IOP Conf. Series: Materials Science and Engineering **230** (2017) 012031 doi:10.1088/1757-899X/230/1/012031

Study on Carbon Reduction of Guizhou Oolitic Hematite by Graphite in Muffle Furnace

Zheng Zhong, Jinzhu Zhang *, Run Huang, Mingming Li and Jie Wu

School of Materials and Metallurgy, Guizhou University, Guiyang 550025, China
E-mail: zjz-yjx@163.com
*Corresponding author

Abstract. Oolitic hematite is an important iron ore resource in China. The mixed powder of the Guizhou oolitic hematite, the graphite, and the calcium hydroxide was pressed in a cylindrical sample mold by a 16 Mpa pressure. The dried samples at 378K for 12h were reduced in a muffle furnace at the temperature between 1323K and 1473K. The microstructure and the metallization degree of the sample were studied by means of optical microscope and chemical analysis. The results show that the higher metallization degree of the Hezhang oolitic hematite was up to 80.2% at 1323K with carbon oxgen mole ratio 1.3, the metallization degree of the sample in a muffle furnace is lower than that in a microwave furrnace, the lower metallization degree of the sample should be concerned with that the redued metallic iron can be oxidized in the muffle furnace with the temperature cooling down very slowly.

1. Introduction

Oolitic hematite is widely distributed in China and mainly distributed in Hubei, Hunan, Jiangxi, Guangxi, Yunnan, Guizhou, Chongqing, and other 11 provinces. Oolitic hematite is an important iron ore resource in China. Oolitic hematite is a deposit sediment by hematite, limonite and gangue mineral such as quartz, clay, etc. generally shows irregular shell layers of parcels in the oolitic particle center outward, forms a multilayer structure. There are not obvious boundaries between iron rich ores and gangue layer, coated or tightly intereconnected with finely laminated.

The depth reduction of oolite hematite and direct metallization has become a new research hot spot. The growth of the metallic iron particles is affected by both interface reaction velocity and diffusion speed in the deep reduction process of the oolitic hematite. The metallic iron particles is developed, continually grew up, gathered by the smaller ones, and gradually tured into the larger ones at enough high temperature with the reduction time prolonged. Generally speaking, raising the reduction temperature and prolonging the reduction time are all beneficial to the iron grains growth, but the over-high binary basicity is bad for the iron grain growth [1]. It is reported that the microstructure of oolitic hematite has been changed and the oolitic structure has been damaged seriously after heating by microwave. The microwave heating is selectivity. The iron oxides in the oolitic hematite has a microwave absorptive capacity, otherwise, the apatite and silicate in the oolitic hematite. It is beneficial for the reduction of iron oxides in a microwave furnace [2].

In this study, the binary basicity was selected as 1.5, the holding time at reduction temperature was taken as 4h, the atomic ratio of Carbon in the graphite to Oxygen bonded with iron atoms in the oolitic hematite from1.1 to 1.4, and the reaction temperature between 1323K and 1473K in a muffle furnace were all taken into consideration to understand the effects on the iron metallization degree of Hezhang oolitic hematite.

2. Experiments

2.1. Oolitic hematite and reagent

The oolitic hematite ores taken from HeZhang of Guizhou province in China were crushed and ground into powder [3]. The main chemical composition of the oolitic hematite was shown in Table 1. The hematite is the main form of the component Iron. The main chemical composition of the graphite taken as reducing agent is as follows: 98.0% (mass percent) fixed carbon, 1.2% ash, 0.5% volatile, and 0.24% moisture. The analytically pure calcium hydroxide ($Ca(OH)_2$) was used as a basic oxide to adjust the binary basicity of the samples.

