Powder Technology 335 (2018) 103–113

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

An integrated approach for production of stainless steel master alloy from a low grade chromite concentrate

Deqing Zhu [a], Congcong Yang [a,b,*], Jian Pan [a], Liming Lu [b,**], Zhengqi Guo [a], Xinqi Liu [a]

[a] School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
[b] CSIRO Mineral Resources, Kenmore QLD 4069, Australia

ARTICLE INFO

Article history:
Received 21 July 2017
Received in revised form 4 April 2018
Accepted 10 May 2018
Available online xxxx

Keywords:
Chromite concentrate
Iron ore
HPGR
Cr-bearing sinter
Blast furnace smelting process
Stainless steel master alloy

ABSTRACT

As an alternative process, the production of stainless steel master alloys in blast furnace (BF) exhibits high economic efficiency and great potential to use low-grade chromite resources. To produce desirable sinter products required by the blast furnace smelting process, sintering tests of ore mixtures made from a low grade South African chromite concentrate (Cr_2O_3/FeO = 1.99) and Chinese magnetite concentrate were performed in a sinter pot in terms of various sintering parameters including coke dosage, mix moisture, sinter basicity and proportion of magnetite concentrate, *etc.* An integrated process comprising "high pressure grinding rollers (HPGR) pretreatment, pelletizing, coke coating, pre-drying and non-fluxed sintering" steps was proposed based on the pellet-sintering technique. The quality of Cr-bearing sinters was evaluated. The results show that high quality Cr-bearing sinters can be obtained through the proposed process. Addition of 40% or more magnetite concentrate in ore blends promises to yield desirable sinters of proper chemical composition and good metallurgical properties required by the blast furnace smelting process. The smelting performance of the Cr-bearing sinter made from the 40% chromite and 60% magnetite mixture was assessed under simulated blast furnace smelting conditions. It is feasible to use the Cr-bearing sinters in blast furnace for stainless steel master alloy production. A stainless steel master alloy containing 71.75% Fe, 19.52% Cr and 7.84% C with phosphorus and sulfur contents (<0.015%) is obtained at Fe and Cr recovery rates of 92.55% and 87.53%, respectively, when smelting at 1550 °C for 60 min with slag compositions (10% Al_2O_3, 10% MgO and R_2 = 1.0). The bonding mechanism of Cr-bearing sinters and the formation mechanism of liquid phase were further revealed by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy-dispersive spectrometer (EDS). Both slag bonding (10 to 20% silicate) and solid bonding (recrystallization of spinel phase) contribute to the consolidation of the Cr-bearing sinters. Increasing the basicity of sinter made from 100% chromite concentrate or addition of magnetite concentrate in the ore blend at natural basicity lead to the formation of low-strength slag bonds, which generally reduces the sinter strength.

1. Introduction

Chromite ore is an essential raw material for production of ferrochromium, metallic chromium and stainless steel products in the metallurgical industry. Currently, with the depletion of high grade lumpy chromite ores, the efficient utilization of low grade chromite fines and concentrates becomes increasingly important not only for its higher significant economic efficiency to increase the competiveness of products, but also for sustainable utilization of chromite resource [1].

Considering the offgrade chromite ores were not suitable for high carbon ferrochromium alloy production through traditional submerged arc furnace (SAF) smelting process, a series of physical and chemical techniques were developed in order to beneficiate and upgrade the chromite ores from lower grades to applicable metallurgical grade by selectively removing iron for increasing Cr_2O_3/FeO ratio of raw materials [2–6]. While these techniques do provide a reasonable way for the utilization of low-grade chromite ores, some new issues may emerge, for example the economic efficiency of processes and the treatment of waste liquors and tailings. A novel process [7] was proposed for Cr, Ni-bearing alloy production from a low grade chromite overburden (14.9% Cr_2O_3 and 0.8% NiO) at 1400 °C. A Fe-Cr-Ni metal assayed 87.4% Fe, 7.2% Cr and 1.4% Ni was achieved, but the results also showed severe chromium and iron loss in final slag due to the low reduction temperature. Meanwhile, some researchers advocated the direct utilization of low-grade chromite ores by blending with high-grade ores [8,9]. Evidently, this idea is effective and easy to apply. However, due to the severe shortage of natural chromite resources in China, it is possible for the industry to confront the disruption of the normal supply of imported materials for any reason. From this point of view, technologies to use overseas or domestic low-grade chromite ores and chromium-bearing resources would be extremely attractive.

