Decarburization of ferrochrome and high alloy steels with optimized gas and slag phases towards improved Cr retention

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Abstract: Chromium is a high value metal and the retention of the same during the refining of high carbon ferrochrome as well as high alloy steel has significant economic and environmental impacts. The loss of chromium during the decarburization is generally minimized using argon-oxygen mixtures thereby reducing the oxygen partial pressure (P_{O2}) of the oxidant gas. In the current study, experiments were carried out in an induction furnace and CO_2 was introduced with the view to partly reduce P_{O2} and partly as an oxidizer. During these experiments, the decarburization of molten Cr-alloy was conducted using pure O_2, pure CO_2 or O_2+CO_2 mixtures.

The results demonstrated that the Cr loss can be minimized under CO_2 introduction. The kinetic analysis showed that the mass transfer is effective due to the production of 2CO gas molecules from one CO_2 molecule during the reaction which will improve the stirring of the bath. Besides, CO_2 reacts with carbon in melt is an endothermic reaction, introduction of CO_2 could be a cooler during the refining process, hence the temperature could be controlled by controlling the diluting gas amount, in this case, the overheat of bath refractory could be prevented and the lifetime of refractory could be extended.

Keywords: CO_2, Cr retention, partial pressure, decarburization, temperature control

1. Introduction

Traditionally, O_2 is selected as an oxidizer for decarburization in ferrochrome refining process and also Electric Arc Furnace (EAF) process. However, as reported by earlier researchers, it is realizable to decarburize with CO_2 as well. The principle of decarburization of Fe-C melts using CO_2 has been expounded by Mannion and Fruehan [1]. Their results showed that nearly one-fifth of CO_2 supplied was consumed during the decarburization reaction. Zughbi [2] reported higher decarburization rate and more vigorous reaction when O_2 was used as the oxidizing gas instead of CO_2. Sain and Belton [3] have studied the decarburization of liquid iron by CO_2 at great length. CO_2 was also introduced into the argon-oxygen refining process by Heise et al.[4]. It is reported that the carbon removal efficiency in argon-oxygen decarburization process (AOD) was improved by using CO_2 in argon-oxygen mixtures. Some authors [5-8] also carried out the study on the surface decarburization of Fe-Cr-C melts. Besides this, there are some researchers who investigated as to how to reduce the Cr loss during ferrochrome refining and also the high alloy steel making process. AOD as a traditional and effective way is being used widely in the world. Steam (H_2O) is another profitable alternative for Cr retention

during AOD process according to UHT's (Uvån Hagfors Teknologi AB, Sweden) references and experience through its CLU technology [9,10]. To the knowledge of the present authors, no systematic investigation has been carried out with respect to the simultaneous decarburization and Cr-loss in Fe-Cr-C melts with introduction of CO_2.

In the present study, the Cr retention during M-LCFeCr making process and high alloy steel making process is investigated with introducing CO_2 in the gas system.

2. Theoretical analysis

The order of oxidation ability for O_2, CO_2 and $\underline{O}$ in Fe-C melts is shown in Table 1. The overall chemical reaction of decarburization with CO_2 can be described by equation (1). In the present calculations, $w[i] = 1\%$ (Henrian) was chosen as the standard state of $\underline{C}$ and $\underline{O}$.

Table 1 The oxidation ability for O_2, CO_2 and $\underline{O}$.

Reactions	No.	$\Delta_r G^0 = \Delta H^0 - T\Delta S^0$	ΔG^0, J/mol (1873K)
$\underline{C} + \frac{1}{2}O_2(g) = CO(g)$	(1)	$\Delta_r G^0 = -138905 - 41.63T$ Weak exothermic	-216697
$\underline{C} + CO_2(g) = 2CO(g)$	(2)	$\Delta_r G^0 = 140170 - 125.6T$ Weak endothermic	-97909
$\underline{C} + \underline{O} = CO(g)$	(3)	$\Delta_r G^0 = -21755 - 38.74T$ Weak exothermic	-94082
$2\underline{Cr} + \frac{3}{2}O_2(g) = Cr_2O_3(s)$	(4)	$\Delta_r G^0 = -1170480 + 350.41T$ Strong exothermic	-514162
$2\underline{Cr} + 3CO_2(g) = Cr_2O_3(s) + 3CO(g)$	(5)	$\Delta_r G^0 = -321505 + 97.47T$ Weak exothermic	-138944

It is seen in Table 1 that CO_2 is a weaker oxidizing agent compared to O_2. From a thermodynamic point of view, it is possible to use CO_2 as an oxidizer for decarburization, realizing that Cr will also be oxidized by CO_2 during this process from reaction (5). One point to be noticed is that reactions (1), (3), (4) and (5) are exothermic while reaction (2) is an endothermic reaction. With mixing CO_2 in the gas system, the temperature of the bath could be decreased and also controlled in some extent.

