CONTROL OF Cr-LOSS TO THE SLAG PHASE IN HIGH ALLOY STEELMAKING

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ABSTRACT

The Cr-loss to the slag phase in high alloy steel production has been investigated as a function of oxygen partial pressure during the decarburization step. The aim of the project was to minimize Cr-losses to the slag in view of the economic and environmental impacts. The oxygen partial pressures were controlled by mixtures of O_2 *and* CO_2*. Bench-scale experiments without a receptor slag for oxidation products and 1 kg scale experiments with a receptor slag were carried out for the decarburization in Fe-Cr-C melts using* CO_2*-*O_2 *gas mixtures. The decarburization reaction that followed could be represented as:*

$2\underline{C} + O_2(gas) = 2\ CO\ (gas)$

$\underline{C} + CO_2\ (gas) = 2\ CO\ (gas)$

The results of the present experiments demonstrate that the Cr-losses are minimized when CO2 is used as the deoxidizer. The results are discussed in the light of the thermodynamics of the slag system. The advantages of decarburization of steel using CO_2*-*O_2 *mixtures and the consequent minimization of Cr-loss are clearly evidenced in the present results.*

INTRODUCTION

With increasing demand for raw materials in high alloy steel making, it is essential to minimize the loss of the valuable metals to the slag phase. In the case of chromium in the slag, the oxidation to Cr^{6+} makes it extremely cancerogenic and thus, the slag poses an environmental hazard. From economic as well as environmental view points, it is essential that the loss of Cr is minimized during the decarburization of high alloy melts.

The Cr-loss during high alloy steel production is directly related to the partial pressure of O_2 prevailing. During the decarburization step, a higher oxygen partial pressure leads to a higher level of oxidation of Cr with a consequent loss to the slag phase. In the traditional practice, the partial pressure of O_2 in the gas phase is reduced by mixing the same with Ar. Choulet *et al.* [1] have indicated that dilution of oxygen by argon was effective in lowering chromium oxidation. Besides, Fulton and Ramachandran [2], Nelson [3] have also carried out investigations regarding the improvement of the efficiency of Ar in protecting chromium in molten steel from oxidation. Fruehan [4] had reported from his investigations, that the concentrations of chromium decreased approximately linearly with time in 90 mins when blowing 1:1 oxygen: argon. It has also been pointed out by Fruehan [5] that the rate of chromium oxidation was considerably faster than that of carbon.

It is to be noted that a decrease in the oxygen partial pressure in the gas injected for decarburization should not lead to a significant decrease in the process efficiency with respect to the decarburization itself as it will have a strong negative impact on the process economy. At the same time, if the oxygen partial pressure exceeds the threshold limit, this will lead to a high degree of Cr oxidation. An optimum level is to control the oxygen partial pressure continuously taking into account the activities of C and Cr in the metal phase and the activity of chromium oxide in the slag phase. A higher oxygen potential in the gas during the initial stages of decarburization and a lower limit towards the end could be a suitable solution. Introduction of CO_2 in suitable amounts could thus offer a unique solution as an environmentally undesired gas is being used for decarburization. The principle of decarburization with CO_2 has been expounded by Mannion and Fruehan [6]. Their results show that nearly one-fifth of the CO_2 supplied was consumed during the decarburization reaction. Zughbi [7] reported higher decarburization rate and more vigorous reaction when O_2 was used as oxidizing gas instead of CO_2. Sain and Belton [8] have studied the decarburization of liquid iron by CO_2 at great length. To the knowledge of the present authors, no systematic investigation has been carried out with respect to the decarburization of Fe-Cr-C melts.

The present work presents the investigations carried out in the laboratory with respect to the decarburization of Fe-Cr-C melts by O_2-CO_2 mixtures and examining the extent of decarburization and Cr oxidation.

EXPERIMENTAL DETAILS

All the materials including the gases used in the present experiments, together with their purity and the suppliers are presented in Table 1.

