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ENHANCED SLAG-METAL REACTIONS

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Synopsis:
Most slag-metal reactions in steelmaking and refining are electrolytic in nature. This is not surprising since the components in a slag are predominantly, if not exclusively, in the ionic state. This fact has been established in many different investigations over the last forty years or so, and our present understanding of the structures and properties of slags is firmly based on this concept. With the recent introduction of commercial D.C. arc furnaces, D.C. plasma furnaces, and D.C. ladle furnaces, there is a new impetus to evaluate the effects of electrolysis in steel melting and refining. In this work, a transferred arc D.C. plasma was applied to a steel-slag system in order to study the effects of polarity on desulfurization, oxide reduction reactions and the behaviour of nitrogen.

Key words: Plasma enhanced refining; desulfurization reactions; reductive alloying; nitrogen behaviour.

Introduction

The only reaction for which the electrolytic aspect has been explored in any depth is desulfurization. The early work of Ramachandran, King and Grant (1) substantiated the existence of an electrochemical mechanism controlling sulfur transfer between metal and slag. The overall reaction is the interfacial exchange reaction:

$$\underline{S} + (O^{=}) = (S^{=}) + \underline{O} \qquad (1)$$

where the underlined components are in liquid steel and the bracketed components are in molten slag. This can be broken into its component half reactions:

$$\underline{S} + 2e = (S^{=}) \qquad (2)$$

$$(O^{=}) = \underline{O} + 2e \qquad (3)$$

Thus desulfurization is cathodic in nature and electroneutrality is maintained by anodic reactions such as reaction 3. Other possible anodic reactions in the steel/slag system may be:

$$Fe = (Fe^{2+}) + 2e \qquad (4)$$

$$\underline{Mn} = (Mn^{2+}) + 2e \qquad (5)$$

$$\underline{Si} = (Si^{4+}) + 4e \qquad (6)$$

$$(O^{=}) + \underline{C} = CO + 2e \qquad (7)$$

Once the electrochemical nature of slag-metal exchange reactions was established, considerable interest developed in the enhancement of desulfurization rates by application of electric current. Several investigators confirmed that desulfurization rates increased with increasing current density with the anode in the slag (2-6). Ward and Salmon found that sulfur reversion took place when the applied current was switched off, and that reversion was accelerated when the current was re-applied with opposite polarity (3). El-Gammal and co-workers suggest that, due to their ionic nature, slags tend to separate by ionic groups and develop internal concentration gradients (5). This causes slag basicity to increase in the direction of the cathode.

With the application of current, it is possible for reactions 2 and 3 to both proceed in the direction of reduction. Thus increased basicity and accelerated reduction reactions at the slag-metal interface are responsible for vast improvements in desulfurization capability of slags with applied current with the melt acting as the cathode.

In light of the positive results of early experimental work, it may seem somewhat surprising that electrochemical desulfurization did not find industrial application. However, Ward and Salmon concluded that the efficiency of sulfur transfer, on the order of a few percent was too low to form the basis of an economical desulfurization process on a large scale (3). The current input required for a ladle of steel in order to achieve an average current density of about 1.0 A/cm^2, which is approximately that required for reasonably accelerated desulfurization, is on the order of 10^5 A. This represents a significant power input which would be difficult to justify on the basis of desulfurization alone. However, if the power input is present for other reasons, as is the case with electroslag remelting (ESR) and arc reheating, the current type and polarity could be chosen to advantage.

Given the above line of thought, one might expect desulfurization during the ESR process to be best achieved with a D.C. positive electrode. The work of Swinden, however, showed that desulfurization was greatest with A.C., least with D.C. negative electrodes, and intermediate with D.C. positive electrodes during consumable electrode ESR (7). The D.C. positive electrode mode of operation did not live up to expectations for several reasons. The electrolytic half reactions are oxidizing at the anode and reducing at the cathode. The metal droplets melting off at the electrode are therefore resulfurized, counteracting the desulfurization that takes place in the cathode pool. Also, less heat is generated at the cathode than at the anode, resulting in a lower sulfide capacity of the slag and a shallow molten pool in the ingot. The net result is less effective desulfurization than can be achieved with an A.C. electrode.