Except for the possibility to use CO_2 as a decarburizer, the Cr retention during the decarburization process needs to be considered as well. It is also well known that, in order to prevent Cr in the molten metal phase from oxidation, at the same time decarburization, reaction (6) given below should be prevented. This can be illustrated by introducing the parameter, referred to in the present work as the 'critical temperature Tc' for $\underline{Cr}$ and $\underline{C}$. Critical temperature is the temperature at which $\Delta_r G_6 = 0$.

$$3CO(g)+2\underline{Cr}=Cr_2O_3(s)+3\underline{C} \tag{6}$$

The standard states of $\underline{Cr}$ and $\underline{C}$ were chosen as w[i] = 1% (Henrian). In the case of Cr_2O_3 in the slag, pure substance standard state was taken. The standard state of 1 atm was for CO. $\Delta_r G^0$ of equation (6) is given by equation (7).

$$\Delta_r G_6^0 = -748740 + 476.68T \, (J/mol) \tag{7}$$

Assuming that the activity of (Cr_2O_3) is 1 (precipitated as pure Cr_2O_3, without considering the dissolution in the slag phase,

$$\Delta_r G_6 = \Delta_r G_6^0 + RT \ln \frac{a_C^3 \cdot a_{(Cr_2O_3)}}{a_{Cr}^2 \cdot (p_{CO}/p^\theta)^3} = \Delta_r G_6^0 + RT \ln \frac{f_C^3 \cdot \omega[C]_\%^3}{f_{Cr}^2 \cdot \omega[Cr]_\%^2 \cdot (p_{CO}/p^\theta)^3} \tag{8}$$

where, a refers to thermodynamic activities and f refers to Henrian activity coefficients; p_{CO} is the pressure of CO gas and p^θ refers to total pressure.

Here,

$$\log_{10} f_c = e_C^C \cdot \omega[C]_\% + e_C^{Cr} \cdot \omega[Cr]_\% \tag{9}$$

$$\log_{10} f_{Cr} = e_{Cr}^{Cr} \cdot \omega[Cr]_\% + e_{Cr}^C \cdot \omega[C]_\% \tag{10}$$

The interaction parameter values of $e_C^C, e_C^{Cr}, e_{Cr}^C$ and e_{Cr}^{Cr} can be obtained from literatures [11, 12, 13].

The value of the Gibbs energy change for reaction (6) thus is given by:

$$\Delta_r G_6 = -748740 + 476.68T + 19.14T \left\{ \begin{array}{l} 0.66\omega[C]_\% - 0.0714\omega[Cr]_\% + 3\lg\omega[C]_\% \\ -2\lg\omega[Cr]_\% - 3\lg(p_{CO}/p^\theta) \end{array} \right\} \tag{11}$$

The critical temperature T_c was calculated at different situations and the result is presented in Table 2. Cr can be kept in the metal bath only if the temperature of the melt exceeds T_c. This indicates that a lower value of T_c is better for the retention of Cr if the bath temperature is constant.

Table 2 The critical temperature T_C for different [C] and [Cr].

No.	Composition of steel		PCO /Pa	$\Delta_r G_6 (J/mol)$ $\Delta_r G_6^0 = -748740 + 476.68T (J/mol)$	T_c /K
	ω[C]%	ω[Cr]%			
1	3.5	15	101325	$-748740 + 486.61T$	1538

2	2.5	15	101325	$-748740 + 465.52T$	1608
3	1.5	15	101325	$-748740 + 440.22T$	1701
4	0.5	15	101325	$-748740 + 400.19T$	1871
5	3.5	18	101325	$-748740 + 479.49T$	1561
6	3.5	12	101325	$-748740 + 494.39T$	1514
7	3.5	9	101325	$-748740 + 503.30T$	1487