Table 1: Details of materials

Materials	Purity	Supplier
Pig iron	4.5wt% Carbon	SSAB Svenskt Stål AB
Armco iron	≥99.9%	KIMAB
Chromium block	≥99.9%	Sigma Aldrich
Iron powder	99%	Sigma Aldrich

MgO powder	99%	Sigma Aldrich
Al_2O_3 powder	99.7%	Sigma Aldrich
CaO powder	99.7%	Sigma Aldrich
SiO_2 powder	99.5%	Sigma Aldrich
Argon	ICP-5.0	AGA Gas AB
Oxygen	ICP-5.0	AGA Gas AB
Carbon dioxide	**ICP-5.0**	**AGA Gas AB**

In the present work, Fe-Cr-C molten alloy was allowed to react with O_2-CO_2 gas mixtures at 1873 K. Experiments were divided into two parts. One was carried out in a horizontal furnace with the gas passing above the sample, the other was processed in an induction furnace with blowing gases into it to refine. The former experiments were conducted in slag-free atmosphere, where the oxide activity will be unity, while the latter experiments were conducted with the metal submerged in a slag.

Decarburization Experiments without Contact with Slag Phase

Experimental Set-up

A high temperature horizontal resistant furnace was used in the present experiments. The gases were carefully cleaned and mixed before passing into the furnace. The details for gas cleaning system are described elsewhere [9]. The flow rates of the gases were measured by pre-calibrated flow meters. The furnace arrangement is shown in Figure 1.

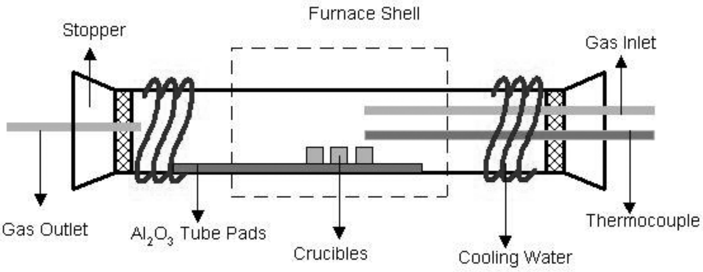

Figure 1: The schematic diagram of the experimental arrangement

Procedure

Iron powder was mixed with pig iron and chromium to achieve the targeted composition of the steel melt as Cr 11 wt% and C 3.5 wt%. The exact composition of some of the post-melted sample was determined by chemical analysis. 25 g of the alloy was held in an alumina crucible of dimensions ID 16 mm, OD 20 mm and height 30 mm. The initial composition of steel was kept the same in all the experiments. The following gas mixtures were used for imposing different oxygen partial pressures above the steel melt: *viz.* 100% O_2, 64% O_2 + 36% CO_2, 30% O_2 + 70% CO_2, 13% O_2 + 87% CO_2, 100% CO_2.

The alumina crucibles holding materials were introduced into the uniform temperature zone of the reaction tube under the protection of Ar and kept at 1873K for 5 hours for melting and homogenization. The oxidant gases were then introduced into the reaction tube. The total gas flow rate was kept at constant at 350 ml/min. The flow rate of reaction gases was stable during the experiments. In each experiment, 3-4 samples were kept in the reaction tube.

The reacted samples were taken out after oxidation at intervals of 10 min up to 60 min by pulling out the samples to the cold end of the furnace over alumina runners. The cooled samples were stored in desiccators. The chromium content of the samples was analyzed by X-ray fluorescence spectroscopy and the total carbon content by LECO combustion method.

Decarburization Experiments with Steel Covered by a Slag Phase

As the above bench-scale experiments may not be representative of the real situation without a slag receptor, a series of experiments were designed with samples masses of 1 kg steel in an induction furnace with a slag phase above and the oxidant gases being injected.

Experimental Set-up

A schematic diagram of the experimental apparatus is presented in Figure 2. The steel and slag samples were placed in an Al_2O_3 crucible of 45 mm I.D. and 130 mm in height and positioned inside an outer graphite crucible, which, in turn, was positioned inside an induction furnace. The decarburizing gas was blown into the liquid melt through an alumina lance of 3.5 mm in I.D. The lance was immersed into the melt to a depth of 50 mm from the melt top.