Because of its failure in ESR applications, the idea of a steel refining process utilizing electrolytic desulfurization was largely abandoned after the early 1970's. However, with the recent introduction of commercial D.C. arc furnaces, D.C. plasma furnaces, and D.C. ladle furnaces, there is a new impetus to evaluate the effects of electrolysis in steel melting and refining. Obviously, the same polarity which favors Reaction 2 should favor other cathodic reactions such as the reverse of Reactions 4 to 6, which are oxide reduction or "reductive alloying" reactions.

Experimental Aspects

The apparatus used in this work is shown in Figure 1, and has been described previously (8-10). Briefly, the equipment consists of a 25 kW induction furnace lined with a 90 wt % MgO ramming compound. The induction power allows melt temperature and plasma power to be independently varied. It also inputs stirring energy to the melt and permits quick melting of the charge. The D.C. plasma is applied with an axially drilled graphite electrode, with 2.5 l/min of argon injection for arc stabilization. A 500 A D.C. welding supply is used as the plasma power source. Voltage and current are monitored continuously.

In the previous work, it was noted that the plasma produced by a negative electrode had enough force to part the slag layer and expose a liquid metal surface, while that produced by a positive electrode was more diffuse, permitting the maintenance of a continuous slag layer. Also, due to the forces imparted by induction power, the molten metal surface is convex, causing the slag layer to thin in the central region which is the area of plasma impingement. Since, in this study, it was desired to maintain a continuous slag layer, and since the use of a large slag volume is impractical, lower induction power was used to flatten the surface of the molten steel bath.

With constant plasma power and decreased induction power, experiments had to be performed at a lower temperature. In order to lower its liquidus temperature, 4 wt % carbon was alloyed to the stainless steel. The carbon also acted as a deoxidizer and aluminum additions were, in most cases, not made. Experiments were conducted at 1400°C with 5 kg melts and 500 g slag weights. With these conditions, and a minimum plasma column length of 3 cm., a continuous slag layer could be maintained on the surface of the melt with both positive and negative polarity D.C. plasma heating.

During the course of experiments, suction samples were taken from the melt with 3mm I.D. quartz tubes. Slag samples were taken by quenching onto a cold steel bar. Melt and slag compositions were determined by X-ray fluorescence. Carbon and sulfur analyses were by combustion of samples in a Leco carbon-sulfur determinator. Temperature was monitored with a Pt-13 % Rh versus Pt thermocouple.

In order to more clearly delineate differences in desulfurization rates and equilibrium sulfur values, initial sulfur levels in the melt were about 0.2 wt %. An example of desulfurisation with and without the plasma slag heating is shown in Figure 2. In both cases, the slag and metal compositions and volumes, along with the temperature, were the same. Desulfurisation was very effective with the well-mixed, reactive slag layer achieved by plasma heating. In contrast, the induction heating alone left the slag cold, crusty and non-reactive, resulting in rather poor desulfurisation. Similar results were obtained for deoxidation and fluxing of inclusions.

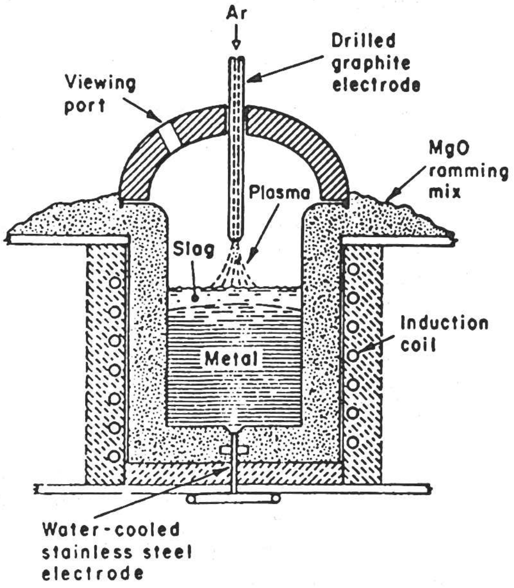

Fig. 1 Schematic diagram of experimental apparatus.

