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EXPERIMENTAL STUDY ON THE REDUCTION OF IRON ORE COAL MIXED PELLETS OF HIGH PHOSPHORUS HEMATITE PRE-TREATED BY MICROWAVE IRRADIATION[1]

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Abstract

In order to make full use of high phosphorus oolitic hematite and the advantage of microwave applied in metallurgy, the experimental study on the reduction of iron ore and coal mixed pellets pre-treated by microwave irradiation was carried out. Through the analysis of microstructure of pellets after reduction, the paper concludes that microwave irradiation could raise the reduction degree of iron ore and coal mixed pellets through descending the activation energy of molecular orbital and enhancing the surface free energy of pellets. The results showed that the reduction degree of iron ore coal mixed pellets was raised from 64% to 90% after microwave irradiation.

Key words: High phosphorus oolitic hematite; Microwave; Non-thermal effect; Reduction degree.

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1 INTRODUCTION

In recent years, with the rise of the price of iron ores in the global market, the supply of iron ores has created tremendous pressure on the development of our country's steel industry. The iron and steel companies in China have to increase the proportion of low grade and complex iron ores in iron-making production, which is one of the basic ways to protect the persistent and stable development of steel industry[1].The Ningxiang iron ore deposit is one of the important iron ore types in China, which is distributed in Hubei, Hunan, Jiangxi, Yunnan, Guangxi, Guizhou, Sichuan, concentrated in Yichang and Enshi[2].There are 7,000 million ton high phosphorus oolitic hematite in our country. The phosphorus content of this iron ore is high, the ore grade is low, the separation is very difficult, so these iron ores have been not used significantly. Recently, there are many studies about making use of iron ore coal mixed pellet self-reduction under high temperature reducing the hematite to metallic iron.(3) Metallic iron will accumulate and grow up under high temperature, destroying the oolitic structure of the green ore, changing the Fe's occurrence mode, and then getting extra-high grade concentrate by magnetic separation.
The frequency range of microwave is from 0.3 to 300GHz. Microwave application in synthesis of organic chemistry, sintering of ceramics and metallurgy has been more and more important because of thermal effects and non-thermal effects of microwave[4]. Through the analysis of reduced microstructure of iron ore coal mixed pellets pre-treated by microwave irradiation, this paper wants to study the effect of non-thermal effects of microwave on the reduction degree of pellets.(5,6) It has a great sense to lower the reduction temperature of iron ore coal mixed pellets and explore a new way of using high phosphorus oolitic hematite.

2 EXPERIMENTAL

2.1 Materials

The high phosphorus oolitic hematite samples(<90 mesh) were provided by a mining company of Yidu, Hubei. The quicklime samples(<90 mesh) were provided by sintering works at AISC. The chemical compositions of them are given in Table 1.The anthracite samples (<120 mesh) was from Dandong, and the chemical compositions of it is given in Table 2.

Table 1. Chemical compositions of iron ore and quicklime，%

	ω(TFe)	ω(FeO)	ω(CaO)	ω(SiO_2)	ω(P)
Iron ore	46.48	5.60	8.75	8.22	0.98
Quicklime	—	—	75.60	2.46	—

Table 2. Chemical compositions of Dandong anthracite，%

FC_{ad}	V_{daf}	A_d	M_{ad}
79.44	8.44	12.05	1.28

2.2 Methods

Firstly, the iron ore coal mixed pellets were made by the briquetting machine according to C/O mole ratio 1.0 and slag basicity 1.3 of the experimental materials; Secondly, the range of the microwave power level and pre-treatment time on the iron ore coal mixed pellets should be determined by the temperature measurement during microwaving; In

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the end, through the analysis of degree of reduction between the raw pellets and the modified pellets the paper could determine both microwave power level and pre-treatment time optimally. The design is given in Table 3.The degree of reduction quoted in the fifth reference is defined as follows:

$$R = \frac{\Delta W_\Sigma - \Delta W_C - \Delta W_V - \Delta W_w}{M_0} \times 100,\% = \frac{4}{7M_0}(\Delta W_\Sigma - f_{A-P}W) \times 100,\% \qquad (1)$$

In the formula, R-reduction degree; ΔW_Σ -total weight loss, g; ΔW_C -total carbon loss, g; ΔW_V -Vdaf loss, g; ΔW_w -Mad loss, g; M_0 -oxygen content in iron oxide, g; f_{A-P} - weight loss percentage of alumina and coal,%; W -raw pellets weight, g;