* Correspondence to: C. Yang, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China.
** Corresponding author.
E-mail addresses: smartyoung@csu.edu.cn (C. Yang), Liming.Lu@csiro.au (L. Lu).

https://doi.org/10.1016/j.powtec.2018.05.018
0032-5910/

Approximately since 1990s, several semi-industrial and industrial-scale blast furnace (volume: 3.0 to 255 m^3) smelting tests have been successfully conducted in China to produce stainless steel master alloy with 5 to 21.3% chromium and 0 to 4.5% nickel [10–13]. The beauty of this process lies on its higher economic efficiency than the traditional SAF smelting process because of its better adaptability to the offgrade chromite ores [14]. However, the industrial tests also showed that two major problems were remained to hinder its further application: 1) high coke rate due to a conservative approach for BF operations at the time and direct use of raw chromite ores without preliminary agglomeration; and 2) high phosphorus content in the Fe-Cr master alloys (the original P content of raw materials was not strictly controlled). When the chromite ores are converted into pre-reduced, sintered or oxidized agglomerates, it is believed that they have great potential to reduce energy consumption and improve smelting efficiency in the blast furnace than lumpy chromite ores [9,15]. Moreover, the P content in the master alloys can be regulated to an acceptable level by applying low P raw materials.

The sintering process is an effective way to agglomerate chromite fines (or concentrates) on account of its low requirement of particle size or specific surface areas for sinter feeds. And because of this, the sintering process usually possesses cost advantage over the pelletization process. The sintering characteristics of 100% chromite fines had been studied previously [9,16,17], showing that the traditional sintering process was suitable to agglomerate coarse chromite fines. Relying on approximately 20% liquid phase and solid-state connections of chromium oxide particles, the chromium-bearing sinter possessed satisfactory mechanical strength at a quite high fuel rate. Sintering of high ratio of fine chromite concentrate may encounter even worse problems of poor permeability, low sinter productivity and high fuel rate. Therefore, a pellet-sintering technique was developed and performed in a conventional sinter pot [18]. Through the pellet-sintering technique, higher sinter strength and yield and lower fuel rate were achieved compared with traditional sintering process. However, the aforementioned sintering processes are all relevant to the traditional SAF smelting process, and there was a lack of investigations on the sintering of chromite concentrates (or fines) for production of stainless steel master alloy in blast furnace.

The objective of this work is to produce a high quality sinter from a low-grade chromite ore and magnetite concentrate for Fe-Cr master alloy production in blast furnace.

2. Material and methods

2.1. Raw materials

The chemical compositions of raw materials including a South African chromite concentrate (*Ch*), a Chinese magnetite concentrate (*Ma*), bentonite, limestone and coke breeze are shown in Table 1. The concentrates were deliberately selected for the purpose of good availability, low cost and low impurities, *e.g.*, phosphorus. The XRD patterns of the *Ch* and *Ma* concentrates are shown in Fig. 1. The South African chromite concentrate consisted mainly of the chromite spinel phase and small quantity of siliceous gangue, and was assayed at 42.55% Cr_2O_3 with a low Cr_2O_3/FeO ratio of 1.99. The magnetite concentrate is expected to improve the softening-melting performance of sinter products from the chromite concentrate. All the raw materials have a low phosphorus content (<0.04%), which is required for the production of low-phosphorus Fe-Cr master alloy. It is noteworthy that although the sulfur content in the magnetite concentrate, bentonite and coke breeze is a bit high (>0.1%), the majority of the sulfur can be released into the waste gas as sulfur oxides (SO_x) during the sintering process [19]. The coke breeze has a high fixed carbon content of 80.29% and a calorific value of 28.36 MJ/kg, which can provide sufficient heat for the sintering process.

