~~COO-4725-6~~

Kinetics of the Desulfurization of Molten Iron

Final Report

MASTER

D.R. Gaskell
University of Pennsylvania
Philadelphia, Pennsylvania 19104

March 1981

Prepared for
The U.S. Department of Energy
Under Contract Number EM-78-S-02-4725

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

There is no objection from the patent
point of view to the publication or
dissemination of the document(s)
noted in this letter.

BROOKHAVEN PATENT GROUP

4/3 1981 By

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

10 24
BOOK IN THE
RECEIVED
ACQUISITION & ASSISTANCE

1981 MAR 30 AM 9 53

11/21/81

Abstract

Experimental work has involved the fabrication of impervious slip-cast CaO crucibles, measurement of the rate of desulfurization of liquid iron by solid CaO and measurement of the rate of desulfurization of liquid iron by CaO-saturated liquid FeO. The rate of desulfurization by solid CaO is determined by diffusion of sulfur in the liquid iron. Above some minimum sulfur level, which is in the range $0.087 < \text{wt}\% \text{S} < 0.67$, the activity of FeS is high enough to form a liquid phase in the system CaO-Fe-S. With lower sulfur levels CaO does not cause any desulfurization of the liquid iron. When CaO-saturated liquid FeO is brought into contact with a liquid Fe-S alloy a rapid initial rate of desulfurization occurs due to surface tension-induced local convection at the slag-metal interface. After this initial period, the rate of desulfurization is determined by diffusion of sulfur in the metal. No change occurs in the oxygen content of the metal during desulfurization and hence the half cell reactions occurring in the electrochemical transfer process are $[\text{Fe}] \rightarrow (\text{Fe}^{2+}) + 2e^-$ and $[\text{S}] + 2e^- \rightarrow (\text{S}^{2-})$. The sulfur content of liquid iron in equilibrium with CaO-saturated liquid FeO at 1600°C is 0.012 wt% and the equilibrium partition ratio, $(\text{wt}\% \text{S})/[\text{wt}\% \text{S}]$, is 5.1. The addition of 4.5 wt% CaF_2 to the CaO-saturated slag has no effect on the kinetics of the desulfurization reaction.

Introduction

Experimental work on this project has involved,

- A) the fabrication of impervious slip-cast CaO crucibles capable of containing liquid iron and CaO-saturated slags at 1600°C,
- B) study of the desulfurization of liquid iron by solid CaO at 1600°C, and
- C) study of the desulfurization of liquid iron by CaO-saturated slags at 1600°C.

All the experimental laboratory studies of the kinetics of desulfurization of liquid iron by liquid slags, prior to the present study, have used graphite crucibles to contain the slag-metal couples. Consequently, these studies have been concerned with the measurement of the rate of transfer of sulfur from carbon-saturated iron to low oxygen potential slags based on the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. The transfer of sulfur from slag to metal involves a reduction reaction $[\text{S}] + 2\text{e}^- \rightarrow (\text{S}^{2-})$ which occurs as the cathodic half-cell reaction in an overall electrochemical transfer reaction. With carbon-saturated iron, the possible anodic half-cell reactions are the oxidation of Si, C and/or Fe and the complexity of graphite-saturated systems is such as to prohibit determination of the factors which control the relative contributions of the half-cell reactions to the overall process of desulfurization.

The present work was undertaken in an attempt to identify the rate-controlling step by simplifying, to the maximum extent possible, the chemistry of the system. The project was designed to study the

rate of desulfurization of liquid iron by CaO-saturated liquid FeO contained in CaO crucibles. With this arrangement the only two possible cathodic half-cell reactions are $(O^{2-}) \rightarrow [O] + 2e^-$ and $[Fe] \rightarrow (Fe^{2+}) + 2e^-$.

A. The fabrication of impervious slip-cast crucibles

In principle, the slip-casting of ceramics involves poring a slip or slurry of suitable density and particle-size distribution into a plaster of paris mold and allowing the liquid phase to be absorbed by the mold. The green slip-cast crucible is removed from the mold and fired at an appropriate temperature. The particular difficulties encountered in slip-casting CaO are hydration during handling and processing and the very large contraction of volume which occurs when green slip-cast CaO is fired. The optimum conditions required were determined by trial and error. High purity CaO powders, suspended in water-free ethyl alcohol, were milled with alumina grinding media, in batches, for periods of time ranging from 100 to 300 hours. The optimum particle size-distribution, determined as average size 1 micron and maximum size 3 microns, was obtained by suitable mixing of the powders ground for varying times. Figs. 1 and 2 illustrate the progress of sintering and densification which occur upon firing. Fig. 1 shows the pore distribution after firing in air at $1300^{\circ}C$ for 48 hours. This heat treatment causes a 50% reduction in volume of the green crucible and yields a density in the range 95-97% of theoretical. The majority of the pores

are interconnected and the crucible absorbs slag. Fig. 2 shows the influence of resintering at 2200°C in argon for 6 hours. During this treatment the porosity decreases and the pores become concentrated at the center of the wall section, providing, thus, a dense inner surface which is impervious to liquid slag.