Table 1. Main chemical composition of the oolitic hematite [mass percent,%]

composition	FeO	Fe_2O_3	SiO_2	Al_2O_3	CaO	P	MgO
content	9.44	62.65	9.78	8.71	1.56	0.69	0.71

Table 2. The size distribution of the oolitic hematite [mass percent,%]

Particle size [mm]	-0.074	0.074-0.098	0.098-0.125	0.125-0.2	0.2+
percentage	18.83	31.32	18.18	31.16	0.51

2.2. Experimental scheme

The binary basicity was selected as 1.5, the holding time at reduction temperature was taken as 4 hour, the atomic ratio of Carbon in the graphite to Oxygen bonded with iron atoms in the oolitic hematite were set as 1.1, 1.2, 1.3 and 1.4 respectively, and the reaction temperature was selected as 1323K, 1373K, 1423K and 1473K respectively, in a muffle furnace were all taken into consideration to understand the effects on the iron metallization degree of Hezhang oolitic hematite.

2.3. Experimental processes

Oolitic hematite was crushed and ball milled for 15 minutes. The powder particle distribution of the oolitic hematite in the experiment was shown in Table 2. The powders of the oolitic hematite, the graphite, and the calcium hydroxide were weighed according to the experimental parameters and mixed uniformly and completely. The mixture was extruded into the cylindrical pieces with a 30mm diameter and about 12mm height in the mold by a 16MPa pressure and dried at 378K for 12h. Then, the cylindrical sample was placed into the alumina crucible with a outer graphite crucible, covered with a graphite plate and an invert Φ91×85 mm graphite crucible, heated in a muffle furnace up to setting temperature, and held for the designed time. Four samples were placed closely to the right and left sides of the heating electrode rod in the chamber of muffle furnace [4].

The samples cooled to room temperature in the furnace were sawed off radially into four equal parts by hand. One part was used for microstructure determination, two parts were crushed and milled to 0.075mm or below for X-ray diffraction and chemical composition analysis.

3. Results and analysis

3.1. Effects of temperature on metallization degree of the sample

The metallization degree of the sample was decreased with temperature increase from 1323K to 1423K, increased from 1423K to 1473K, on the condition that the binary basicity was selected as 1.5, the holding time at reduction temperature was taken as 4 hour, the atomic ratio of Carbon in the graphite to Oxygen bonded with iron atoms in the oolitic hematite were set as 1.3 (see figure 1). The lowest metallization degree of the sample was gotten at 1423K, and the largest gained at 1323K.

Generally speaking, in the early stage of the sample reduction, the chemical reaction plays a dominant role for the reaction speed control; in the middle stage of the sample reduction, both the chemical reaction and the mutual diffusion of carbon atoms or iron atoms become the dominant speed control step; in the late stage of the sample reduction, the diffusion of carbon atoms is the dominant speed control step. Meanwhile, the diffusion of iron atoms plays a dominant role for the metallic iron grains growth. Based on the reduction of the oolitic hematite and the diffusion of iron atoms in the sample, the metallic iron particles were developed, continually grew up, gathered by the smaller ones, and gradually turned into the larger ones at enough high temperature with the reduction time prolonged.

The metallization degree of the sample in this study is lower than that the carbon reduction [5] is executed in a microwave furnace. That the slag formation reaction can hinder the mutual diffusion of carbon atoms or iron atoms may be a main reason for the lower metallization degree, and the higher the temperature, the larger the effect. Moreover, the lower metallization degree of the sample should be concerned with that the reduced metallic iron can be oxidized in the muffle furnace with the temperature cooling down very slowly.

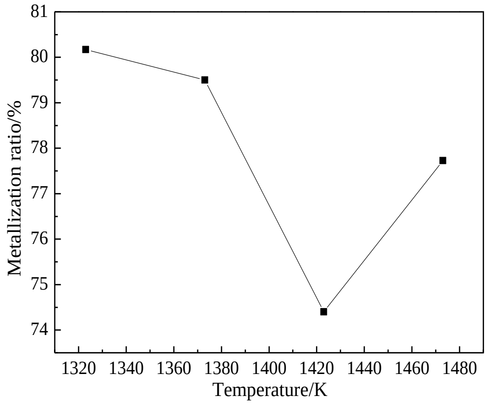


Figure 1. Effect of temperature on the metallization degree of the sample at Carbon Oxgen mole ratio1.3