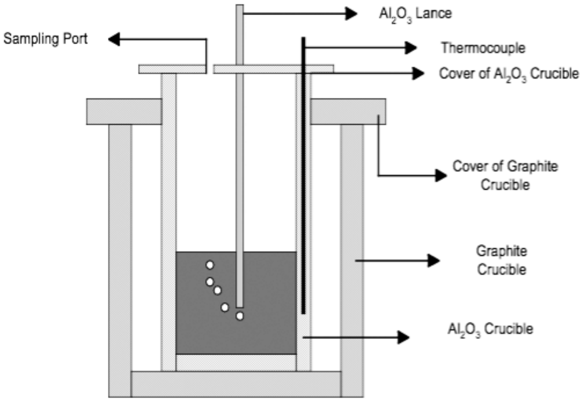

Figure 2: A schematic plot of the induction furnace experiment

Experiments in an Induction Furnace

The composition of the slag used is shown in Table 2.

Table 2: The compositions of slag

Composition	CaO	MgO	SiO_2	Al_2O_3
Wt%	40	10	40	10

All the oxide powders were dried and mixed well before they were made into pellets. About 1.5 kg slag pellets were melted in a graphite crucible at 1773 K in an induction furnace. The steel sample was prepared by pre-melting 20 kg of the targeted alloy mixture. 1 kg of this was used in each experiment. The amount of slag which was added in each experiment corresponded to 5% in weight of the steel taken. The steel and the slag were melted under the Ar atmosphere and the oxidant gas was blown into the liquid metal at 1873 K. Gas flow rate was kept at 1670 ml /min for some experiments. Samples of the steel melt were taken at appropriate time intervals using quartz sampler tubes of ID 6 mm and quenched in cold water. The samples were analyzed to obtain carbon and chromium compositions.

RESULTS

Decarburization Experiments without Contact with a Slag Phase

These experiments were carried out in order to study the impact of oxygen partial pressure on decarburization and Cr-loss. The initial composition of the steel sample as determined by chemical analysis was: Cr 10.4 wt% and C 3.31 wt%.As mentioned earlier, 5 different oxygen partial pressures were used varying from 100% O_2 to 100% CO_2.

The Effect of CO_2 in the Retention of Cr

Figure 3 shows the changes of Cr and carbon contents in steel with time under pure oxygen and pure CO_2 in the horizontal furnace. The carbon content decreased from 3.3 wt% down to about 1.0 wt% in both the above gas atmospheres after 50 min.

The Cr-loss from the metal samples in the two cases showed a significant difference. With pure oxygen, the Cr content decreased sharply from the initial value of 10.4% to less than 3%. On the other hand, in the case of 100% CO_2, the line corresponding to Cr content was almost horizontal indicating insignificant oxidation of Cr. It should be pointed out that the Cr amount was nearly equal in the case of both pure O_2 as well as pure CO_2 during the first 10 min. Beyond this, the Cr loss was significant with pure O_2 as the oxidizer.

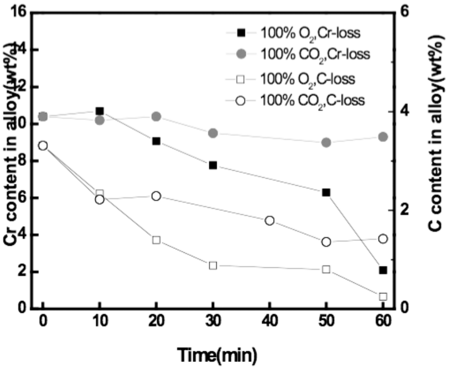

Figure 3: The change in the Cr and C contents during the reaction of Fe-Cr-C alloys with pure O_2 and CO_2 in a horizontal furnace

When the reaction time was less than 30 min, the carbon loss with pure O_2 as oxidant was almost twice that for pure CO_2. This is in agreement the theoretical analysis that for every molecule of O_2 injected, 2 moles of C from the melt can be removed; however, for every mole CO_2, only one carbon atom in the melt will be removed. With the progress of the reaction, the carbon amount in steel would be less and the carbon diffusion would be the rate-limiting step.