Table 3. Design on iron ore coal mixed pellets pre-treated by microwave irradiation

Number	Microwave power（W）	Time（s）
1	—	—
2	132	60
3	132	120
4	264	60
5	264	120
6	396	60
7	396	120
8	528	60
9	528	120

3 RESULTS AND DISCUSSION

3.1 Temperature Increase of Iron Ore Coal Mixed Pellets

The results of microwave heating on the pellets are shown in Fig.1. Fig.1 shows that the pellets were a good microwave-absorbing material and they were heated up quickly under microwave irradiation. According to the thermodynamics of carbothermic reduction on iron oxide, the iron oxide was reduced by carbon at the temperature of 280℃ in the standard state. To prevent the iron ore coal mixed pellets from self-reduction, the pellets should be treated by microwave irradiation under the temperature of 280℃. According to concerned papers, the pyrolysis of coal had come up above the temperature of 200℃.In order to descend the loss of volatile matter of coal, the coal should be treated by microwave irradiation under the temperature of 200℃.

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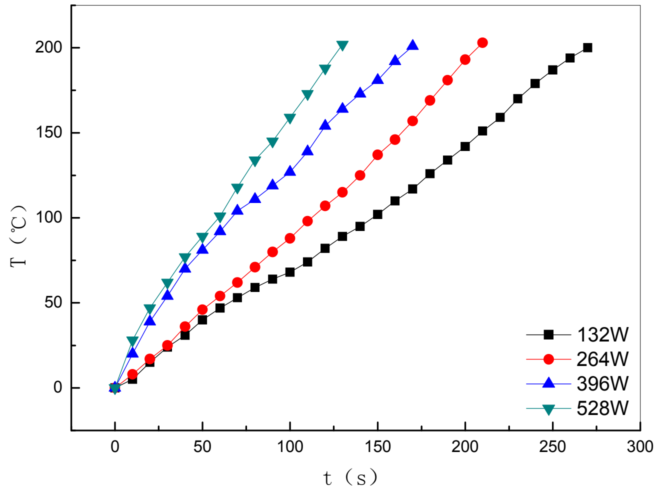

Figure 1 Temperature increase of pellets heated by microwave power at 132W,264W,396W and 528W, respectively.

Considering the above both conditions, the iron ore coal mixed pellets should be treated by microwave irradiation under the temperature of 200℃.In order to test the effect of non-thermal effects of microwave on pellets，it should analyze the degree of reduction between the raw pellets and the modified pellets. And further to determine both microwave power level and pre-treatment time optimally.

3.2 Reduction of Iron Ore Coal Mixed Pellets

Put the raw pellets and the modified pellets in the shaft furnace respectively and make them have 30 minutes reduction under the temperature of 1100℃.And then test their reduction degree, which is given in Table 4.

Table 4. Reduction degree of iron ore coal mixed pellets pre-treated by microwave

Number	Microwave power（W）	Time（s）	Reduction degree（%）
1	———	———	84.04
2	132	60	90.16
3	132	120	88.50
4	264	60	86.71
5	264	120	88.12
6	396	60	88.86
7	396	120	86.85
8	528	60	89.19
9	528	120	84.64

Table 4 shows that the reduction degree of modified pellets are greater than that of raw pellets. And the second degree of reduction reached a maximum pre-treated by microwave irradiation. Make the results of reduction degree form the bar chart,and the concrete analysis is given in Fig.2.

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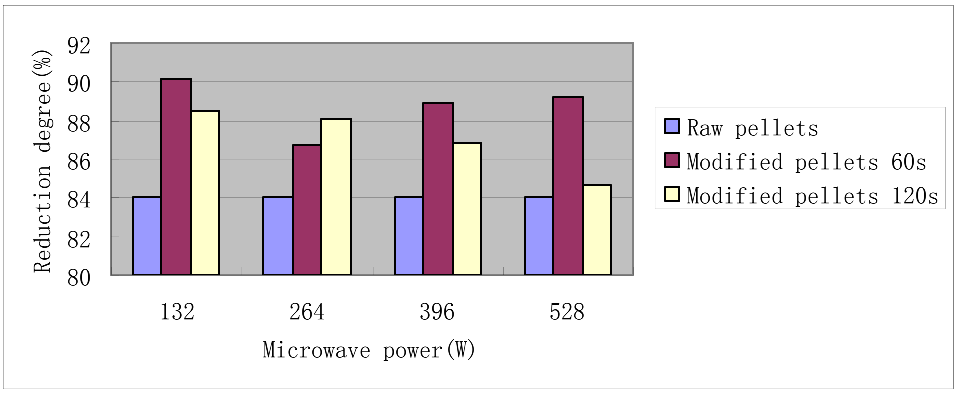

Figure 2 Effect of microwave pre-treatment(132W, 264W,396W,528W) on reduction degree of pellets.

