EVALUATION ON HEAT AND MATERIALS BALANCE OF CO_2 INVOLVED IN CONVERTER PROCESS FOR M-LCFECR PRODUCTION

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ABSTRACT

During the production of Medium-Low Carbon Ferrochromium (M-LCFeCr) or Medium-Low Carbon Ferro-manganese (M-LCFeMn) in converter process with introduction of oxygen, the oxidation reactions of main and tramp elements by oxygen are all exothermic reactions, hence lead to energy surplus in the production process.

Essentially there are three practical strategies to deal with energy surplus:

- *Dilute the surplus energy by adding coolants.*
- *Remove the surplus energy by blowing inert gases (like argon).*
- *Neutralize the surplus energy by injecting part CO_2.*

The first method is used frequently nowadays, but the additional coolants including silicochromium and M-LCFeCr are costly and cause the temperature variation in a wide margin. The second way is not cost effective to remove small amount of heat by introducing the expensive argon. The last method could be moderate and worth to study. CO_2 introduction is aimed to realize controlling the bath temperature flexibly because $C+CO_2=2CO$ is an endothermic reaction, enhancing the yield of Cr (Mn) because of its weaker oxidation ability, prolonging the life time of the converter lining because of less thermal shock. However, those advantages need to be proved by theoretical and experimental work. The heat and material balance calculation can provide a theoretical basis for the production practice with introduction of CO_2 in converter process. The authors pay attention to this aspect with the aim to optimize the amount of CO_2 and the materials requirements. The optimal ratio of CO_2 and O_2 for producing M-LCFeCr and M-LCFeMn with different carbon content has been determined.

KEYWORDS: *Heat and Materials Balance, CO_2, Converter, M-LCFeCr*

1. INTRODUCTION

The argon-oxygen-decarburization (AOD) process is a common metallurgical treatment to decarburize by using oxygen and insert gas injection through bottom tuyeres and a top-lance. AOD converters are characterized by a fast and efficient decarburization[1]. Compared with electro-silicothermic process, the heat required for the smelting process during the AOD process mainly comes from the reactions between O_2 and elements in the melt, such as C, Si, Fe, without additional electric energy or fuel. Therefore, it is an economical way to produce M-LCFeCr and M-LCFeMn. However, there are many problems to produce M-LCFeCr and M-LCFeMn with the AOD process. When O_2 is injected into the bath, elements in the melt will react with O_2, and release a large number of heat, which is far more than the heat required for smelting M-LCFeCr or M-LCFeMn. The surplus energy will lead to the increase of bath temperature and accelerate the erosion of refractory[2,3]. The present authors[4,5] found it is feasible to control the bath temperature with introduction of CO_2 through the earlier experiments. It was also showed that CO_2 had a high efficiency for decarburization, especially at high initial carbon content. Many researchers have studied the application of CO_2 in the field of metallurgy. Yin[6,7] had studied the theoretical temperature change with different proportion of CO_2 injection at the fire district and pointed out that the theoretical temperature decrease with the proportion of CO_2 increase, which can enhance the yield of metal, so as to reduce the amount of dust during the steel-making process. Zhu and Wei[8,9] had researched the decarburization during the refining process of stainless steel and set up a mathematical modeling of the argon-oxygen decarburization. The results such as temperature and carbon content obtained through this mathematical model could be in good agreement with the real production based on a few assumptions.

Based on the positive results obtained from the experiments and the lack of energy data of CO_2 introduction during AOD process, it is essential to make an estimation of heat and material balance with introduction of CO_2, and find out the optimized CO_2 amount as well as the corresponding material input. This work has been presented in this paper.

2. THERMODYNAMIC ANALYSIS

It should be noted that carbon dioxide is a weaker oxidizing agent compared with oxygen during the steelmaking process, which had been proved by Zughbi[10]. But it can react with C, Fe, Si, Cr and some other elements under the smelting temperature of ferrochrome. The thermodynamic data of interrelated chemical reactions[11,12] are shown in Table 1 and the relationship between Standard Gibbs free energy and the temperature can also be found. The standard state of [C], [Fe], [Si] and [Cr] is chosen as [%i] =1 (Henrian), and the standard state of the composition of slag such as (FeO), (SiO_2), (Cr_2O_3) is used as the pure substance. The standard state of O_2, CO and CO_2 is 1 atm.