Fig. 1 illustrates the variation of T_c with respect to Cr and C contents. From this figure, it can be seen clearly that Tc increases with the increasing of Cr content when C content is a constant. Further, Tc decreases with the increasing of C content when Cr content is stable. Thus, if the temperature of the melt is kept constant, Cr-loss will increase with the progress of decarburization. Or in case the temperature is kept constant, if the partial pressure of CO is decreased, the Cr will be kept in the melt and the C will be removed. To realize decrease p_{CO}, dilute gas such as Ar could be used (the principle to AOD process) from the thermodynamics point of view. Besides thermodynamic aspects, kinetic aspects should also need to be considered. Ar introduction could increase the stirring of the bath, hence increase the contact between carbon and Cr_2O_3 that eventually is oxidized, thereby restoring the Cr back to the melt. In the present study, CO_2 was used as the stirring gas. It should be noted that the activity of Cr_2O_3 was assumed to be unity in the above calculations. If the activity of chromium oxide is decreased due to the dissolution in the slag, chromium oxidation will be favored.
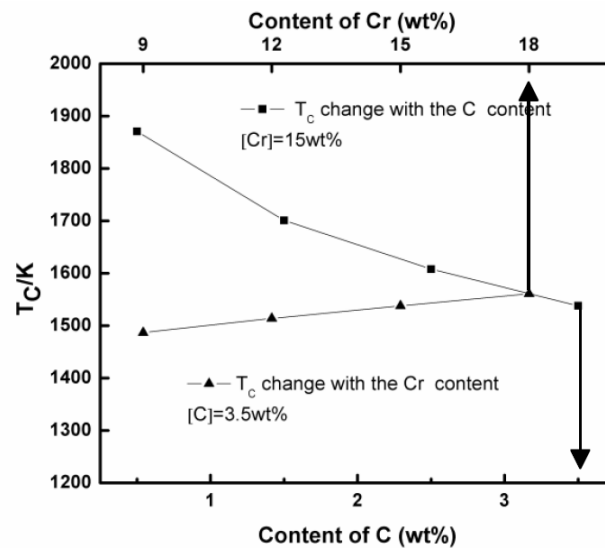

Fig. 1 The effect of C and Cr contents on Tc.

Another aspect to be considered with respect to the reduction of Cr_2O_3 formed by the carbon dissolved in the steel is the formation of 3 molecules of CO gas according to reaction (12):

$$Cr_2O_3(s) + 3\underline{C} = 3CO(g) + 2\underline{Cr} \qquad (12)$$

$$(FeO)(l) + \underline{C} = \underline{Fe} + CO(g) \qquad (13)$$

The formation of 3 molecules of CO by the reduction of Cr_2O_3 in the melt is similar to the oxidation of Cr in the melt as represented by reaction (5). The CO gas bubbles thus formed either by reaction (5) or by reaction (12) will not further react with the components in the metal bath.

One of the significant differences between O_2 and CO_2 injections is 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. Accordingly, in order to achieve the same metal composition at the end of the blowing, one needs to blow twice the amount of CO_2 compared to O_2. It may be also noted that for every CO_2 bubble injection, two CO bubbles are formed; the number of CO bubbles will be twice that corresponding to O_2 injection. This can facilitate good mixing between metal and slag phases leading subsequently towards a near-equilibrium situation, corresponding to equations (12) and (13).

In the above considerations, the temperature of the metal bath was assumed to be constant. In reality, decarburization with O_2 injection (reaction (1)) would be exothermic while, reaction (2) will be endothermic. Thus, decarburization with CO_2 would require additional energy input in order to keep the temperature of the metal bath constant.

For refining of ferrochrome or high alloy steel, the temperature must be controlled during decarburization period, to ensure that it is neither too low to lead Cr oxidized strongly nor too high to lead furnace lining damaged. The real production experience showed that the temperature around 1700℃ is optimum according to Rick [14], and this temperature is normally used in high alloy steel refining as well as HCFeCr refining.

3. Experiment

A series of experiments were carried out in an induction furnace with samples masses of 1kg metal and with a slag phase above. The schematic diagram of experimental set-up is illustrated in Fig.2.
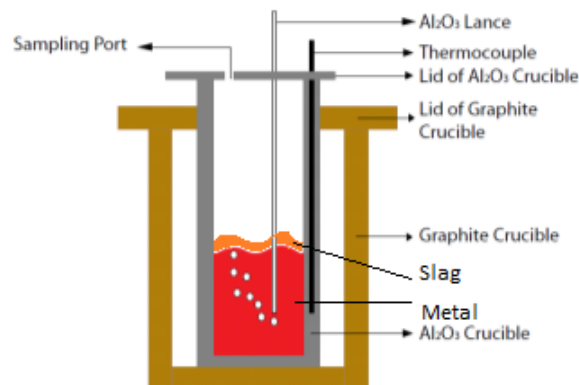

Fig.2 A schematic drawing of the induction furnace

An Al_2O_3 crucible of 45mm I.D. and 130mm in height was adopted in the experiment to carry metal and slag samples and it was positioned inside an outer graphite crucible and heated in an induction furnace. The decarburizing gas was blown into the liquid melt through an alumina lance from the melt top and lance was immersed in the melt during experiment.

