EPD Congress 2016
Edited by: Antoine Allanore, Laura Bartlett, Cong Wang, Lifeng Zhang, and Jonghyun Lee
TMS (The Minerals, Metals & Materials Society), 2016

THE COOLING ABILITY STUDY ON CO_2 AND O_2 MIXED INJECTION IN VANADIUM EXTRACTION PROCESS

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Keywords: Vanadium extraction, O_2-N_2 Mixed injection, O_2-CO_2 Mixed injection, CO_2 cooling ability

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Abstract

Carbon dioxide could be utilized as a weak oxidant and a kind of coolant to oxidize elements, meanwhile, helping control the temperature during the converter vanadium extraction process. However, the optimum content of CO_2 and the cooling effect of CO_2 at low content have not been reported. In this study, experimental research based on the influence of different CO_2 contents from 0% to 25% injected to the vanadium-containing hot metal was carried out, as well as contrast experiments of O_2-N_2 mixed blowing. The results indicated that the optimum content of CO_2 was 15%. Under the optimum condition, the oxidation of [C] was the lowest and the oxidation rate of [V] was 96.9%, while the temperature was also lower than the O_2-N_2 mixed blowing. This paper provide a potential property for utilizing CO_2 during the converter vanadium extraction process.

Introduction

With an increasing attentions to the problems of global warming, many research teams are working on how to reduce the carbon dioxide emissions and taking use of it.[1-4] It is high time for iron and steel industry, which plays a big role in the emissions of CO_2, to make some changes.

Nowadays, lots of studies on applications of CO_2 during steelmaking process have been carried out. In these papers, CO_2 are used as protective gas, reaction media and stirring gas.[5-8] They found some applications will improve the quality of molten steel and rolled steel. However the application of CO_2 in the vanadium extraction process has not been reported yet.

At present, steel mills always use pure O_2 to oxidize [V] into (V_2O_3)[9] during converter steelmaking process. However, the strong reaction between O_2 and the elements in hot metal will cause the temperature to increase too highly. There will be some energy wasted and more solid coolants will be used. Those solid coolants will influent the quality of molten steel.

Therefore, it is necessary to do some studies on the cooling ability of CO_2 by using CO_2-O_2 gas as oxidizer during the converter vanadium extraction. This work was supported by National Natural Science Foundation of China (project No.51334001) and Sharing Found of Large Scale Equipment, Chongqing University (project No.201406150044).

Experimental

The vanadium-bearing metal was provided by PZH Steel, China. The chemical compositions of the vanadium-bearing metal are shown in Table 1.

Table 1. Composition of vanadium containing hot metal

composition	C	Si	Mn	V	P	S
Wt%	3.73	0.0535	0.14	0.325	0.075	0.145

Experimental Set-up

Figure 1 shows the equipment for the experiments, which includes a $MoSi_2$ electric resistance furnace and the flow rate control system. The flow rate control system consists of 4 valves, 4 flowmeters and 3 different kinds of gases: O_2, CO_2, N_2. The use of the flow rate control system is to decide which one or two gases can be blown into the furnace and control its flow rate.

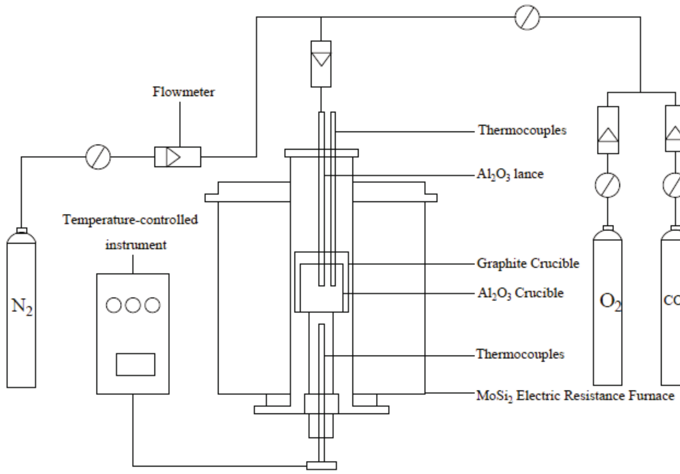

Fig. 1. Schematic drawing of experimental apparatus

Experimental Method

350 g vanadium-bearing metal was charged into a corundum crucible (inner diameter, 46 mm; height, 120 mm) which was then placed in another graphite crucible (inner diameter, 55 mm; height,135 mm). They were placed in the furnace at 1573K(1300℃) and held at 1573K for 30 min to ensure the metal melted completely. Then the blowing was began and lasted for 15min. Total flow rate of the CO_2 and O_2 mixed blowing was controlled at 0.6L/min, and with varied proportions of CO_2 as 0%, 5%, 10%, 15%, 20%, 25% in the mixed gas, the rest of which is pure oxygen.

