concentration increases past 0.05 wt pct. They observed that flow rate of the gas mixture has a relatively small effect on the decarburization rate compared to the oxidant partial pressure in the gas mixture. It was thus concluded that the process is a mixed controlled scenario of both gas phase mass transfer and dissociative chemisorption of carbon dioxide.

Sun and Pehlke[6] have studied the kinetics of carbon oxidation in the presence of silicon and manganese in iron. They observed preferential oxidation of carbon when the alloy (3.35 wt pct C, 2 wt pct Si, 0.36 wt pct Mn) was exposed to 20 pct CO₂-80 pct N₂ gases. Oxidation of Mn and Si only began when carbon levels were sufficiently low and the rate limiting step changed from CO₂ transport in the boundary layer to solute diffusion in the liquid metal. It was found that sulphur, in the range of 0.002 to 0.5 wt pct has negligible effect on the decarburization rate.
Work by Simento et al.\textsuperscript{[7]} has shown that the rate of decarburization of Fe-C, with initial carbon concentrations between 3.38 and 4.18 wt pct C, by CO\textsubscript{2}-N\textsubscript{2} gas mixtures is jointly controlled by CO\textsubscript{2} diffusion in the gas phase and subsequent dissociative chemisorption at the gas-metal interface. Small amounts of P (0.1 wt pct), Cr (0.5 wt pct), and S (up to 0.27 wt pct) were alloyed with the Fe-C melt to determine their effect on the decarburization behavior. From their experimental results, mostly at 1723K, the effect of sulphur on the rate was found to obey the Langmuir isotherm for sulphur adsorption. For the melt compositions pertaining to their work, both chromium and phosphorus did not exhibit a noticeable effect on the rate.

It is clear from the above that, for high carbon melts, the rates of CO\textsubscript{2} decarburization were found to be controlled by either diffusion in the gas phase, surface chemical kinetics, or a mix of both. However, limited mention was made with regard to the effects of other alloying elements commonly found in high alloy steel grades on the kinetics of decarburization by CO\textsubscript{2}.

It has been indicated\textsuperscript{[8-11]} that sulphur plays an important role in the kinetics of decarburization by CO\textsubscript{2}. The presence of sulphur, even in low concentrations, was found to significantly decrease the decarburization rate. It is generally understood that the blocking of available reaction sites by chemisorbed sulphur is responsible for the rate retardation. As shown in Figure 1, decarburization rate is hampered by the increasing sulphur concentration in the melt. However, the results from a recent study by Wu et al.\textsuperscript{[12]} suggest that 0.01 wt pct sulphur in the presence of 20\% Cr, did not have an adverse effect on the decarburization rate of Fe-Cr-C droplets. It can be seen from Figure 1 that chromium-containing melts with 0.01 wt pct sulphur (□) have similar behavior to that of essentially sulphur-free melts (Δ). This trend is consistently observed within a range of gas flow rates, specifically, between 500 mL/min and 1500 mL/min.
Figure 1 Effects of gas flow characteristics and melt sulphur content on the rate of carbon removal.

The presence of chromium in significant concentrations may have contributed to this observation due to its effect on reducing the sulphur activity at steelmaking temperatures. This would imply that chromium can mitigate the effect of sulphur coverage. In order to gain some insight into the specific mechanism, re-examination of the rate data was performed. Thus the present discussion is aimed at providing some insight into the effects of chromium in the presence of sulphur on the decarburization kinetics involving CO$_2$ as the oxidant gas.

**Development of Rate Equation**

As discussed in the previous work\textsuperscript{[12]}, the rate of carbon loss is linear down to about 1 wt pct C, which suggests that mass transport in the liquid phase is not the rate-limiting step. If decarburization is limited solely by the transport of CO$_2$ from the bulk gas to the interface, the rate can be expressed as follows:

\[
\frac{d(\text{wt pct C})}{dt} = -\frac{1200A}{W} \frac{k_g}{RT_f} (p_{CO_2}^b - p_{CO_2}^l)
\]  

(1)
where $k_g$ is the gas phase mass transfer coefficient, $P_{CO_2}^b$ is the $CO_2$ partial pressure in the bulk gas on the edge of the boundary layer and $P_{CO_2}^l$ is the $CO_2$ partial pressure at the interface. In the gas phase controlled scenario, $P_{CO_2}^l$ is expected to approach zero.