Table 1
Chemical composition of raw materials.

Constituents (*wt%*)	SA chromite concentrate (Ch)	Magnetite concentrate (Ma)	Bentonite	Limestone	Coke breeze
Fe_{Total}	22.61	65.12	1.28	0.07	2.08
FeO	21.38	27.67	–	–	–
Cr_2O_3	42.55	–	–	–	–
Cr_2O_3/FeO ratio	1.99	–	–	–	–
SiO_2	3.40	3.61	62.12	0.40	7.58
CaO	1.92	0.98	4.17	55.79	0.44
MgO	9.02	1.49	0.23	0.20	0.10
Al_2O_3	13.58	1.42	14.20	0.37	5.73
P	0.006	0.021	0.027	0.008	0.038
S	0.047	0.190	0.100	0.007	0.400
LOI[a]	1.03	0.99	7.42	42.59	82.68

[a] Loss on ignition.

Table 2 shows the particle size distributions of the raw materials. The *Ch* concentrate possesses a coarse size distribution with nearly 88% particles in the size range of 0.075 mm to 0.5 mm. In contrast, the *Ma* concentrate is much finer with approximately 85% passing 0.075 mm. Therefore the *Ch* concentrate is too fine for traditional sintering process but too coarse to be pelletized effectively. It lack effective granulating nucleus particles, resulting in poor granulation efficiency, inferior sintering productivity and high fuel rate [18,20]. On the other hand, preliminary pretreatment is required for the *Ch* concentrate to improve its ballability before the pelletizing step [21]. Both the bentonite and limestone powder are suitable for pelletizing with over 94% passing 0.075 mm. However, the coke breeze is relatively coarse with 90% particles smaller than 3 mm.

2.2. Experimental methods

2.2.1. Pellet-sintering test

The sintering characteristics of chromite-magnetite mixtures were studied based on the pellet-sintering technique in a sinter pot. Fig. 2 illustrates the experimental flowsheet of the pellet-sintering process. It includes four major steps, *i.e.*, pretreatment of sinter feeds, pelletization, coke coating and sintering. Details of the pellet-sintering process are summarized below.

High pressure grinding rollers (HPGR) pretreatment was applied in this work due to its superior advantages in reducing grinding energy and improving the ballability of feeds over the traditional ball milling pretreatment [21–23]. An open circuit HPGR process was adopted to

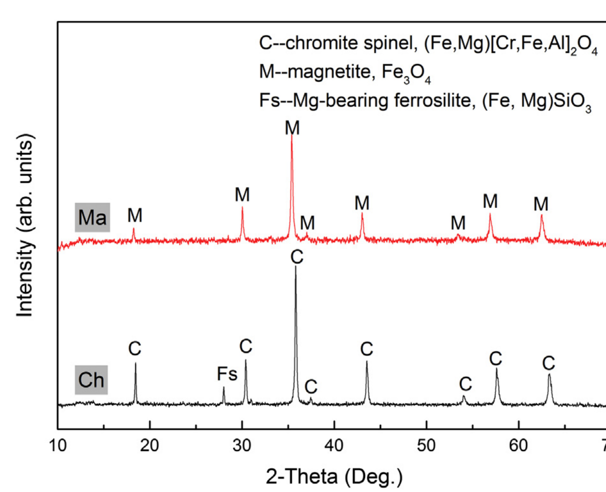

Fig. 1. XRD patterns of South African chromite (*Ch*) and Chinese magnetite concentrates (*Ma*).