Decarburization at Different O_2 Partial Pressure

The decarburization at different O_2 partial pressures, obtained in the present experiments is shown in Figure 4.

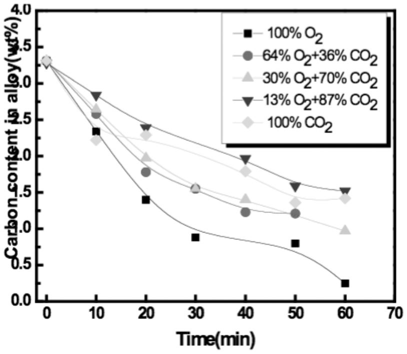

Figure 4: Decarburization with different O_2 partial pressure in a horizontal furnace

It shows that C content loss quickly from 3.3% down to 0.2% while treatment with pure O_2. In general, the rate of decarburization is seen to increase with the raising of O_2 partial pressure, except when the gas composition was 13%O_2 + 87%CO_2, as can be seen in Figure 4. The carbon loss in this case was less than that corresponding to pure CO_2. According to Sain and Belton [8] and Cramb and Belton [10], the rate of dissociation of CO_2 on the surface is the limiting step when decarburization with CO_2, as shown in Equation (1),

$$CO_{2(ads)} \rightarrow CO_{(ads)} + O_{(ads)} \tag{1}$$

When adding O_2 to the CO_2 system, the equilibrium will move to the left side. In other words, the decomposition of CO_2 will be suppressed by adding some content of O_2. Since the decarburization reaction occurs due to both O_2 gas as well as oxygen by the dissociation of CO_2, the impact of the latter may not be felt at higher oxygen levels in the gas mixture. At lower oxygen levels in the gas, the effect of the dissociation of CO_2 is likely to be significant. This aspect needs to be examined further and experiments are conducted presently to understand the phenomenon.

Chromium Loss with Different Partial Pressure of Oxygen

Cr-loss at different partial pressures of oxygen was studied with a horizontal furnace and the result was shown in Figure 5.

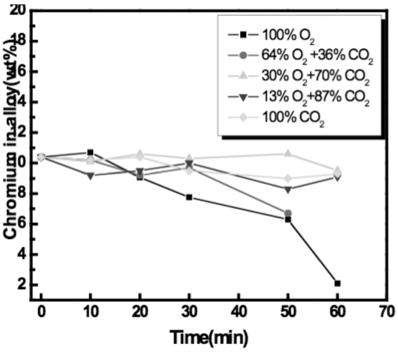

Figure 5: Change of Cr content in steel at the different partial pressure of oxygen in a horizontal furnace

As mentioned earlier, the ratio of CO_2 to O_2 was changed in the present experiments. The results of these studies are presented in Figure 5. In all the cases, the Cr-content in the metal does not show any significant change during the first 20 min. of oxidation irrespective of the prevailing oxygen partial pressure. It is also seen in the figure that the Cr-loss is significant at later stages in pure O_2 as well as 64% O_2+ 36%CO_2 atmospheres, albeit the oxidation of Cr was somewhat less in the latter case. With O_2 content in the gas 30% or less, the Cr loss was negligible. The scatter between the points is due to the uncertainties during sampling and analysis.

From these results, it is reasonable to assume that the optimal ratio of O_2:CO_2 was 3:7 considering both the decarburization and Cr-loss.

Decarburization Experiments with Steel Covered by a Slag Phase

In the case of the experiments with a slag phase, the composition of the slag and the steel phases were similar for all the experiments. These trials were focused on the impact of the gas flow rates apart from the change of oxygen partial pressure in the gas.

The Effect of Gas Flow Rate in Cr-loss and Decarburization

In these experiments, the composition of steel was as follows: C: 2.65-3.25 wt% and Cr: 11.8-15.1 wt%. The effect of the impact of gas flow rate on decarburization and to Cr-loss was studied by injecting pure CO_2 at different flow rates (350, 930, 1360 and 1670 ml/min). The results are shown in Figure 6.

