ATLANTIS PRESS

Advances in Engineering Research (AER), volume 143

6th International Conference on Energy and Environmental Protection (ICEEP 2017)

The Development of Calcium Ferrite Pellet Used as Dephosphorizing or Slagging Agents for Steelmaking and its Application

WU Wei[1,a] LIU Yue[2,b]

(1. Metallurgical Technology Research Department of Central Iron & Steel Research Institute, Beijing 100081; 2.Hai Yi Tong Special Material Co., LTD, Wuhan 430082; a. wuweineu@163.com; b. Lyht18@126.com)

Key words: The calcium ferrite; Dephosphorizing agents; Slagging agents; Hot metal dephosphorization

Abstract: In order to meet the demands of slag formation without fluorite the calcium ferrite pellet is developed in laboratory. The lime and iron oxides combining in different proportion are used as raw material of the calcium ferrite pellet. The melting properties of the calcium ferrite pellet is determined in resistance furnace as basis for the optimum recipe. The results of test show that recipe c has better melting, which is used as composition of the calcium ferrite pellet and compared with other slag formation material for their melting characteristics. In order to the target of removing the higher phosphorus of hot metal the calcium ferrite pellet is used as dephosphorization and cooling agents to replace the sintered ore in 300t converter. The results show that the consumption of slag formation material is 71kg per ton steel and the dephosphorization rate of hot metal is over 85% by single slag manner to melting the hot metal with 0.105~0.13% phosphorus using the calcium ferrite pellet. The slag basicity is same, T.Fe content is reduced 3% and P_2O_5 content is increased 0.2% obtained by the calcium ferrite pellet comparing with the sintered ore.

Introduction

With the demands of decreasing the consumption of slag formation material and replacing fluorite for steel plant [1,2], it is very important to develop the fluxing agent of the furnace burden. According to the research results of the fluxing agent [3-7], most fluxing agent is the laterite and alumina bauxite to slag formation without fluorite in LD converter. There are greatly influences of the laterite and alumina bauxite on slag melting, however slag formed by the laterite and alumina bauxite has bad effects on the hot metal dephosphorization and slag basicity, which may increase the steelmaking cost. Hiromi S et al [8] studies the effects and mechanism of the calcium ferrite melting lime, Takashi S et al [9] studies the hot metal dephosphorization effect by slag formation of the calcium ferrite producing the high carbon steel. Guomin M et al [10] studies the preparation methods of synthesis calcium ferrite and their hot metal dephosphorization effects. According to the above research results the calcium ferrite slag as the dephosphorizing and slagging agents may achieve good results, which can completely replace fluorite. However most calcium ferrite slag product is made at the high temperature, which application is restricted for its high cost. So the calcium ferrite slag without being pre-melted is developed and applied to hot metal dephosphorization for steelmaking instead of fluorite slag formation, which provides evidence for decreasing the consumption of raw materials and improving the effects of hot metal dephosphorization.

the development of the calcium ferrite pellet

In the phase diagram of calcium oxide and iron oxide there are three kinds compounds of C_2F

($2CaO·Fe_2O_3$), CF ($CaO·Fe_2O_3$) and CF_2 ($CaO·2Fe_2O_3$). The melting point of them is respectively 1449°C, 1228°C and 1205°C. The calcium ferrite is the important slag formation material because of its low melting point and containing calcium oxide and iron oxide. So the calcium ferrite is used as the best substitute for the fluorite, which is widely applied to the hot metal dephosphorization process in abroad. However there is few application of the calcium ferrite product in our country at present.

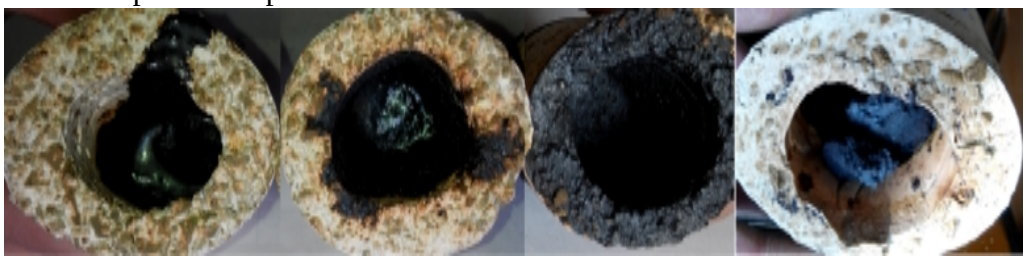
Table 1 is the physicochemical index of pre-melted calcium ferrite by metallurgical standard YBT-4266-2011. The chemical composition of calcium ferrite slag A, B, C, D is determined according to the requirement of table 1, which is composed of iron oxide red with containing total iron 55% and lime powder and their proportion is separately 1.3 :1；2:1；3:1；4:1 corresponding to the composition in table 1 being CF-45, CF-50, CF-55, CF-65.