The interfacial reaction for dissociative chemisorption of $CO_2$ can be written as:

$$CO_2^l + v = CO^* + O^*$$ (2)

where $v$ represents a vacant reaction site at the droplet surface and the superscript $i$ and * denote interface and adsorbed species, respectively. Ignoring the reverse reaction, the rate of decarburization is given by:

$$\frac{d(wt \text{ pct } C)}{dt} = \frac{-1200A}{W} k_c (1 - \theta_S) P_{CO_2}^i$$ (3)

where $k_c$ is the chemical rate constant for the forward reaction described in Equation (2). The fractional surface coverage by sulphur, $\theta_S$, can be described using the Langmuir adsorption model:

$$K_S = \frac{\theta_S f_S^*}{(1 - \theta_S - \theta_u) a_S}$$ (4)

where $K_S$ is the sulphur adsorption coefficient, $a_S$ is the activity of sulphur in the melt, $\theta_u$ represents the fraction of surface sites that cannot be occupied by sulphur, and $f_S^*$ is the activity coefficient of sulphur in the adsorbed layer, which can be taken as unity at carbon saturation\[9]. For carbon saturated alloys, Sain and Belton\[9] provided an expression for $K_S$, in wt pct$^{-1}$, which was based on measurements taken between 1553K and 1873K:

$$\log K_S = \frac{3600}{T} + 0.57$$ (5)
The $\theta_u$ term was introduced to account for the residual rates observed by many investigators\cite{5,7,9} who noted that increase in sulphur content beyond 0.1 wt pct does not further decrease the decarburization rate. Lee and Rao\cite{5} have obtained a value of 0.085 for $\theta_u$ from kinetics analysis of their study involving levitated droplets. For convenience, Equation (4) can be rearranged in terms of available reaction sites:

$$
(1 - \theta_S) = \frac{f_S^* + a_S K_S \theta_u}{f_S^* + a_S K_S}
$$

When the process of decarburization is jointly controlled by both the gas phase mass transfer and the interfacial reaction, the overall rate may be derived by combining Equations (1) and (3). The resulting expression takes the form:

$$
\frac{d (wt \ pct \ C)}{dt} = \frac{-1200 A k_g k_c (1 - \theta_S) P_{CO_2}^b}{W RT_f k_c (1 - \theta_S) + k_g}
$$

Effect of Chromium

As shown in Figure 2, experimental measurements by Lee and Rao\cite{4} has demonstrated the effect of sulphur concentration on the overall rate. The result from Wu et al.\cite{12}, obtained under similar experimental conditions, is also superimposed on the plot. It can be seen that the process of decarburization of Fe-C alloys containing 20 wt pct chromium (represented by ●) is 33 pct faster than chromium-free melts (represented by ○) containing the equivalent amount of sulphur, based on the experimental results by Lee and Rao\cite{4}.
According to Equation (7), the fractional surface sites available for the CO\textsubscript{2} dissociative reaction, \((1 - \theta_S)\), is an important parameter in decarburization kinetics. It is evident from Equations (6) and (7) that the rate would become a sole function of \(a_S\) if parameters such as droplet weight, temperature, gas composition and flow rate remain constant. Hence the effect of an alloying element such as chromium on the decarburization rate is reflected by virtue of the effect on the sulphur activity coefficient, and consequently \((1 - \theta_S)\). The interaction parameter for effect of Cr on S as a function of temperature is given by the equation:\[^{13}\]

\[
e_S^{Cr} = -\frac{94.2}{T} + 0.040
\]  

(8)

At 1873K, \(e_S^{Cr}\) has a value of -0.0103. Using this figure, the effect of chromium on surface coverage by sulphur can be computed using Equation (6). Results of the calculations are summarized in Figure 3. For instance, melts with identical sulphur concentration of 0.01 wt pct, the fraction of available sites is approximately 31 pct higher in the melts containing 20 wt pct chromium compared with chromium-free melts. With more available sites on the surface of the droplet, the contribution from chemical rate to the overall rate equation is expected to increase. Since the interfacial reaction takes place much faster than the transfer of gaseous oxidant across the boundary layer, this phenomenon translates to an enhanced rate as indicated by Figure 2. In
other words, melts containing 0.01 wt pct sulphur and 20 wt pct chromium can exhibit
decarburization behavior that is similar to melts which are essentially free of sulphur. This
finding is particularly significant to the industrial development of decarburization of stainless
steels by CO$_2$.

![Figure 3](image-url)

Figure 3 Change of available surface sites with melt sulphur and chromium contents.

**Summary and Conclusions**

The objective of the present work was to provide some insights into the effects of chromium, at
higher concentrations, on the decarburization kinetics involving CO$_2$ as the oxidant gas. It was
observed that the rate for Fe-20Cr-C alloys containing 0.01 wt. pct. S was 33pct faster than that
reported for chromium-free melts with the same sulphur content and essentially the same as that
for Fe-C alloys containing zero sulphur and zero chromium. The increase in decarburization rate
of iron-chromium-carbon-sulphur droplets can be explained by the attraction between chromium
and sulphur solutes in the liquid phase which decreases the sulphur activity and results in fewer
surface sites occupied by surface active sulphur.

**References**