Synthetic slag with the composition: CaO 40 mass%, MgO 10 mass%, SiO_2 40 mass%, Al_2O_3 10 mass% was used to cover the metal. The slag composition corresponds to Al_2O_3 saturation so that composition changes due to crucible dissolving in the slag could be avoided. The crucible was specially designed and produced in the present laboratory. A Pt.30% Rh – Pt. 6%Rh thermocouple was place inside the wall of the crucible with the aim to monitor the temperature of the melt accurately. The crucibles were preheated in a furnace at 573 K overnight in order to remove adsorbed moisture and then preheated to 1273 K in a muffle furnace at a heating rate of 3 K/min.

The slag sample was melted at 1773 K in an induction furnace. The amount of slag added was approximately 5% of the metal mass. The "mother alloy" was produced in significant amounts by pre-melting alloy mixture of targeted composition in an induction furnace in order to get homogenous alloy. It was then cut into even pieces of 1 kg and was used in each experiment.

During the decarburization running, Ar atmosphere was introduced during the melting of the steel. After totally melted, oxidant gas was blown into the liquid metal at 1873K. Samples of the steel melt were taken at appropriate time intervals using quartz sampler tubes of I.D. 6mm and quenched in cold water. The samples were analyzed to obtain carbon and chromium compositions.

4. Results and Discussions

Table 3 presents a selected part of the results from the significant number of experiments carried out in the present work. The initial carbon contents of FeCr alloy are selected as 0.3mass% and 3.0 mass%, and the results obtained are presented in this table. Only pure O_2 and pure CO_2 were tested in current experiments. The experiments were carried out in two different scales, one with 500g materials and the other with1000g materials, both at 1873K.

Table 3 The Cr and C change during refining process

Time	1600℃, 100%O_2, 500g steel 900ml/min gas		1600℃, 100%CO_2, 500g steel 900ml/min gas		Time	1600℃, 100%O_2,1000kg steel 1360ml/min gas		1600℃, 100%CO_2,1000g steel 1360ml/min gas	
	C(mass%)	Cr(mass%)	C(mass%)	Cr(mass%)		C(mass%)	Cr(mass%)	C(mass%)	Cr(mass%)
0 min	0.257	11.1	0.290	10.3	0min	3.02	14.6	2.99	15.1
3.5 min	0.188	10.5	0.283	9.6	6min	2.96	14.9	2.53	14.6
7 min	0.134	9.2	0.253	8.5	12 min	2.90	14.5	2.00	14.8

10.5 min	0.078	7.9	0.224	8.1	18 min	2.75	13.7	1.41	15.0
14min	0.053	6.8	0.183	7.8	24 min	2.55	13.1	1.17	15.2
17.5min	0.030	3.3	0.161	7.6	30 min	1.74	13.8	0.99	14.9
21 min	-	-	0.145	6.8	36 min	1.31	13.5	0.91	15.1

4.1 The relationship between C and Cr content during the refining process
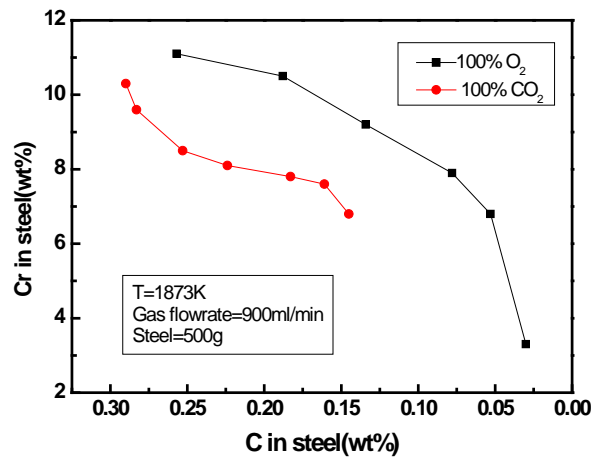
Fig.3 The relationship between Cr and C during refining process with the initial carbon content at 0.3wt%