Table 1 the physicochemical index of pre-melted calcium ferrite

Item	Index (mass fraction)/%					
	CF-75	CF-70	CF-65	CF-60	CF-55	CF-50
Fe_2O_3	≥75	≥70~75	≥65~70	≥60~65	≥55~60	≥50~55
CaO	≥10~15	≥15~20	≥20~25	≥25~30	≥30~35	≥35~40
other requirements	SiO_2≤4.0%;MgO≤6.0%;F≤0.5%,C,P,S≤0.1%, the bulk density≥3.2g/cm^3					

The experimental methods are that firstly the crucible is put into resistance furnace at 1350°C and preheating 15 minutes, then the crucible is taken out from resistant furnace and the sample is put into the crucible, finally the sample and crucible is put into resistance furnace at 1340~1360°C and heat preservation time is 5 minutes.

The sample melting of A, B, C and D at 1350°C is showed as figure1. The operating condition is that the temperature of coming into resistance furnace is about 1340°C, the heating-up time is 5 minutes. It is seen from figure 1 that the surface of sample A begins to melting and there is fluid phase on the surface of the crucible, however the internal of the sample is still powder. The surface of sample B has small amount melting and the internal of the sample is still a little powder. Sample C has completely melting and good fluidity. The surface of sample has a little agglomeration and the internal of the sample is still powder.



(A) (B) (C) (D)

Fig.1 the melting state of different samples at 1350 °C

The melting of sample is investigated placed on the refractory at 1350°C. The results show that the surface of sample A has little sintering and the internal of sample is still powder, the surface of sample B has melting and the internal of sample has no completely melting, sample C has completely melting and good fluidity, sample D is in the liquid and solid mixed state.

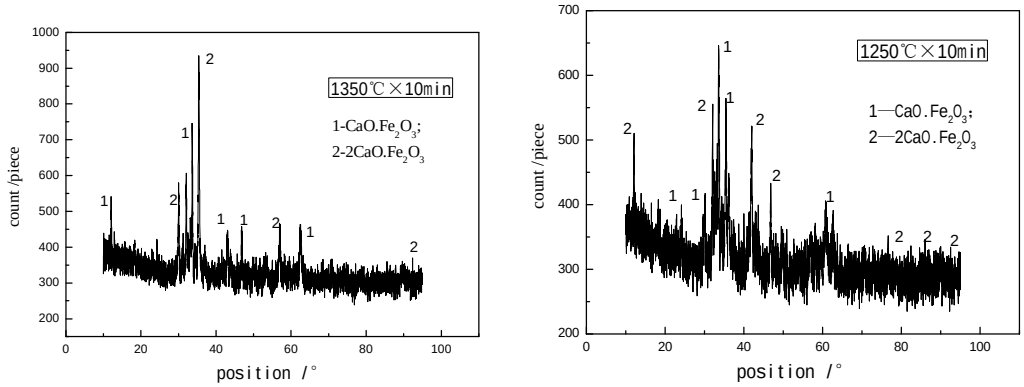
According to above analysis results the sample C is easy to melt and has good fluidity, which is used as the formula of the calcium ferrite pellet. The strength and wear resistance of the calcium ferrite pellet is ensured during the manufacture process to meet the quality requirement as converter burden.

the melting characteristic and mineral composition of the calcium ferrite pellet

The melting state of the calcium ferrite pellet at different temperatures is measured. The experimental process is that firstly the crucible is put into resistance furnace at 1250°C and preheating 15 minutes, then the crucible is taken out from resistant furnace and the sample is put

into the crucible, finally the sample and crucible is put into resistance furnace at the temperature of 1250°C, 1300°C,1350°C and time of holding temperature is 10 minutes. The melting state of sample is immediately observed after cooling.