Table 1: The thermodynamics data of interrelated chemical reactions

reactant	Chemical reaction	$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$/(J.mol^{-1})	No.
CO_2	$CO_2(g) + [C] = 2CO(g)$	$\Delta G^\theta = 34580 - 30.95T$	1
	$CO_2(g) + [Fe] = (FeO) + CO(g)$	$\Delta G^\theta = 11880 - 9.92T$	2
	$2CO_2(g) + [Si] = (SiO_2) + 2CO(g)$	$\Delta G^\theta = -3577967 + 357.27T$	3
	$2[Cr] + 3CO_2(g) = (Cr_2O_3) + 3CO(g)$	$\Delta G^\theta = -321505 + 97.47T$	4
O_2	$1/2\, O_2(g) + [C] = CO(g)$	$\Delta G^\theta = -22219.35 - 91.84T$	5
	$O_2(g) + [C] = CO_2(g)$	$\Delta G^\theta = -166666.534 - 40.8T$	6
	$1/2\, O_2(g) + [Fe] = (FeO)$	$\Delta G^\theta = -459400 + 87.45T$	7
	$O_2(g) + [Si] = (SiO_2)$	$\Delta G^\theta = -866510 + 152.3T$	8
	$4[Cr] + 3O_2(g) = 2(Cr_2O_3)$	$\Delta G^\theta = -2064712 + 510.87T$	9

It can be seen from table 1 that the reactions between O_2 and other elements are exothermic. However, the reactions between CO_2 and C or Fe are endothermic. Although the reactions between CO_2 and Si or Fe are exothermic, the heat output is much smaller compared with O_2 injection. Therefore, the bath temperature could be controlled if the ratio of O_2 and CO_2 was appropriate, so as to enhance the lifetime of converter lining. The coolant is not necessary when CO_2 is available, which can reduce the cost.

3. CALCULATION BASIS

In the AOD process, around 55-60% of the total energy is generated from oxidation of elements, such as carbon, silicon, chromium and iron. And 40-45%of the heat comes from the hot metal. Around 40% of the total energy is retained in the liquid metal, and 17% of the heat contains in slag. While the rest is lost to waste gas, the storage of the lining and cooling, as shown in Figure 1.

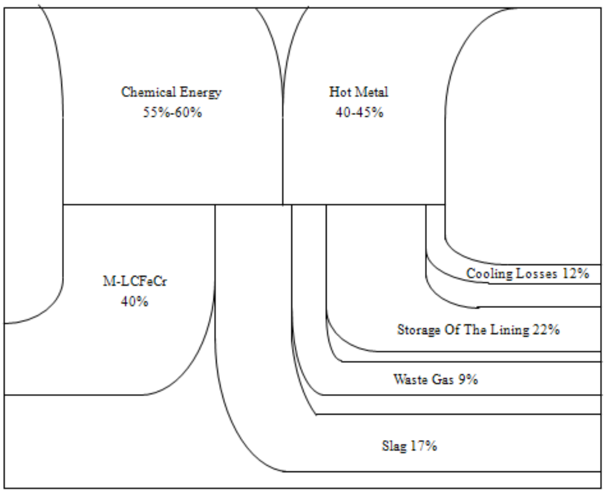

Figure 1: Energy patterns in AOD process

It is easy to determine the total energy input into an AOD converter because energy is supplied to AOD through two ways: the energy of the hot metal and the oxidation of elements, like C, Si, Al, Fe, Cr, and Mn. But the oxidation energy contribution is not only dependent on the oxygen input but also on the chemical composition of the High Carbon Ferromanganese (HCFeCr) and slag.

Before carrying out the calculation, the input and output parameters in the system should be defined in the program. In the present case, all input and output parameters are defined and set according to the practical production parameters. And in the present study on heat and materials balance in AOD process with introducing CO_2 gas, the raw materials consumption and the effect of process parameters, like gas (here CO_2 is replacing partial O_2), HCFeCr (HCFeMn) and slag agent consumption et al. are shown in Figure 2.