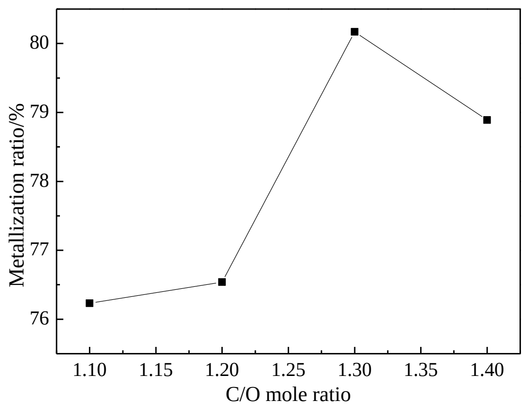


Figure 2. Effect of Carbon Oxgen mole ratio on the metallization degree of the sample at 1323K

3.2. Effects of Carbon Oxgen mole ratio on metallization degree

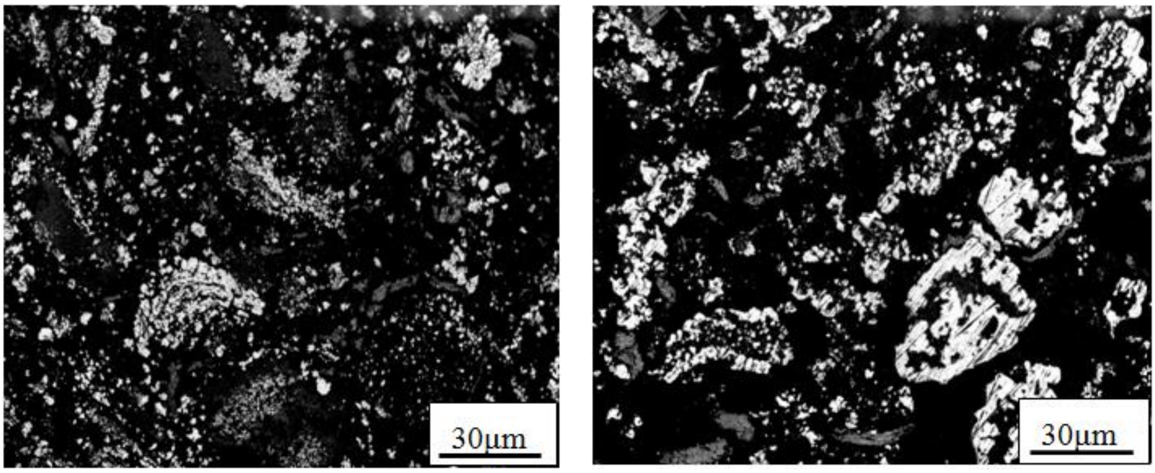
The metallization degree of the sample was increased with Carbon Oxgen mole ratio increase from 1.1 to 1.3, decreased from 1.3 to 1.4, on the condition that the binary basicity was selected as 1.5, the holding time at reduction temperature was taken as 4 hour, the reduction temperature was set as 1323K(see figure 2). The lowest metallization degree of the sample was gotten at 1.1, and the largest gained at 1.3.

At the early stage of the reduction, because the carbon content is not much, metallization rate curve smooth. With the increase of the ratio of carbon, increase the surface area per unit volume of iron oxide with a reducing agent [6], thereby increasing the contact area between the two, help iron oxide with a reducing agent of solid solid reaction, promoted the reduction of oolitic hematite, and with more carbon, total carbon gasification rate the more conducive to the reduction. At the late stage of the sample reduction, metallization rate decline may be at the root of excessive carbon reaction with other image, formed the organization of low density porosity low melting point material, prevented the reduction of its body and the diffusion of gas products.This is different from that of the microwave heating process, and the metallization rate curve will continue to rise.This may be because the heating process of iron oxides and gangue minerals are not consistent, the characteristics of microwave selective heating [7], so the changes are not the same. Due to the temperature difference between material form a larger thermal stress, so the oolitic hematite in the heating condition of the muffle furnace under the structure of no damage under microwave condition is serious.