It is seen from figure 2 that the sample is dried at room temperature for two hours, the calcium ferrite pellet is all melted and liquid at 1300°C and 1350°C. However the calcium ferrite pellet is in melting state at 1250°C, which shows that the melting point is lower than 1250°C. The results of the x-ray diffraction analysis of molten sample at 1250°C and 1350°C show that the composition of the calcium ferrite pellet mineral phase is mainly $CaO•Fe_2O_3$ and $2CaO•Fe_2O_3$.



Sample	Condition	Phase composition	Composition	Melting point
1#	1350°C×10min	$2CaO·Fe_2O_3$	34%	1449
		$CaO·Fe_2O_3$	66%	1228
2#	1250°C×10min	$2CaO·Fe_2O_3$	48%	1449
		$CaO·Fe_2O_3$	52%	1228

Fig. 2 the x-ray diffraction analysis of molten sample at 1250°C and 1350°C

the melting comparison of the calcium ferrite pellet and other slag formation materials

The chemical composition and physical properties of slag formation material in BOF steelmaking are showed as table 2. The bulk density average value of the calcium ferrite pellet is 3.02 g/cm^3 by drainage. In order to better application of the calcium ferrite pellet the melting point of the calcium ferrite pellet and slag formation material of converter is compared. The concrete method is that firstly the crucible is put into resistance furnace at 1280°C~1320°C and preheating 15 minutes, then the crucible is taken out from resistant furnace and the sample is put into the crucible, finally the sample and crucible is put into resistance furnace at the temperature of 1350°C and time of holding temperature is 10 minutes. The melting state of sample is immediately observed after cooling.

Table 2 the chemical composition and physical properties of materials in experiment

material name	the chemical composition and the bulk density of materials
the calcium ferrite pellet	CaO:21-28%; SiO_2≤10%;Fe_2O_3:35~45%;Al_2O_3≤6%;MgO≤4%; P≤0.1%;S≤0.1%, the bulk density:2.8~3.2g/cm^3
the sintered ore	CaO:9.16%; SiO_2:5.18%;TFe:54.3%;P:0.05%; S:0.02%
iron oxide powder（cold rolling iron skin）	The content of total iron is 55%
the iron scale	The content of total iron, silica and water is respectively 70.02%, 1.55% and 8.5%.
lime powder	CaO≥90%

The melting situation of different slag formation material is showed as table 3. It is seen from table 3 that sample of the calcium ferrite pellet is easy to melt and has good fluidity, the sample of the sintered ore has no melting, the sample of the iron oxide powder is still powder without melting, the sample of the iron scale and lime powder has just little liquid phases and is in semi-melt state, however there is no melting lime in the internal of sample.

Table 3 the melting situation of different slag formation material

item	before charged into resistance furnace	After melting experiment	item	before charged into resistance furnace	After melting expeiment
① the calcium ferrite pellet			② The sintered ore		
③the iron oxide powder			④ the iron scale and lime powder mixture		

the application of the calcium ferrite on hot metal dephosphorization

The calcium ferrite developed can accelerate lime dissolution and is beneficial to the hot metal dephosphorization. Japan iron and steel enterprises have used the calcium ferrite as slag formation materials to produce the low phosphorus or ultra low phosphorus steel. The calcium ferrite pellet is used as dephosphorization and cooling agents to replace the sintered ore in 300t converter, which provides evidence for application of the calcium ferrite.

experimental equipment and methods

The experiment is done in 300t converter, the amount of hot metal charged is from 262t to 280t, the average value of hot metal charged amount is 272t, the amount of scrap charged is from 15t to 25t, the average value of scrap charged amount is 20t, the oxygen supply intensity of top blowing is 3.3 Nm^3/t.min, the gas supply intensity of bottom blowing is from 0.02 to 0.08 Nm^3/t.min, the composition and temperature of hot metal is that C 3.66-4.81%, Si 0.11-1.16%, Mn 0.15-0.43%, P 0.102-0.130%, S 0.001-0.01%, T 1220-1420°C.

The detailed experimental method is that two-thirds of lime, all the dolomite and a half of the all sintered ore or calcium ferrite pellet are added in the beginning of blowing. The residual lime is added at one quarter of the blowing time and the residual sintered ore or calcium ferrite pellet is added with dynamic join according to the blowing situation. The constant pressure and variable lance level operation are adopted, the lance level of open blowing, slag melting, process and the lowest is respectively 2.65m, 2.2~2.4m, 2.1~1.9m and 1.9m. The sample of steel and slag at the smelting terminal is taken by a sub lance. The dynamic catch carbon is operated to control the temperature and oxygen content in molten steel by the actual situation of steel grade, rhythm and process. The re-blowing time is determined by the carbon content at the smelting end-point and reducing carbon amount.