Fig.2 shows that the degree of reduction reached a maximum under microwave pre-treatment at 132W, 60s. The reasons might be connect with the non-thermal effects of microwave. On the one hand, the molecules were vibrated by microwave irradiation, which might cause the resonance vibration of chemical bond. As a result, the path of the reaction was influenced by the change of materials. At the same time, microwave irradiation could descend the activation energy of molecular orbital by stored the energy in the molecules[7].On the other hand, the high phosphorus iron ore and the anthracite in the pellets could absorb the microwave irradiation selectively, which enhanced the surface free energy of pellets and increased the activity of anthracite. So the reduction process could be sped up comparatively.

3.3 Microscopic Observation

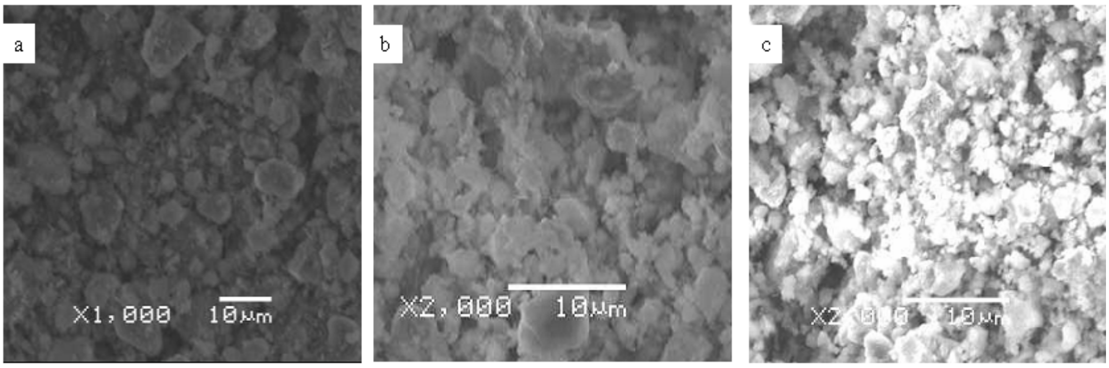

Figure 3 Microstructure of iron ore coal mixed pellets: (a) microstructure of high phosphorus iron ore; (b) microstructure of raw pellets after reduction（C/O=1.0，T=1100℃; (c) microstructure of modified pellets after reduction（C/O=1.0，T=1100℃,132W，60s）

Fig.3(a) shows that the iron oxide grains were distributed in the iron ore in the form of oolitic texture; The phosphorus in these iron ore presents majored in apatite, and disseminated at the edge of iron oxide grain. Some distributed in carbonate or quartz, and only a little occurred in the lattice of iron oxide. The grain sizes of iron oxide and apatite were so minimum that the common beneficiation methods could not raise ore grade and remove phosphorus content.

Fig.3(b) shows that the raw pellets were reduced mostly under the temperature of 1100℃.XPS indicated that the white shiny material was metallic iron, the shallow gray material was the gangue and the black material was blow hole. The oolitic structure of the raw ore after reduction was destroyed by the growing up of the iron grain.

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However ,the size of the iron grain did not grow up significantly.

Fig.3(c) shows that the iron grain in modified pellets after reduction grew up significantly under the temperature of 1100℃.The metallic iron appeared in the pellets in the form of spherical particles. The iron grain destroyed the oolitic structure of the raw ore, and this was benefit for separation between metallic iron and gangue with rich phosphorus.

4 CONCLUSIONS

- The iron ore coal mixed pellets are a good microwave-absorbing material and they are heated up quickly under microwave irradiation. In the present pellets an optimum value of these parameters was obtained with microwave treatment for 60s at a power of 132W.
- Microwave treatment enhanced the reduction degree of iron ore coal mixed pellets. That indicated the non-thermal effects of microwave played a positive role in reduction process.
- Through the observation of microstructure of raw pellets and modified pellets which were reduced it could find that the iron grain in modified pellets were bigger than that in raw pellets. It meant that the reduction temperature of pellets was descended by the non-thermal effects of microwave.

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