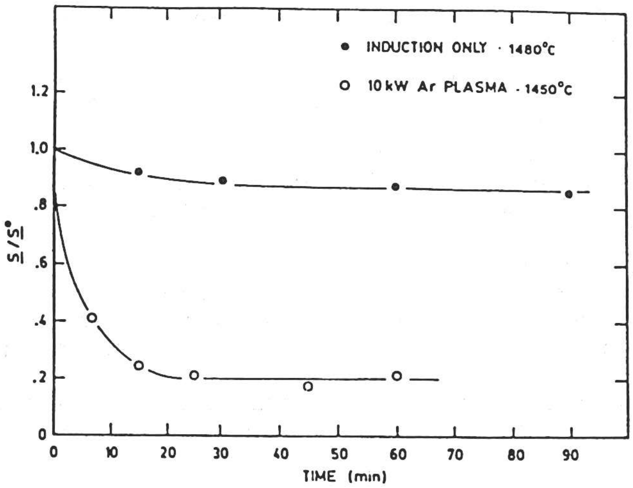

Fig. 2 Desulfurization of stainless steel (type 304) by a 50% CaO, 50% Al_2O_3 slag, with and without plasma heating.

The Effect of Electrode Polarity

In accordance with the work of Ward and co-workers (3), the results of this work show an increased rate of desulfurization as well as lower final sulfur levels in a cathodic melt, as shown in Figures 3 and 4. Contrary to Ward, however, there was no evidence of sulfur reversion upon switching polarity to an anodic melt. The reason for this became clear when mass balances were performed on sulfur. The sum of the sulfur in the slag and the sulfur in the metal accounted for as little as 20% of the total initial sulfur in the system. This loss of sulfur to the gas phase was observed to a lesser extent by Ward and co-workers during desulfurization of a cathodic melt. They observed a 15 % loss of sulfur from the system over a period of 150 minutes. Sulfur lost to the gas phase in the present work amounted to 0-4% for anodic melts and 50-80% for cathodic melts. Desulfurization of metal and slag in the plasma impingement zone during positive electrode heating is shown in Figure 5.

The removal of sulfur from the slag to the gas phase during positive electrode plasma heating can be attributed to two main factors. Firstly, the potential gradient and current through the slag are such that oxidizing reactions are encouraged at the slag/plasma interface. Sulfur can therefore be removed by reactions such as:

$$(S^{=}) + O_2 = SO_2 + 2e \qquad (8)$$

$$2(S^{=}) = S_2 + 4e \qquad (9)$$

The voltage gradient may also cause the slag to polarize, with cations concentrating near the melt and anions concentrating near the gas phase, thereby increasing the activity of sulfur anions, and forcing reactions such as 8 and 9 to the right. Secondly, the high temperature and high gas velocity imparted by the plasma increase mass transport and reaction rates in both the slag and gas phases.

In agreement with reaction 8, it was found that increasing the oxygen content of the gas phase led to a higher desulfurization rate and a lower final sulphur level. This may seem to contradict the established relationship between steel desulfurization and oxygen potential. It should be clearly understood that it applies only to the case where the anodic and cathodic reaction sites are well separated. Only then is the slag acting as a transfer medium or pump rather than as a reservoir for the sulfur. The corollary of this is that the sulfide capacity and hence the basicity of the slag become less critical.

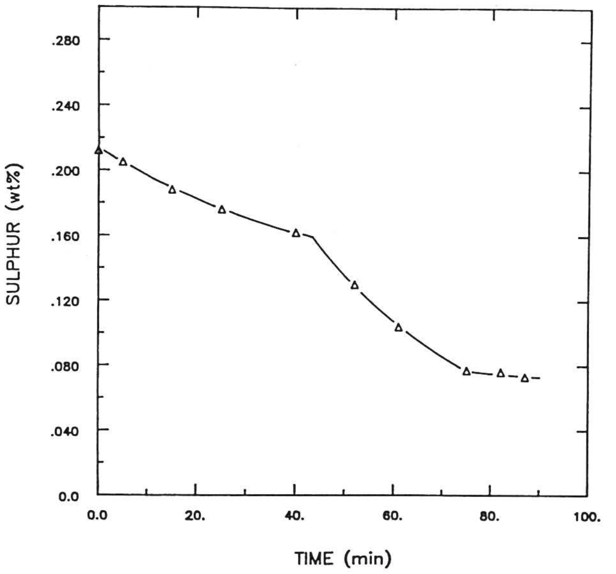

Fig. 3 Sulfur content of the melt with time for cathodic melt from 42 to 75 minutes, and anodic melt for the remainder of time