It is illustrated clearly in Fig.3 that, the rate for Cr loss with decarburization process while blowing pure O_2 is slightly larger than that blowing pure CO_2, when the initial carbon content in the melt was 0.3wt%. This indicates that CO_2 may have superiority in Cr retention. However, comparing the slopes of those above curves starting from carbon 0.3wt% to 0.15wt%, there are very similar. Hence, the CO_2 introduction seems have no impacts on Cr saving during low carbon level. This needs future investigation.
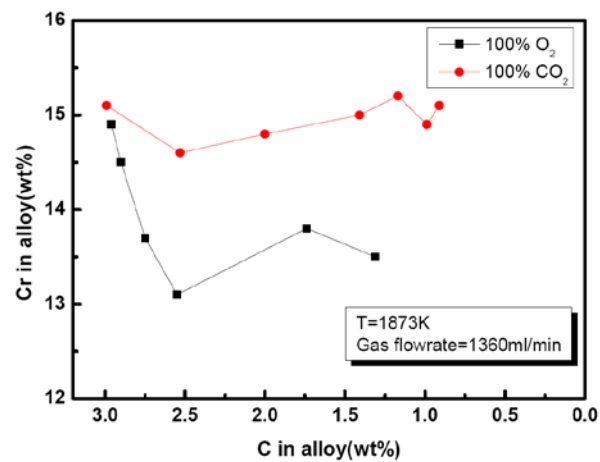

Fig. 4 The relationship between Cr and C during refining process with the initial carbon content at 3.0wt%

It is seen in Fig.4 that, when blowing pure CO_2, the Cr content almost kept constant during decarbuzaiton, while with oxygen blowing, the Cr loss is maximum 2%, with high initial carbon content (approximately 3.0wt%). That indicates the advantage to use CO_2 for Cr retention, especially with high initial carbon content melt. That indicates CO_2 may have big advantages for decarburization of high carbon ferrochrome (HCFeCr) to make medium carbon ferrochrome (MCFeCr) or low carbon ferrochrome (LCFeCr) in ferroalloy industry.

4.2 The effect of CO_2 in Cr- retention at low initial carbon content

The same initial C content was taken to investigate the Cr loss in pure O_2 and CO_2 at low carbon contant (around 0.25%). For $100\%O_2$, the initial steel composition was C:0.257wt%,Cr,11.1wt%; for $100\%CO_2$, the initial composition of steel was C:0.253wt%,Cr,8.5wt%.The Cr-loss in these two situations is shown in Fig.5.
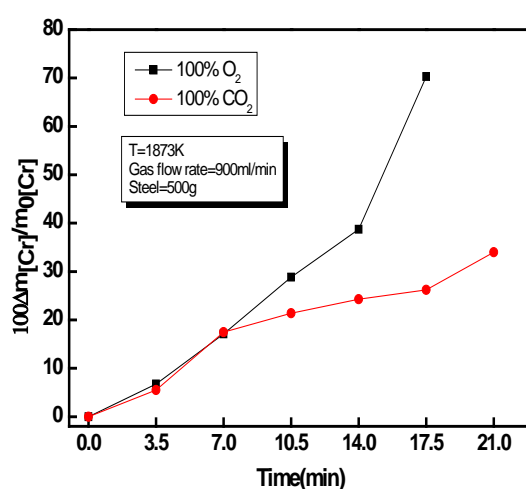

Fig.5 The Cr-loss during refining when blowing pure O_2 and pure CO_2

It is obvious that the Cr-loss rate in $100\%O_2$ and $100\%CO_2$ is almost the same at the beginning 7 mins. But with the progress of refining, Cr-loss rate with blowing $100\%CO_2$ is less than that blowing $100\%O_2$. The maximum Cr-loss with blowing $100\%CO_2$ is about 30% at 17.5min, at the same time, blowing $100\%O_2$, the Cr-loss even reach 75%, which is more than twice that of blowing $100\%CO_2$. This indicates that, O_2 oxidation ability is stronger than CO_2. And if one considers both decarburization and Cr-oxidation, Fig.6 may illustrate clearly.