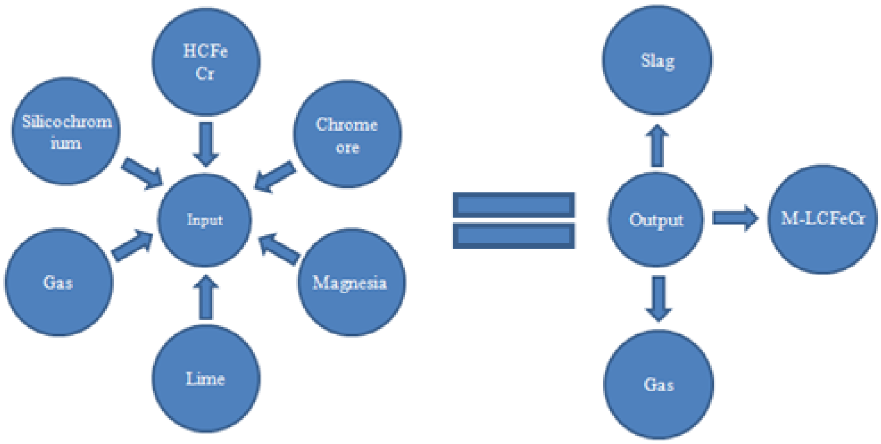

Figure 2: Parameters set on materials balance calculation

4. RESULTS AND DISCUSSIONS

As discussed in chapter 3, CO_2 introduction is an endothermic reaction, which indicates that, the energy surplus can be consumed with the aim to keep the temperature constant. Heat and materials balance with introduce of CO_2 were calculated with different amounts of CO_2. And the results are presented as following.

4.1 The appropriate smelting temperature of different ferrochrome productions

The main task of AOD process for M-LCFeCr is to reduce the carbon content in the melt by blowing oxygen. The main decarburization reaction in the melt has been shown as Equation 10.

$$(Cr_2O_3) + [C] = \frac{2}{3}[Cr] + CO(g) \qquad \Delta F^{\theta} = 60200 - 38.15T \qquad (10)$$

Here, the standard state of (Cr_2O_3) is used as the pure substance. The standard state of CO_2 is 1 atm. And the equilibrium constant of Equation 10 can be described as Equation 11.

$$\log K = \log\frac{a_{Cr}^{\frac{2}{3}}}{a_C} = -\frac{13160}{T} + 8.34 \qquad (11)$$

where: K is the equilibrium constant;

T is the smelting temperature;

a_{Cr} = activity of Cr;

a_C = activity of C.

And it is easy to know that $e_{Cr}^{Cr} = 0.000, e_{Cr}^{C} = -0.100, e_{C}^{C} = 0.220, e_{C}^{Cr} = -0.024$ from literatures[13,14]. The relationship of [Cr], [C] and T can be obtained from above data and Equation 11, and it has been shown as Equation 12.

$$3 * \log[\%C] - 2 * \log[\%Cr] + 0.86 * [\%C] - 0.072 * [\%Cr] = \frac{39486}{T} - 25.02 \qquad (12)$$

From Equation 10, one can see that, with the increase of the bath temperature, the carbon content in the melt decrease, at the same time, the chromium is retained. And the relationship between carbon and chromium at different temperature has been shown in Figure 3[15].