B. The desulfurization of liquid iron by CaO

During the preliminary attempts to contain liquid Fe-S alloys in CaO crucibles it was observed that the crucibles were effecting significant desulfurization of the iron, and hence a study of the kinetics of this desulfurization was conducted. The experimental arrangement was as follows. An empty crucible was secured to a platinum rod, which, in turn, was secured to the lower end of an alumina tube such that the central axes of the crucible and the alumina tube were coincident. This arrangement was lowered into a vertical tube furnace until the crucible was located in the 1600°C constant-temperature hot zone. When thermal equilibrium was established seven or eight grams of a master Fe-S alloy were dropped through the alumina tube into the CaO crucible and, after a predetermined time, the melt was quenched by raising the crucible into the cool upper end of the furnace. Master alloys containing 1.62 wt%S, 0.66 wt%S and 0.087 wt%S were studied and the experimental results are shown in Fig.3 as the variation of the average sulfur content of the iron with t/a^2 where t is the time in minutes and a is the radius

of the iron ingot. Each datum point plotted in Fig.3 was obtained from a separate experimental run and the influence of variation in the inner diameters of the crucibles is accounted for by dividing the time by a^2 . The results were analysed on the assumptions that an equilibrium sulfur partition is established at the crucible-melt interface and the rate of desulfurization is controlled by radial diffusion of sulfur in the iron. The upper line in Fig.3 is the theoretical line calculated for a diffusivity of sulfur in iron, D_S , of $7.3 \times 10^{-4} \text{ cm}^2/\text{s}$, and the lower line is drawn for $D_S = 6.3 \times 10^{-4} \text{ cm}^2/\text{s}$. No desulfurization of the 0.087 wt%S alloy occurred.

X-ray examination of sections of the CaO crucible showed concentrations of Fe and S at the sintered grain boundaries in the crucible. A typical distribution of sulfur is shown in Fig.4. The apparent rapid diffusion of Fe and S in the CaO crucible indicates that, when the activity of FeS in the iron exceeds some minimum value, an FeS-rich liquid is formed in the system CaO-Fe-S. The extent of penetration of the Fe and S into the crucible wall is illustrated in Fig.5. The absence of desulfurization of the 0.087 wt%S alloy by the crucible indicates that the activity of FeS in the melt is less than the minimum required for formation of the liquid phase. The diffusivity of sulfur obtained from these experiments is in excellent agreement with values obtained using classical experimental techniques.

C. The desulfurization of liquid iron by CaO-saturated FeO slag

It was determined experimentally that saturation of liquid FeO by CaO at 1600°C occurs at the composition 58 wt%CaO-42 wt%FeO and a master slag of this composition was prepared. Fig.6 shows a fragment of a CaO crucible which has contained this slag for 10 minutes at 1600°C . The darkening at the inner walls of the crucible is due to absorption of iron to form the equilibrium solid solution of FeO in CaO.

All of the desulfurization experiments were conducted with 0.087 wt%S samples using a technique in which slag was added to the crucible containing the liquid Fe-S alloy at time, $t = 0$ and the experiment was stopped at time t by raising the crucible to the upper end of the tube furnace. The variation of the average sulfur content of the metal with $At^{1/2}/W$, where A is the measured area of the slag-metal interface, W is the weight of the metal and t is the time of the experiment, is shown in Fig.7. The broken line is the expected variation of the average sulfur content with time if the rate of desulfurization were controlled by linear diffusion of the sulfur to the slag-metal interface. This calculation was made using the value of D_S obtained from the data shown in Fig.3 In Fig.7 it is seen that, after an initial period of rapid desulfurization, the experimental line becomes parallel to the broken line up to such time as the conditions for diffusion in a semi-infinite medium break down. It is suggested that the initial rapid rate of transfer of sulfur across the interface