It can be found, the decarburization rate by blowing O_2 is about twice of that blowing pure CO_2 during 3.5min to 14min. while the rates in both cases are fairly constant after about 3.5 min. With respect to Cr-loss rate, the rate with blowing pure O_2 is about 1.6 times that of blowing pure CO_2 when the gas was injected into the bath for 3.5min.With the progress, rate of blowing pure O_2 is seen to increase sharply even over 1.4g/min, but the Cr-loss rate is almost constant at about 0.5g/min. This would imply that when blowing CO_2, the Cr-loss is around 1/3 of the value corresponding to O_2 blowing. However, the decarburization rate with O_2 is just around 2 times of that with CO_2. That indicates CO_2 is good for keeping Cr inside the steel for the same decarburization level.
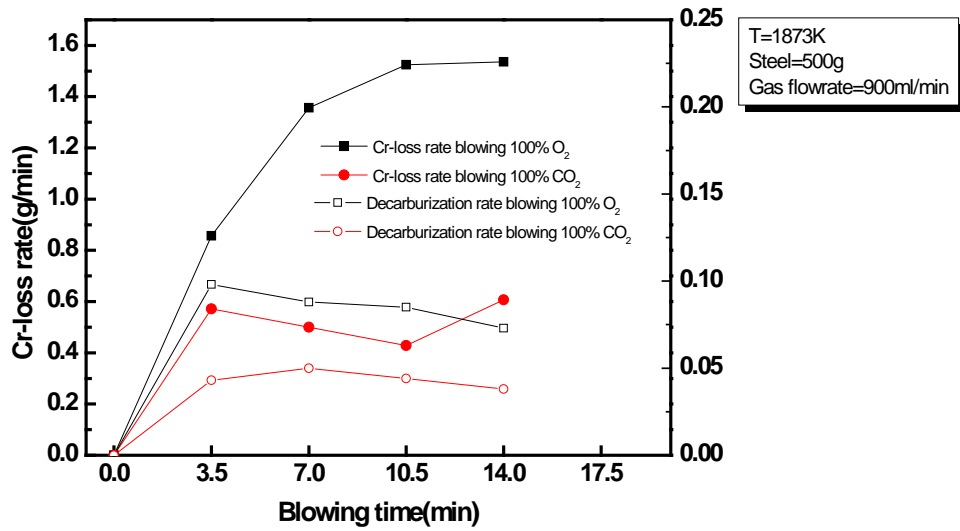
Fig.6 The decarburization rate and Cr-loss rate when blowing pure O_2 and pure CO_2

4.3 The utilization ratio of O_2 and CO_2 in decarburization process

For blowing CO_2, the effective part which is used in decarburization and Cr oxidation is O, as shown in equation (14). Hence, for blowing pure CO_2, the effective part of CO_2 (CO_2 can be calculated as $\frac{1}{2}O_2$) was taken to plot. The amount of effective part of gas (O_2) react with metal was calculated and plotted in Fig.7 and Fig.8 for two different initial carbon content melts.

$$CO_{2(ads)} \rightarrow CO_{(ads)} + O_{(ads)} \tag{14}$$
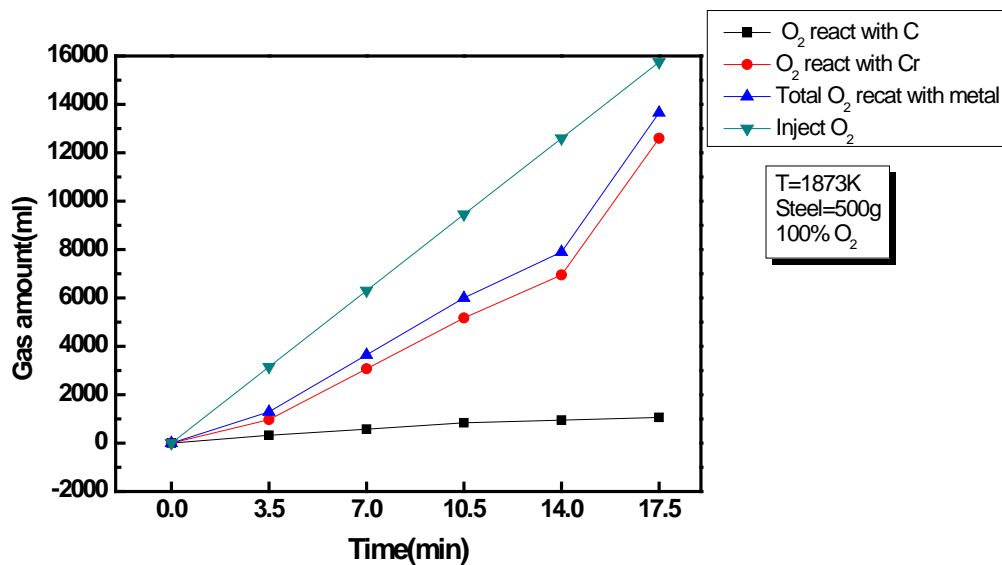
Fig.7(a) The O_2 amount reacting with alloy when blowing 900ml/min O_2 in 17.5 min (Initial C,0.26%,Cr,11.1%; Final ,C,0.03%,Cr,3.3%)
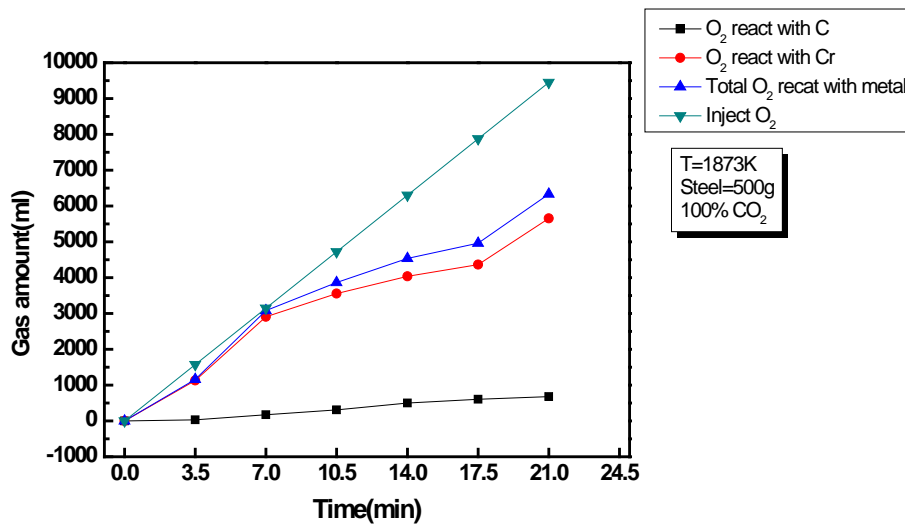
Fig.7(b) The O_2 amount reacting with alloy when blowing 900ml/min CO_2 in 21min (Initial C,0.29%,Cr,10.3%;Final,C,0.145%,Cr,16.8%)