Experiment result and analysis

The 32 heats experiment is done by the slag formation material of the calcium ferrite pellet. The average value of the slag formation materials consumption for smelting hot metal with the phosphorus content being 0.105~0.13% is that active lime is 42kg/t, the dolomite is 18kg/t, the

calcium ferrite pellet is 11kg/t and the total consumption of slag formation material is 71kg/t. The dephosphorization rate of hot metal is averagely 85%.

The 110 heats experiment is done by the slag formation material of the sintered ore. The average value of the slag formation materials consumption for smelting hot metal with the phosphorus content being 0.105~0.13% is that active lime is 43kg/t, the dolomite is 18kg/t, the sintered ore is 18kg/t, the magnesium nodular is 2.1kg/t and the total consumption of slag formation material is 81.1kg/t. The dephosphorization rate of hot metal is averagely 80%. The adding quality of slag formation by the calcium ferrite pellet is 10 kg/t less than that by the sintered ore. The slag chemical composition at the smelting end-point by the calcium ferrite pellet and the sintered ore is showed as table 4.

Table 4 the slag chemical composition obtained by different slag formation methods

category	CaO/%	SiO_2/%	MgO/%	T.Fe/%	P_2O_5/%	S/%	R	number
the calcium ferrite pellet	50.4	18.1	7.1	13.6	2.49	0.023	2.79	32
the sintered ore	49.6	17.9	7.2	16.75	2.29	0.019	2.77	110

It is seen from table 4 that the slag basicity is same, T.Fe content is reduced 3% and P_2O_5 content is increased 0.2% obtained by the calcium ferrite pellet comparing with the sintered ore.

Conclusions

The calcium ferrite slag is developed and applied to hot metal dephosphorization for steelmaking instead of dephosphorization and cooling agents to replace the sintered ore in 300t converter. The results are the followings.

(1) The recipe c has better melting, which is used as composition of the calcium ferrite pellet and compared with other slag formation material for their melting characteristics. The results show that the calcium ferrite pellet has the best melting.

(2) the composition of the calcium ferrite pellet mineral phase is mainly $CaO•Fe_2O_3$ and $2CaO•Fe_2O_3$.

(3) The calcium ferrite pellet is used as dephosphorization and cooling agents to replace the sintered ore in 300t converter. The results show that the consumption of slag formation material is 71kg per ton steel and the dephosphorization rate of hot metal is over 85% by single slag manner to melting the hot metal with 0.105~0.13% phosphorus using the calcium ferrite pellet. The slag basicity is same, T.Fe content is reduced 3% and P_2O_5 content is increased 0.2% obtained by the calcium ferrite pellet comparing with the sintered ore.

Acknowledgements

This research has been financed by the Beijing Natural Science Foundation with project number 2172057 in China.

References

[1] J.B. Wang, T. X. Yuan, Z.H. Tian: Steelmaking Vol. 30(6) (2014), p.1-9
[2] H.D. Ma:Tianjian Metallurgy Vol. 158(2) (2010), p.3-4
[3] Z.Z. Zhang, S.J. Yu, H.Y. Hou: Steelmaking Vol. 29(3) (2013), p.69-72
[4] T. Geng, C. D. Zou, Y.Z. Zhou, Z.T. Ding: Shanghai Metals Vol. 35(4) (2013), p. 24-28
[5] Z.Z. Zhang, H.W. Jie, P. Fei, J. Li: An Gang Technology Vol. 5 (2000), p.5-12
[6] J.S. Meng, M.F. Jiang, Y.X. Zhu: Steelmaking Vol. 21(2) (2005), p.1-3
[7] T.Y. Cao, Z.Z. Yang, S.B. Liu: Wisco Technology Vol. 52(2) (2014), p.14-17
[8] S. Hiromi, T. Satoshi, I. Masakazu, M. Oasmu: J. Soc. Inorg. Mater. Vol. 9 (2002), p. 218-223
[9] S. Takashi, I.N. Kunih, M. Katsumi: TetSu−to-Hagane Vol. 87(10) (2001), p. 643-649
[10] M. Guomin, M. Yasukazu, S. Daisuke, S. Fumio: Shigen-To-Sozai Vol. 115(9) (1999), p. 683-687