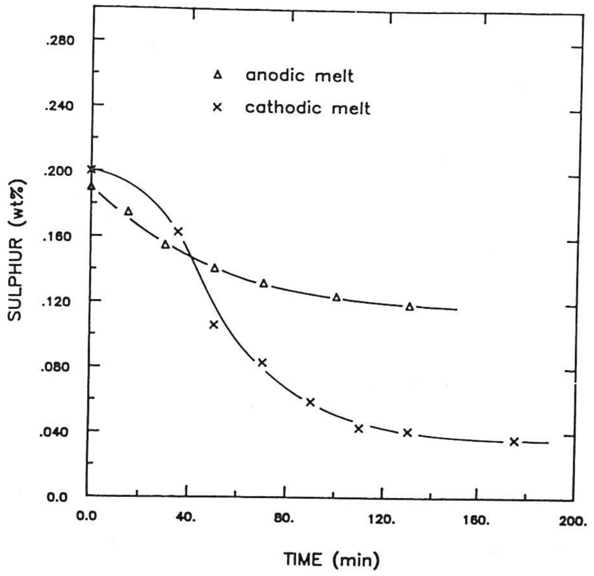

Fig. 4 Sulfur content of anodic and cathodic melts versus time.

Slag Chemistry

The influence of the direction of current flow on slag chemistry is evident in Table 1. An anodic melt increases concentrations of FeO, MnO and Cr_2O_3 in the slag by oxidizing metallic elements in steel. Conversely, a cathodic melt causes reduction of these oxides, as well as of SiO_2. If the slag contains reducible oxides, then the fraction of a given Faradaic current available for reduction of sulfur will be decreased. Consequently, the rate of desulfurization of the melt is reduced, as is evident in Figure 6. Reducible oxides were built up over time by plasma heating with a negative electrode, and then the current direction was reversed. The rate of desulfurization during positive electrode heating was depressed more with a longer duration of prior negative electrode heating. It stands to reason that a higher activity of reducible oxides in the slag would utilize a larger fraction of the Faradaic current, thus curtailing the desulfurization rate.

Table 1: Typical slag compositions (wt%) for a) lime-alumina flux b) after 140 minutes of desulfurization with cathodic melt, c) after 135 minutes desulfurization with anodic melt, d) slag (c) after an additional 65 minutes desulfurization with cathodic melt.

Slag	CaO	Al_2O_3	MgO	Cr_2O_3	FeO	MnO	SiO_2	S
a	46.6	46.6	1.9	---	0.90	---	3.4	0.22
b	44.11	43.80	9.11	0.50	0.25	0.20	1.87	0.56
c	41.13	40.31	5.10	5.35	1.47	2.78	3.36	0.97
d	42.45	41.97	8.12	2.25	1.14	0.99	2.52	0.73

The interesting corollary of this effect is that this technique could be employed advantageously to facilitate addition of alloying elements such as manganese and chromium. The addition of such elements as their oxides, followed by their reduction in situ, could by-pass the need for expensive ferroalloys (especially attractive where the desired carbon content of the melt is low) and thus significantly reduce the cost of alloying. This technique of reductive alloying could be employed after both deoxidation and desulfurization have been completed. It is interesting to note that enhanced oxide reduction is in fact an example of in-bath smelting, which is the subject of intensive research by many companies and groups throughout the world since it is at the heart of most, if not all, of the technologies being developed for direct steelmaking. It is thus possible that the application of D.C. arc technology could have repercussions of paramount importance in this rapidly developing area. It is also conceivable that it could confer significant advantages in the production of ferroalloys, and perhaps even metals such as manganese, silicon and chromium.

In addition to these rather speculative applications, this technology clearly has important applications to several processes already in use. In the field of ladle metallurgy, for example, arc heating is commonly used for raising and controlling temperature. The use of reverse polarity D.C. arcs would not only provide the necessary heating but also permit significant amounts of alloying subsequent to deoxidation and desulfurization, using the relevant oxides rather than ferroalloys, under conditions of low oxygen potential and moderate stirring levels in the steel bath. Such conditions are preferable to the oxidizing environment existing during tapping where much of the alloying is currently carried out.

With induction melting in the steel foundry industry, the ability to carry out reductive alloying under appropriate conditions with the metal stirred inductively and the slag superheated by the plasma power could provide an attractive alternative to the AOD process, by significantly increasing the range of alloy steel specifications which can be made by this route.