It is seen that, at low initial carbon contents, most of the O_2 and CO_2 are used for oxidizing Cr and just a minor part of the injected gas is used for oxidizing C. This indicates that, for low carbon melt, Cr loss is strong. However, if consider the overall gas utilization (effective parts used for reaction), the utilization ratio of CO_2 is more than O_2, especially in the first 7.0min, almost all the effective part of CO_2 is used for oxidizing C and Cr, but just half of O_2 is used for C and Cr oxidation, the rest may have been used for oxidizing Fe or escaped unreacted.

For high initial carbon content, the utilization of gas is also investigated and illustrated in the following figures.
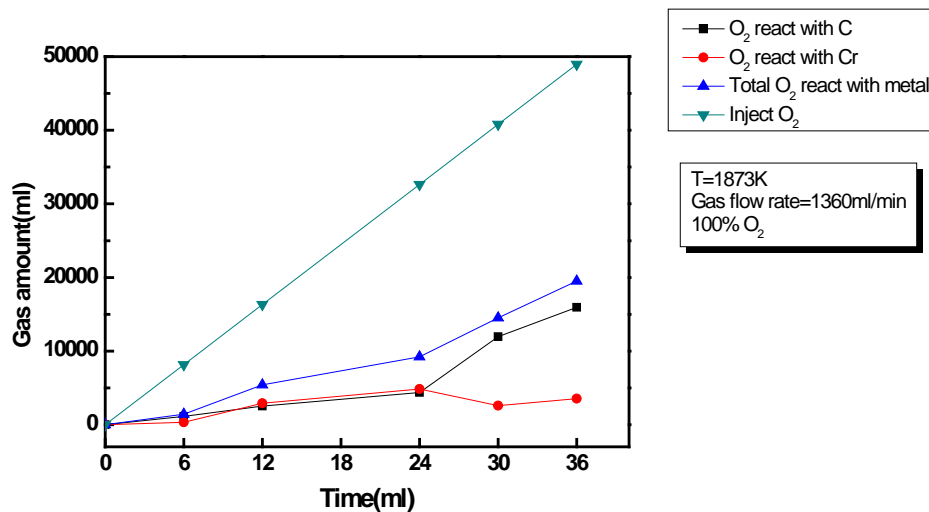

