

INFLUENCE OF PARTICLE SIZE ON REDUCTION KINETICS OF NATURAL LATERITIC IRON ORES

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ABSTRACT

INFLUENCE OF PARTICLE SIZE ON REDUCTION KINETICS OF NATURAL LATERITIC IRON ORES. This work is to report a laboratory investigation on the influence of particle sizes on reduction behavior of natural lateritic iron ore with anthracite coal under isothermal condition. The main minerals content of investigated ore were goethite = 62.8%, hematite = 18.3% and magnetite (Fe_3O_4) = 6.2% and other oxide minerals like alumina = 6.6%, silica = 4.5%, chromate = 3.3% and others. The ore and anthracite coal of -100, -200 and -500 μm size with mol ratio between iron oxide and carbon in the anthracite of 1 : 1.88 were mixed, pressed into a composite of 12 mm diameter and 20 mm long and heated isothermally at four different temperatures for various reduction times. The metallization is determined by the reduction temperature and time. Mostly, effective reduction temperatures were found to be 1100 °C resulted in the highest value of metallization of almost 96 %. The particle size seems has no significant influence on the metallization value at this reduction temperature. However, particle sizes influenced significantly the metallization for reduction temperatures of less than 1100 °C from which values of metallization increased with decreasing in particle sizes.

Key words: Lateritic iron ore, Anthracite, Reduction kinetics, Metallization, Iron oxide/coal composites

ABSTRAK

PENGARUH UKURAN PARTIKEL TERHADAP KINETIKA REDUKSI BIJIH BESI LATERIT ALAM. Dalam makalah ini dilaporkan hasil kegiatan penelitian skala laboratorium tentang pengaruh ukuran partikel terhadap perilaku kinetika reduksi dari komposit antara bijih besi laterit alam dan batu bara antrasit selama proses reduksi pemanasan tetap. Kandungan utama bijih laterit yang dijadikan sasaran penelitian terdiri dari goethite = 62,8%, hematite = 18,3% dan magnetite (Fe_3O_4) = 6,2% dan senyawa-senyawa oksida lain seperti alumina = 6,6%, silika = 4,5%, kromat = 3,3%. Partikel laterit dan antrasit masing-masing berukuran -100, -200 dan -500 μm dicampur dengan perbandingan mol antara oksida besi dalam laterit dan karbon dalam antrasit adalah 1 : 1,88. Material campuran kemudian dipadatkan dalam suatu cetakan dan menghasilkan pelet komposit dengan dimensi diameter 12 mm dan panjang 20 mm. Pelet komposit selanjutnya dipanaskan pada empat suhu tetap berbeda selama berbagai waktu reduksi. Diketahui bahwa metalisasi sangat ditentukan oleh suhu dan waktu reduksi. Dalam banyak hal, suhu efektif untuk menghasilkan nilai metalisasi tertinggi selama proses reduksi adalah 1100 °C yaitu mencapai nilai 96 %. Disamping itu ditemukan bahwa ukuran partikel kurang memiliki pengaruh terhadap pencapaian nilai metalisasi pada suhu efektif tersebut, kecuali pada suhu reduksi kurang dari 1100 °C. Dapat disimpulkan bahwa pada suhu reduksi di bawah 1100 °C nilai metalisasi bertambah besar dengan mengecilnya ukuran partikel.

Kata kunci: Bijih besi laterit, Antrasit, Kinetika reduksi, Metalisasi, Komposit oksida besi/karbon

INTRODUCTION

One of the lateritic ore species is lateritic iron ore which available significantly in the world but the Fe content is < 66% or even less than minimum standard for current commercial iron ore content [1]. However,

the lateritic iron ore can in principle be utilized as raw materials for iron and steel making industry even with its low Fe content by a reduction with a suitable technology e.g. rotary kiln or lateritic iron ore – carbon

composite technology like Iron Technology Mark III or ITmk3 [2-3] but the utilization of lateritic iron ore for those technology is under development.

The main mineral content of lateritic iron ore is goethite, $\text{FeO}(\text{OH})$, among with others like hematite, Fe_2O_3 , magnetite, Fe_3O_4 and other oxides like alumina, Al_2O_3 , etc. When ore is heated, dehydroxilation of goethite takes place at about 200-400 °C and $\text{FeO}(\text{OH})$ is transformed to Fe_2O_3 [4]. Consequently, Fe content increases due to increasing of Fe_2O_3 content.