The N_2 and O_2 mixed blowing was also done as comparison experiment. In the experiment, the proportion of N_2 is 15%.

Results and Discussion

Cooling Ability

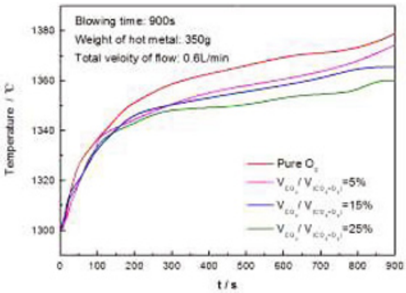

Fig 2. Changes of molten iron temperature with blowing time.

Fig. 2 shows how the temperature of molten iron changes with blowing time in different CO_2 proportion. From the figure 2, it can be seen that the bath temperature increase fast in the first 300s and tend to be constant after 300s. The bath temperature during blowing is lower with the Carbon dioxide content increasing from 5% to 25% after 300s.

The temperature of the iron bath can be influenced by CO_2 which mainly because of the following reactions.

Table 2. The thermodynamics data of interrelated chemical reactions

Chemical reaction	ΔG^0(J/mol)	ΔH^0 (kJ/kg)
$[C]+CO_{2(g)}=2CO_{(g)}$	34580-30.95T	11602.67
$[Fe]+CO_{2(g)}=(FeO)+CO_{(g)}$	11880-9.92	720
$[Si]+2CO_{2(g)}=(SiO_2)+2CO_{(g)}$	-3577967+357.27	-9299
$[Mn]+CO_{2(g)}=(MnO)+CO_{(g)}$	-261507.82+72.905T	-1512
$[Si]+O_{2(g)}=(SiO_2)$	-866510+152.30T	-29202
$[Mn]+1/2O_{2(g)}=(MnO)$	-803750+171.57T	-6594

Table 2 shows that the reactions of CO_2 and C or Fe is endothermic reactions. And the reactions of CO_2 and Si or Mn output only about 30% heat compared with that the reactions of O_2 and Si or Mn.

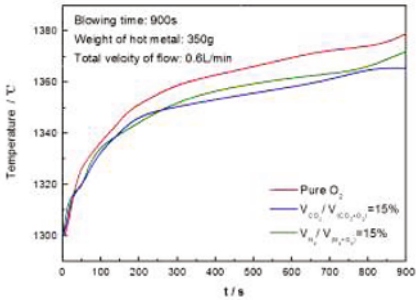

Fig 3. Changes of molten iron temperature with blowing time.

Fig. 3 shows how the temperature of molten iron changes with blowing time in different atmosphere. From the Figure 3, it can be seen that the bath temperature of N_2 and O_2 mixed blowing is higher than that of the CO_2 and O_2 mixed blowing after 300s.

Effect of Cooling Ability

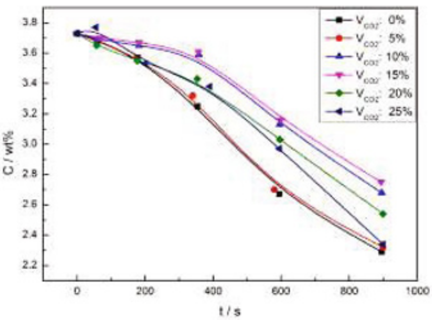

Fig 4. The [C] in molten iron changes with blowing time.