Fig.8(a) The O_2 amount reacting with alloy when blowing 1360ml/min O_2 in 36 min (Initial C,3.02%,Cr,14.6%; Final,C,1.31%,Cr,13.5%)
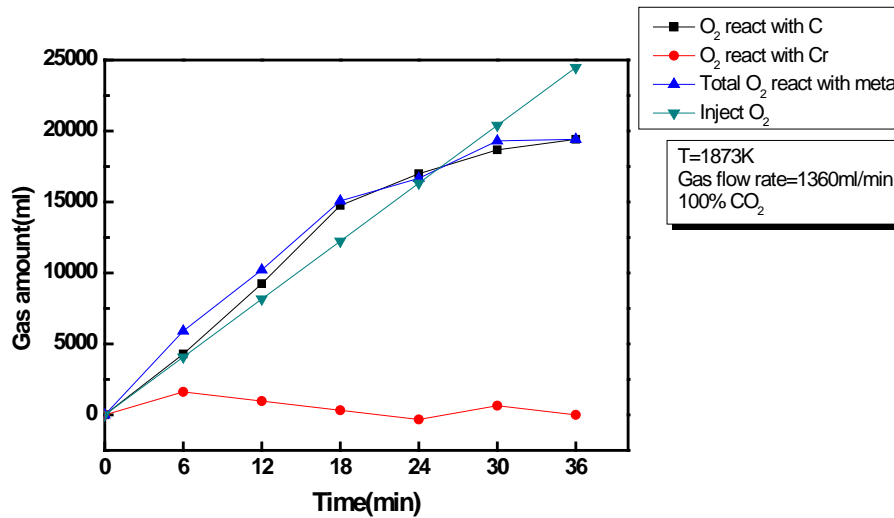
Fig.8(b) The O_2 amount reacting with alloy when blowing 1360ml/min CO_2 in 36 min (Initial C,2.99%,Cr,15.1%; Final,C,0.91%,Cr,15.1%)

The overall utilization of the gases at high initial carbon content shown in Fig. 8(a) and Fig.8(b), is similar to that decarburization of low initial carbon content. The effective part of pure O_2 used for reacting with Cr and C is just half the gas, the rest is oxidizing Fe or just flows away, however, for pure CO_2, almost 100% of the effective gas is used for Cr and C reaction, in this case, around 100% CO_2 is used for decarburization since Cr is almost not oxidized. It is also seen in above figures that, at high initial carbon content, most of the gas is used for oxidizing C and only a minor part is used for oxidizing Cr for both two gas cases. However, for blowing pure O_2, at the beginning 24mins, the gas amount to react with Cr and C are very similar, but for blowing pure CO_2, the gas amount oxidizing C is much larger than that reacts with Cr, which indicates that CO_2 is much more effective in decarburization at high initial carbon content, and also efficient for Cr retention.

5. Conclusions

1) The experimental result shows that CO_2 is effective for Cr retention, especially for high initial carbon content situation. CO_2 can be as diluting gas to reduce partial pressure of oxygen. The endothermicity of the Boudouard reaction can be advantageously used to control the bath and control temperature, which would extend the refractory life.

2) For low initial carbon content, the overall utilization ratio of CO_2 is higher than O_2, especially at the initial stage of decarburization, almost all the effective part of CO_2 is used for oxidizing C and Cr, on the other hand, for O_2 as decarburizer, approximate half of O_2 is used for C and Cr oxidation.

3) For high initial carbon content, CO_2 could be an effective diluting gas for decarburization, since in this situation, CO_2 is very effective for decarburization. At lower initial carbon content, the superiority of CO_2 for decarburization and Cr retention is not obvious.

6. Future work

1) The slag now used is synthesized in order to protect the Al_2O_3 crucibles, however, in the real production, MgO or MgO-Cr_2O_3 lining are normally used in FeCr refining process and high alloy steel refining process. Hence, the slag composition is different and needs to be optimized so that the activity of the oxidation product, viz. Cr_2O_3 would be high in the slag phase. In this case, Cr loss could be reduced.

2) Based on positive results obtained now, pilot plant trials are currently being planned at Uddeholms AB, Hagfors, Sweden. In order to maximize decarburization, a computer program based on a kinetic model was developed as part of this work. This is being adopted to control the gas composition and flow rate. The program will also take into account the extra energy need in the process in view of the endothermicity of the above reaction, by controlling the ratio of O_2+CO_2. This also would enable the prevention of overheating and would have a positive impact on the refractory life. These trials are expected to be followed by plant trials at Uddeholms AB, where the process is expected to be implemented.

3) For high carbon ferrochrome refining, the use of CO_2 as a decarburizer needs to be future-investigated. The current results show that CO_2 is more efficient at higher carbon content. For high carbon ferrochrome, the carbon content is around 7wt%, hence the decarburization with CO_2 appears to be promising

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