decreases the interfacial energy to an extent which produces local instabilities and local convection at the interface. As the rate of transfer decreases, the interfacial tension increases and convection ceases, after which time the rate of desulfurization is controlled by diffusion of sulfur in stagnant iron. The equilibrium sulfur content of the iron is 0.012 wt% and the equilibrium partition ratio between the slag and metal, $(\text{wt}\% \text{S})/[\text{wt}\% \text{S}]$, is 5.1. The initial oxygen content of the Fe-S alloy was 705 ppm, which is virtually that value required for equilibrium with CaO-saturated liquid FeO at 1600°C (corresponding to $a_{\text{FeO}} = 0.3$ in the slag). The variation of the oxygen content of the iron with time is shown in Fig.8, which shows that, within experimental error, the oxygen content remains constant. Thus, by elimination, the half-cell reactions occurring at the slag-metal interface are

and

Evidence for the transfer of Fe and S across the interface is shown in Fig.9 which shows the build-up of a "head" on the iron ingot with time. This head develops as the result of dissolution of the CaO crucible at the line of crucible-metal-slag contact.

A CaO-saturated slag of composition 4 wt% CaF_2 -53 wt% CaO-43 wt% FeO was prepared and used in a series of experiments. The variations of sulfur and oxygen contents with time, shown in Figs.7 and 8 respectively, are identical with the results

obtained with the binary slag, as is required if diffusion in the metal is rate-controlling.

Recent developments in the approach to the problem of desulfurization in iron- and steelmaking .

Within the life-time of the present contract a major change has occurred in the approach to the problem of desulfurization in iron- and steelmaking. At the time that the present project was proposed the burden of desulfurization fell on the steelmaker and interest was focussed on identification of substitutes for fluorspar (CaF_2) as the flux in steelmaking slags which would permit acceptable desulfurization in the steelmaking process. The sulfur problem had been steadily increasing in severity due to ever-increasing sulfur loading in the blast furnace and was becoming critical with the need to change fluxing practise in the steelmaking operation. As the extent of desulfurization achieved within the blow-time in a BOF vessel is determined more by the rate of desulfurization occurring during the fixed time of blowing than by the equilibrium distribution between the tapping slag and the liquid steel, identification of the rate-controlling mechanism in the desulfurization reaction would have greatly aided the process of identifying a substitute flux.

However, at about the same time, what has become known as the "alkali problem" was identified in blast furnaces. This problem is caused by trace-amount quantities of alkali oxide,

(mainly Na_2O) which are present in the ore fed to the blast furnace. On descent through the stack, a temperature is reached at which the alkali oxides volatilize and rise with the ascending gases. Upon sufficient cooling the alkali oxides sublime and are again carried downwards with the burden. After sufficient recycling of the alkali oxides within the stack, scabs and crusts begin to form which, eventually, cause unacceptably uneven descent of the burden. This problem has been eliminated by decreasing the basicity of the blast furnace slag to a level at which the alkali oxides are fluxed at an activity lower than that which permits evaporation at the highest temperatures in the blast furnace. As a result, the alkali oxides are passed through the blast furnace, but the required decrease in the basicity of the slag has caused a commensurate increase in the sulfur content of the hot metal produced. Depending on the slag practice, the hot metal sulfur levels can be in the range 0.06 to 0.08 wt%, which is much higher than can be dealt with by a single-slag process in the BOF. Consequently, steelmakers faced with the alkali problem have been forced to introduce external desulfurization of the hot metal prior to its conversion to steel. Desulfurizing agents in current use include mag-coke, CaC_2 and salt-coated Mg. The extents of desulfurization being obtained are sufficiently great that the problem of desulfurization in the steelmaking process has been virtually eliminated. Thus the focus of interest has

been changed from the steelmaking process to external desulfurization of blast furnace hot metal.

FIG 1. Section of CaO crucible wall after firing at 1300°C for 48 hrs. (Mag x20)

FIG.2 Section of crucible wall after firing at 1300°C for 48 hrs. + firing at 2200°C for 6 hrs.(x20)

FIG 3

DESULFURIZATION OF LIQUID IRON AT 1600°C BY LIME CRUCIBLES

↓ melt-crucible interface (iron on left
CaO on right)

↑
FIG.4 Distribution of sulfur
(light areas) in CaO crucible (x150)

FIG.5 Penetration of crucible wall
by FeS.

DESULFURIZATION OF LIQUID IRON AT 1600 °C BY LIME-SATURATED SLAGS

FIG 8

FIG.6 Crucible and contained slag ($\times 5$)

FIG.9 Build-up of a "head" on the iron ingot
(Increasing time from left to right).

RECEIVED BY TIC

APR 9 1981