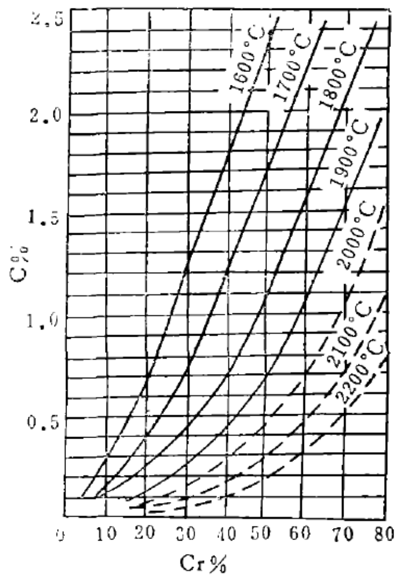

Figure 3: The relationship between carbon and chromium at different temperature

From the Figure 3, one can see that the bath temperature should be 1769℃ if the carbon content is reduce to 2mass% for the production containing 65mass% Cr. Accordingly, the temperature should be 1944℃ if the carbon content is reduce to 1mass%. And the temperature should be 2159℃ if the carbon content is reduce to 0.5mass%. Based on the above discussion, one can see that the suitable smelting temperature varies for different specifications of ferrochrome product. Therefore, it is necessary to calculate the appropriate amount of CO_2 to keep the temperature constant according to different ferrochrome productions.

4.2 The bath temperature change with different CO_2 and O_2 ratio

The parameters for current calculations were taken as following: AOD process for MCFeCr refining, the weight of HCFeCr is 1t, aim C content is 2mass%. The input raw materials include hot metal, chrome ore, magnesia, lime and silicochromium. The compositions of raw materials have been shown in Table 2-6 respectively. The parameters of raw materials during the AOD process have been shown in Table 7. And the compositions of final production and slag are shown in Table 8-9 respectively. The parameters of MCFeCr and slag are shown in Table 10.

Table 2: Compositions of HCFeCr in mass percentage

HCFeCr	Cr	Fe	C	Si	P	S
Mass%	63.00	26.92	7.00	3.00	0.04	0.04

Table 3: Compositions of chrome ore in mass percentage

Chrome ore	Cr_2O_3	FeO	SiO_2	Al_2O_3	MgO	CaO
Mass%	46.88	23.96	5.21	13.54	8.33	2.08

Table 4: Compositions of magnesia in mass percentage

Magnesia	MgO	SiO_2	CaO
Mass%	97.50	1.00	1.50

Table 5: Compositions of lime in mass percentage

Lime	CaO	SiO_2	$CaCO_3$
Mass%	95.00	4.00	1.00

Table 6: Compositions of silicochromium in mass percentage

Silicochromium	Cr	Si	Fe
Mass%	28.28	48.49	23.23

Table 7: Parameters of raw materials during the AOD process

	HCFeCr	Chrome ore	Magnesia	Lime	Silicochromium
Amount/kg	1000.00	50.00	12.00	55.86	50.00
Temperature/℃	1550	25	25	25	25

Table 8: Compositions of final production (MCFeCr) in the percentage

MCFeCr	Cr	Fe	Si	C	S	P
Mass%	66.41	30.50	1.02	2.00	0.04	0.03

Table 9: Compositions of slag in the percentage

Slag	Cr_2O_3	FeO	SiO_2	CaS	$Ca_3(PO_4)_2$	Al_2O_3	MgO	CaO
Mass%	24.27	2.94	41.15	0.02	0.24	2.77	6.48	22.13

Table 10: Parameters of MCFeCr and slag

	MCFeCr	Slag
Amount/kg	932.784	245.057

The bath temperature has been calculated with introduction different O_2 and CO_2 according to the above conditions, and the result is shown in Figure 4.