Reduction kinetics in iron ore reduction deal with the rate at which iron oxides are converted to metallic iron by the removal of oxygen [5-6]. It is important if the process is carried out under the iron melting point like in ITmk3 and Direct Reduction process, the rate at which the ore can be reduced determines the production rate. The production rate largely determines its economic feasibility and its competitiveness with other process. It is well known that the rate of chemical reaction increases as the temperature increases.

The rate determining steps in ore reduction is associated with the nature of the ore. This property is often called the reducibility which determines the ease with which oxygen can be reduced from iron oxides in the ore by reductants. One of the ore properties which determine the reducibility is particle size. Larger particle provides less surface area.

The reducibility of an iron ore can be determined experimentally in many ways, one of them is measuring of the time require to reach an arbitrarily chosen reduction degree, some people use 90 % and others use 50 % reduction degree [7]. It can be said that the reducibility is the time required to reach a certain reduction degree, in industrial case 90 % figure is often used. For the reduction reactions to take place the reductant must come in contact with the surface of the iron oxides [8], the reductants must diffuse inwards and the product gas outwards at least at the outer layer to reach the wustite layer.

In this paper, some results in kinetic studies of laterite-anthracite composites reduction process under isothermal heating are reported. Metallization which is defined as a ratio between reduced iron and total iron in the ore is used throughout results of reduction kinetics. Quantitative analyses by X-ray diffractometer (XRD) was employed in order to derive fraction of phases during reduction processing.

EXPERIMENTAL METHOD

Materials under investigation were lateritic iron ores from Sebu island of Indonesia. Phase identification of materials based on X-Rays Diffraction (XRD) indicated that materials consisted of goethite and other minerals identified as quartz (SiO_2), hematite (Fe_2O_3), nickel oxide (NiO) and chromite (Cr_2O_3) as reported previously [9]. The ores and anthracite coals

with 1 : 1.88 mol ratios between iron oxides and carbon content in the ores and anthracite respectively were co-milled to -100, -200 and -500 μm sizes by a ball mill apparatus. The milled mixture powders were pressed into a composite of 1.2 cm diameter and 2 cm length. The composite was then heated isothermally at four different reduction temperatures 800, 900, 1000 and 1100 °C for various reduction times from 15 to 90 minutes at each reduction temperature. The heating was carried out in an auto glass bead furnace with normal atmosphere. All of reduced materials were analyzed with XRD and the diffraction traces were further analyzed quantitatively employing General Structure Analysis System (GSAS) software. The anthracite composition was the following = fixed carbon = 85.57 %; ash = 10.88 %; Lost of ignition (LoI) = 89.12 %; volatile matter = 5.5 % and water content = 1.84 %.

RESULTS AND DISCUSSION

The fitted XRD profiles of reduced materials which resulted in residues of almost zero intensities for the whole diffraction range were plotted in Figure 1. The convergen fitting process was achieved at acceptable c^2 values of 1.818, 1.585 and 1.228 for samples coded MTZ17 (reduced at 900 °C), MTZ 42 (reduced at 1000 °C) and MTZ 94 (reduced at 1100 °C) respectively. Phases and respective weight fraction which were identified and derived from fitted profiles are listed in Table 1. It indicates that a reduction temperature of 900 °C was inadequate to achieve a complete reduction in which the fraction of Fe was obtained in a relatively small ~ 13.0 %. The reduction was predominantly in

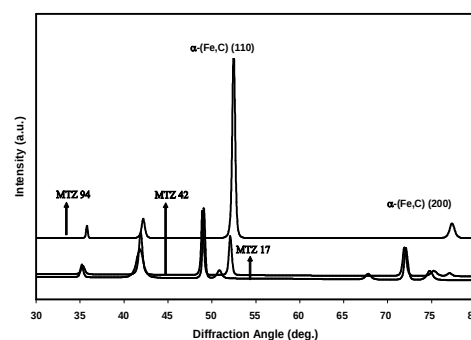


Figure 1. XRD profiles of reduced lateritic iron ore for reduction temperatures of 900 °C (MTZ 17), 1000 °C (MTZ 42) and 1100 °C (MTZ 94)