Fig. 4 shows that the [C] in the molten iron decrease continuously with blowing time. More [C] participated in the reaction as the proportion of CO_2 (volume%) increasing from 0% to 15%. However, the more proportion of CO_2 (volume%) blew, the lower [C] existed when the proportion of CO_2 (volume%) was from 15% to 25%. It is mainly because of the following reactions.

$$[C]+1/2O_{2(g)}=CO_{(g)} \quad \Delta G^0=-136990-43.51T(J/mol) \quad (1)$$

$$2/3[V]+1/2O_{2(g)}=1/3(V_2O_3)_{(g)} \quad \Delta G^0=-387160+109.58T(J/mol) \quad (2)$$

$$2/3[V]+CO_{2(g)}=1/3(V_2O_3)_{(g)}+[C] \quad \Delta G_1^0=-250170+153.09T\ (J/mol) \quad (3)$$

$$[C]+CO_{2(g)}=2CO_{(g)} \quad \Delta G^0=34580-30.95T(J/mol) \quad (4)$$

$$[C]+[O]=CO_{(g)} \quad \Delta G^0=-17166-42.5T(J/mol) \quad (5)$$

$$CO_{(g)}+[O]=CO_{2(g)} \quad \Delta G^0=-131945+87T(J/mol) \quad (6)$$

Eq.(1)-(3) shows that there is a selective oxidation temperature T_{trans}=1634K(1361℃; ΔG_1^0 =0). When bath temperature is over T_{trans}, more [C] will participate in the reaction with O_2 and the oxidation of [V] will be inhibited. However, According to other researchers' study[10], decarburization reaction of hot metal is influenced synthetically by the Eq.(4)-(6) and especially when the amount of CO_2 in the mixed gas is large. So the carbon in the molten iron decreased with CO_2 proportions increasing from 15% to 25%.

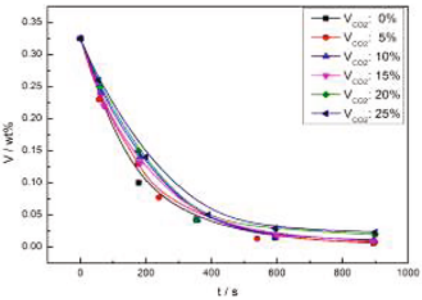

Fig 5. The [V] in molten iron changes with blowing time.

Fig. 5 shows that the [V] in the molten iron decrease continuously with blowing time and reached equilibrium state when blowing time was about 600s. It can be seen that the oxidation rate of [V] was 96.9% when the proportion of CO_2 was from 0% to 15%, while the oxidation rate of [V] was 92.1% when the proportion of CO_2 was from 20% to 25%. That is mainly because that CO_2 is a weak oxidant which will weaken the oxidation of [V]. However, all these can meet the demand of industry standard which demands the content change rate of V is more than 90%.

According to the thermodynamic analysis and the experimental results above, there is a proper proportion of CO_2 in mixed gas, which can match the objective of industry to extract more vanadium and keep more [C] in the molten steel.

The vanadium extraction process ended at 600s, as shown in Fig. 5. So the ratio of the oxidation quantity of [C] to the oxidation quantity of [V] at 600s is an important parameter to reflect the effect of vanadium extraction and carbon preservation process. The higher the ratio is, the better the vanadium extraction process is. In these experiments, the $\Delta V/\Delta C$ reached the peak value when the content of CO_2 was 15%, as shown in Fig. 6.

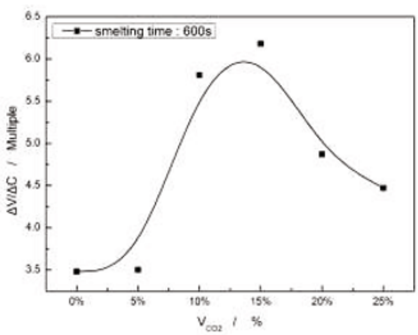

Fig.6. The $\Delta V/\Delta C$ changes with the proportion of CO2(volume%) at 600s

Conclusions

Based on the theoretical analysis and lab-scale experimental study above, the following conclusions can be drawn.

[1] The test of temperature control in CO_2 and O_2 mixed blowing vanadium extraction process shows that the bath temperature (after 300s) has continued to decrease as increasing the proportion of Carbon dioxide. Compared with N_2 and O_2 mixed blowing, CO_2 and O_2 mixed blowing has a better effect on the temperature controlling.

[2] The cooling ability of CO_2 has remarkable effect on vanadium extraction process. With the proper proportion of CO_2 , more vanadium will be extracted and more [C] will be kept in molten steel. In these experiments, the proper proportion of CO_2 is 15%, under which condition the oxidation rate of [V] is 96.9% and the $\Delta V/\Delta C$ reach the peak value.

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