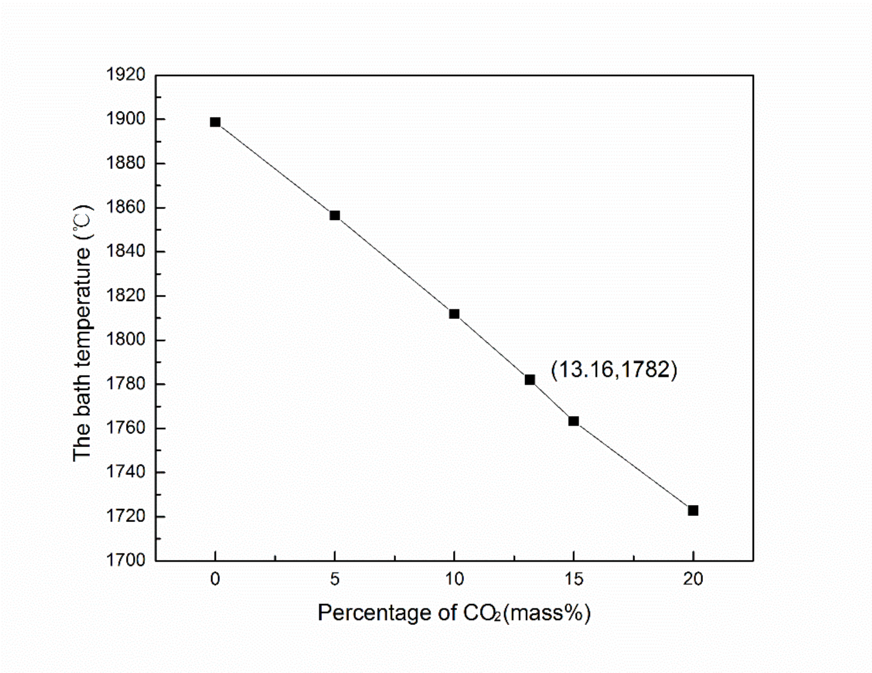

Figure 4: The bath temperature change with increase of CO_2 for different proportioning

It is easy to obtain from Figure 4 that, with the increase of CO_2 addition, for the same melt, the bath temperature is decreased. The melt temperature is about 1900℃ with introduction of pure oxygen. And this temperature is far more than that of ferrochrome, whose aim carbon content is 2mass%. Decarburization with O_2 will increase the temperature in AOD leading to serious damage to the refractory lining of the furnace, which affects the productivity seriously. Meanwhile, too high temperature will cause the "boiling" of slag in the furnace. If part of oxygen is replaced by CO_2 during the refining process, this may reduce the increase of temperature during decarburization. In this case, control the bath temperature, prolonging the lifetime of the furnace lining can be achieved if the ratio of O_2 and CO_2 is appropriate. The slag "boiling" during decarburization would be minimized as well.

4.3 The suitable amount of CO_2 for ferrochrome smelting

The appropriate amount of CO_2 is an important parameter for ferrochrome smelting. If CO_2 ratio is too large, that will cause problem for the ferrochrome refining process since the heat is not sufficient based on the heat balance calculation and analysis. If CO_2 ratio is too small, the energy surplus will lead to the bath overheat and the lining of the furnace could be damaged heavily. For the production of MCFeCr containing 2mass% C and 66.41mass% Cr, the most suitable temperature is 1782℃, which can be calculated by Equation 12. Based on above data, the suitable amount of CO_2 has been calculated and the result is 13.16mass% CO_2 when the total amount of gas is 148.149kg, which can be seen from Figure 4.

6 CONCLUSIONS

Through the present calculation and analysis, one could conclude that:

1) The introduction of CO_2 will consume the surplus energy in the converter which leads to the decrease of the bath temperature. And it is feasible to reduce or avoid the coolant consumption by this way, so as to reduce the production costs.
2) Surplus energy which causes by the reactions of O_2 and C, Cr, Fe can be compensated by introducing CO_2. And the bath temperature increases from 1550℃ to 1900℃ when pure O_2 has been introduced. On the contrary, the temperature can be decreased to a reasonable range when use CO_2 to replace O_2 partly.
3) For producing 2mass% C, 66.41mass% Cr productions, the suitable amount of CO_2 is 13.16mass% when the total amount of gas is 148.149kg. This is because the heat required by the MCFeCr could be satisfied, at the same time, the lining of the furnace could be protected at the maximum extent. Of course, the suitable amount of CO_2 is variable and it is determined by the requirements of raw materials and the final production.

7 FUTURE WORK

CO_2 introduction during AOD process involves complicated physical and chemical reactions, such as Cr-retention, decarburization, dephosphorus, desulphurization, which need to consider both thermodynamic and kinetics aspects. Furthermore, there are many differences between the theory and production practice. Therefore, it is necessary to adjust the ratio of CO_2 and O_2 according to the different smelting environment in order to obtain high-quality L-MCFeCr (M-LCFeMn) and find out the economical way to produce products. Besides, heat and material balance calculations need to be supported by the experimental work, which is planned to carry out in the future.

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