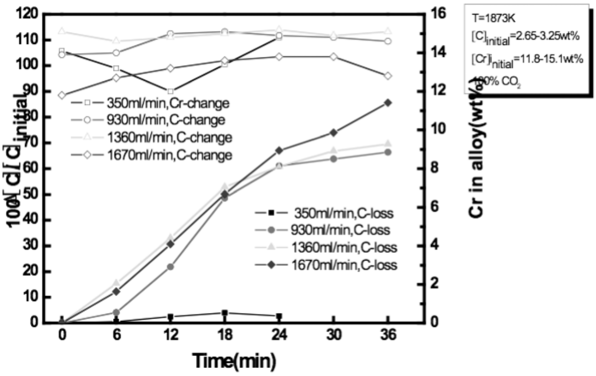

Figure 6: The effect of gas flow rate in Cr-loss and decarburization

As shown in Figure 6, the carbon content does not change when the gas flow rate was 350 ml/min CO_2. But the carbon loss increases sharply, to nearly 80% in 36 mins, as soon as the flow rate was enhanced to 930 ml/min. and is almost independent of the flow rate beyond this. In the present series, a constant flow rate of 1670 ml/min was used for the different gas mixtures. It is to be noted that the Cr-content in the steel does not show any significant change as can be seen in Figure 6.

The Effect of Partial Pressure of O_2 in Cr-loss and Decarburization

The relationship between Cr and C loss with partial pressure of oxygen was investigated and the results are shown in Figure 7.

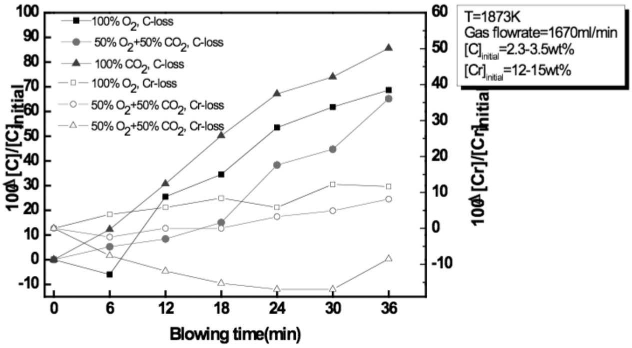

Figure 7: The Cr and C change with different PO_2 in an induction furnace

It can be seen clearly in Figure 7 that the carbon loss was about 70-85% in pure CO_2, pure O_2 as well as the gas mixture with equal amounts of these gases during 36 mins. The decarburization effect with 50% O_2+50% CO_2 is similar to that with pure O_2. In the case of pure CO_2, carbon loss showed a near-linear increase up to about 18 min, beyond which the curve shows a decrease in slope. It is also seen that the decarburization with CO_2 was better than the other two oxidant gases including pure O_2. This positive result of using CO_2 as a decarburizing agent is being examined in further studies.

On the other hand, Cr-loss was higher with O_2 as the oxidant. With 100% CO_2 the Cr content was nearly unchanged up to 36 min, showing thereby the advantage of using CO_2 as the decarburizing agent.

DISCUSSION

The present results, in the case of the experiments with and without slag phase indicate that the use of CO_2 in the decarburizing gas is advantageous with respect to Cr loss. A comparison of the two experimental results is made in Figure 8 with respect to C-loss.