Nitrogen Behaviour

In experiments conducted with carbon saturated iron and aluminum killed steel melts contained under a lime-alumina slag, nitrogen removal was not significantly enhanced by the presence of an argon plasma. This contrast to the behaviour observed with sulfur may be due to the more complex forms in which nitrogen can exist in the slag i.e. as free nitrogen ions, as nitride ions incorporated within the network, and in the presence of carbon, as cyanide ions. Further work has been conducted with a variety of slag compositions from systems including BaO-TiO_2 and CaO-CaF_2 (11). Again however, the argon plasma had very little effect on nitrogen desorption. It is worth noting however that the rates of nitrogen removal from carbon saturated iron were greater than those observed with aluminum killed steel. As mentioned earlier, with carbon saturated iron, nitrogen can be absorbed in the slag in the form of cyanide ions. At the elevated temperatures of the present experiments, cyanogen is unstable, and consequently cyanide in the slag can be removed to the gas phase in the form of nitrogen gas.

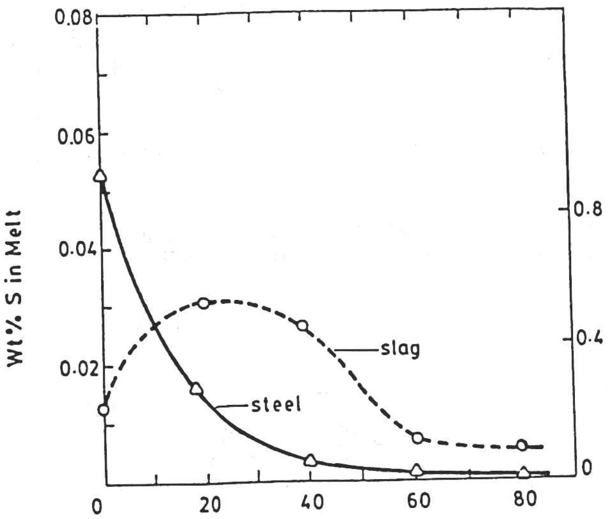

Fig. 5 Sulfur content of steel and slag in the plasma impingement zone with time (cathodic melt).

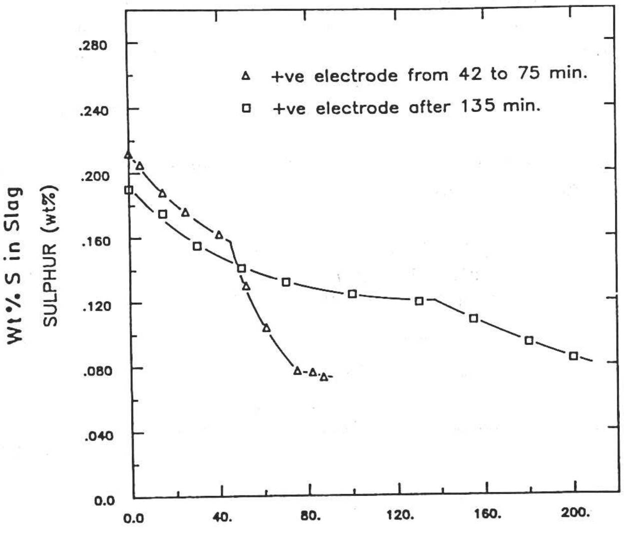

Fig. 6 The effect of prior negative electrode plasma heat duration on subsequent desulfurization with positive electrode plasma heat.

Conclusions

There are four benefits to be gained from the use of DC electrode positive polarity (that is a cathodic melt or reversed polarity), together with a fluid, basic flux. Firstly, greatly accelerated sulfur transfer from metal to slag. Secondly, much lower sulfur contents in the melt than those dictated by chemical equilibrium, since up to 80% of the sulfur is removed from the slag-metal system by oxidation reactions at the anode. Thirdly, very low oxygen activity and total oxygen contents, and hence low inclusion contents in the solidified steel, provided that the flux employed has high capacity for the deoxidation product (usually either silica or alumina). Finally, reductive alloying which can provide alloying elements such as nickel, manganese and chromium by in situ reduction of their oxides and so reduce both alloy losses to the slag phase and the need for expensive ferro alloy additions (12, 13).

In contrast to the benefits mentioned above, very little enhancement was observed with respect to the removal of nitrogen from metal to slag under plasma conditions. This may be due to the different complex forms in which nitrogen can exist within the slag phase.

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