3.3. Effect of temperature on the microstructure of the sample

The microstructure of the sample under various reduction temperatures [8] is different, on the condition that the binary basicity was selected as 1.5, the holding time at reduction temperature was taken as 4 hour, the

atomic ratio of Carbon in the graphite to Oxygen bonded with iron atoms in the oolitic hematite were set as 1.3(see figure 3).
When the temperature reaches 1323K, as shown in figure 3 (a), light grey part is iron oolite and matrix interaction. The oolitic structure was destroyed, and the metal iron were fundamental to the small particles scattered. When the temperature reaches 1493K, from figure 3 (b) can be seen in the disappearance of ooide the structure, iron particles in gangue material as crystal nucleus [9] grew up together. More and less dispersed iron particles, metallic iron ring mostly grew up together. This is due to the increase of temperature, the nucleation driving force for iron particles, reaction of activated carbon increased significantly, the dynamic conditions have been improved, which is beneficial to the iron particles grew up together. However, at this temperature, the damage degree is less than the extent of microwave heating. Because microwave heating in the muffle furnace. It is through the internal heating mode [10] increases the temperature of a substance. Iron oxides and gangue minerals in the microwave processing conditions, the disorganization.



（a）1323K （b）1493K

Figure 3. Effect of reduction temperature on the microstructure of the sample at carbon oxgen mole ratio 1.3

4. Conclusions

(1) The metallization degree of the Hezhang oolitic hematite in a muffle furnace is lower than that in a microwave furrnace.
(2) The lower metallization degree of the sample should be concerned with that the redued metallic iron can be oxidized in the muffle furnace with the temperature cooling down very slowly.
(3) The higher metallization degree of the sample was up to 80.2% at 1323K withr carbon oxgen mole ratio 1.3.
(4) The metallic iron particles were grew up, gathered by the smaller ones, and gradually tured into the larger ones with the reduction temperature increase.

References

[1] Yongli L, Tichang S, Jue K, Chengyan X, Zhanhua L and Qian G 2012 Advanced materials research *Industry test on phosphorus removal and direct reduction of High-phosphorus oolitic hematite ore* chapter 32 pp 1538-1542
[2] Haonan C 2016 Guizhou university *The reduction of oolitic hematite and separation of metallic iron* chapter 26 pp 23-25
[3] Yushu Z, Yazhuo D and Wenqi G 2010 Metal mine *Progress of beneficiation on oolitic hematite ore* chapter 136 pp 92-96
[4] Shuwen C, Yongzhen Z and Qiping C 1997 Metal mine *Direct reduction of oolitic hematite ore based on magnetism produced in Guizhou* chapter 24 pp 14-17
[5] Guanglong J, Jinzhu Z, Benjun X and Song Y 2014 Advanced materials research *Study on the reduction of oolitic hematite ores in N_2-CO atmosphere* chapter 22 pp 3275-3280
[6] Wei W, Jianjun G, Jiaqing Z, Yuanhong Q, Jianchang W and Xidong Z 2016 Journal of iron and steel research international *Reduction of carbon-bearing pellets of oolitic hematite in a Shaft Furnace* chapter 26 pp 23-26

[7] Fengjiu L 2011 Applied mechanics and materials *Study on dispersion character of fine oolitic hematite ore particle* chapter 412 pp 1156-1159
[8] Jia Y, Wen N and Fei Z 2010 Metal Mine *The Growth Characteristics of Metallic Iron Grains in Depth Reduction of Oolitic Hematite* chapter 412 pp 52-56
[9] Dongbo H, Yanbing Z, Rufei W, Wei G and Xiaoming L 2016 Journal of iron and steel research international *Direct reduction of high-phosphorus oolitic hematite ore based on biomass pyrolysis* chapter 22 pp 23-32
[10] Yongsheng S, Shufei L, Guangquan S, Yuexin H and Yanjun L 2009 Metal mine The deep investigation of oolitic hematite ore reduction experiments chapter 21 pp 80-83

Acknowledgment

The authors are especially grateful to the Program of National Natural Science Foundation of China (Grant No. 51274074).