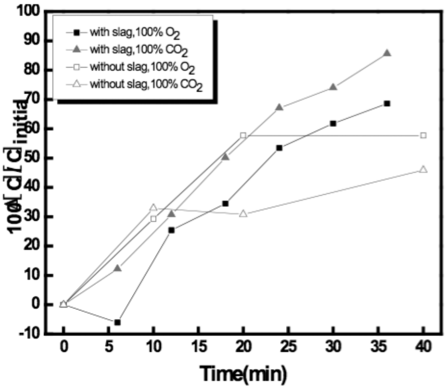

Figure 8: The C-loss in steel with slag on the top and without slag

In the case of the experiments without slag, the decarburization with pure O_2 was rapid during the first 20 min. reaching 60% decarburization beyond which there is practically no decarburization. In the case of pure CO_2, the final decarburization level stops between 30 and 40%. The results of the induction furnace experiments show clearly that decarburization with 100% CO_2 has a high rate and reaches a maximum value of nearly 85%. There is a linear region, indicating chemical reaction, followed by a parabolic region. Strangely, the decarburization with pure oxygen is slower in the initial stages and carbon removal gets accelerated after the first 20 minutes.

In order to examine these differences critically, it is important to look the Cr-loss in both cases. This is presented in Figure 9.

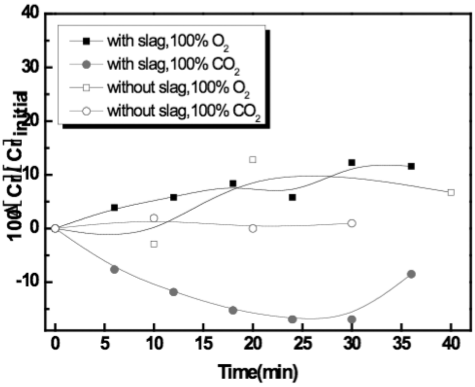

Figure 9: The Cr-loss in steel with slag on the top and without slag

It is seen that Cr losses are significant in the case of the trial with 100% O_2 both with a slag phase involved and without a slag phase. In the other cases, the total Cr loss is negligible. With respect to 100% CO_2 with a slag phase, the Cr loss is negative, which is most probably caused by sampling.

It is admitted that a direct comparison between the two types of experiments is not possible as the conditions in these experiments are different. These can be summarized in Table 3.

Table 3: A comparison of the experimental conditions between the two types of experiments in the present work

Experiments without slag	Experiments with slag
No slag phase	Slag phase
Gas streaming above the sample	Gas injected into the sample
Static experiment	Induction stirring
Diffusion in the melt –main mechanism	Convection -important
Product oxide above molten steel	Slag phase involved in the convective flow
Activity of Cr_2O_3=1*	Activity of $Cr_2O_3 \neq 1$ before saturation*

* The stable oxide was assumed to be Cr_2O_3 due to the oxidation conditions prevailing in the present experiments

However, it is seen in both types of experiments that the introduction of CO_2 as the decarburizer has a positive impact on Cr-loss. The 1 Kg experiments show that CO_2 is effective with respect to decarburization. The activity of Cr_2O_3 may have some importance in altering the driving force towards the oxidation of Cr in the steel. Dong *et al.* [11] have carried out measurements of Cr_2O_3 activities in slags containing $CaO-Al_2O_3-SiO_2$ system at 1873 K using a gas-equilibration technique involving $CO-CO_2-Ar$ gas mixtures. These authors conclude that the activity of Cr_2O_3 tends to show a positive deviation from a Raoultian behavior. This would dampen the driving force for Cr-oxidation to some extent. Beyond the saturation solubility of Chromium oxide, a solid oxide phase might be precipitated.

The slight increase in the Cr-loss seen in Figure 9 around 5 min. could be due to the instantaneous oxidation of Cr from the steel sample by the oxidant gas. The chromium oxide thus formed would subsequently be reduced by the carbon dissolved in the molten steel.

The present results have a strong implication in the manufacture of high alloy steels involving Cr. It is clear that a gas mixture containing a significant amount of CO_2 can be used as a decarburizing agent with advantage. The design of the chemistry of the receptor slag phase is important so that the chromium oxide activity is kept high. Induction stirring appears to help decarburization. This suggests that stirring is important. The formation of 2 molecules of CO would contribute to extra stirring effect. Thus, the present results support a pursual of the deployment of CO_2 as a decarburizer. Implementation in a larger scale unit requires a modeling of the process, taking into account the impact of various process parameters. Such a modelling effort is currently pursued in the present laboratory.

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