Table 1. Summary of quantitative analysis by XRD on phase composition of reduced materials

Phase	Weight Fraction		
	MTZ17 (%)	MTZ42 (%)	MTZ94 (%)
Hematite (Fe_2O_3)	1.3	0	0
Magnetite (Fe_3O_4)	17.3	4.9	1.58
Wustite (FeO)	67.9	59.3	6.5
Ferrite, α -(Fe,C)	13.5	36	91.7
Metallization (%)	16.6	42.1	93.7

Table 2. Summary of Root mean square deviation (RMSD) evaluated from experimental data for Metallization

First Stage T (°C)	RMSD		
	Av	FO	PB
800	0.565	0.456	0.508
900	1.760	0.050	1.578
1000	0.092	0.001	0.888
1100	0.100	3.278	2.182
Σ First stage	2.516	3.785	5.157
Second stage			
800	N/A	0.307	3.324
900	3.46	--	--
1000	N/A	11.312	1.076
1100	N/A	0.521	0.494
Σ Second stage	3.46	12.140	3.894

favour of wustite (FeO) formation with a quantity of ~ 68 %. The value is significantly higher when compared with that of magnetite (~ 17.3 %). At a higher reduction temperature 1000 °C, similar results were also obtained in which the reduction was also by wustite formation but with the fraction of Fe almost triple. Thus, magnetite seems an intermediate phase which is less favourable to form in an overall reaction for direct reduction in lateritic iron oxide coal composite.

Included in Table 1 is metallization obtained from three different reduction temperatures. Metallization was defined as the weight fraction ratio between iron obtained after reduction and total of iron containing in the sample prior to reduction processes. It is shown that the most effective temperature for reduction reaction of iron oxides/coal composite was found at 1100 °C in which composite materials were reduced to Fe with quantities of more than 93 %. Reduction kinetics of iron oxides/coal composite at any isothermal temperature showed that the metallization increases as reduction temperature and time increased.

However, metallization obtained at 1100 °C and 1000 °C was very significantly different compared with that of 800° and 900 °C. It is noted that metallization at temperature 800 °C was almost zero and only ~ 10 % at 900 °C at a reduction time of 30 minutes. The rate of metallization for the whole reduction temperature is consequently not the same. To find out what kinetic models govern the metallization at any reduction temperature, values of metallization obtained at different reduction temperatures were then fitted with Avrami (Avr), first order (FO) and phase boundary (PB) models [10].

When applying the Avrami model, values of order constants (n) derived from all experimental data for each reduction temperature are not all relied in the range 1-4. However, when data are divided into two stages, the n values for each temperature are now in the acceptable range though only applicable at the first stage and complete stage for reduction temperature of 900 °C. Consequently, n values derived from data of second stage are mostly not acceptable.

Thus, kinetic of metallization is to follow the Avrami model only at the first stage and reduction at temperature 900 °C. Further kinetic model is thus required to fitt the experimental data of the second stage. When root mean square deviation (RMSD) parameter is applied to the three kinetic models, values of RMSD for each model were obtained and these were listed in Table 2. It can be seen that among the three total RMSD values, the smallest for the first stage reduction kinetic was obtained from Avrami model and followed by FO and PB respectively. For the second stage of reduction kinetic in which Avrami model is not applicable (N/A) except for the temperature 900 °C, PB model resulted in a total RMSD value of 3.894 which is much lower when compared with that of FO model (12.140).

In Figure 2, experimental data of metallization at isothermal temperatures for 100 µm particle were replotted in which theoretical plot of Avrami equation which valid only for the first stage kinetic is now included. Except, a theoretical plot of kinetic at 900 °C, the theoretical plot was extended in the second stage employing PB equation. The whole theoretical plots showing well fitted with the experimental data of metallization.

This suggests that a reduction kinetic of two stages relation with reduction times seems applicable to the lateritic iron ore reduction. It is clear that reduction of lateritic iron ore-carbon composite at isothermal condition of 800 -1100 °C governs by a two stages kinetic. The first stage of reduction is nucleation and growth control in which the reduction is controlled by chemical reactions. Further growth is governed by a kinetic of lower reduction rate due to diffusion of reducing agent into the core interfaced by boudary layers of reduced iron. Kinetic of diffusion control is to follow a PB model. The latter is lowering the slope of PB kinetic as reduction temperature increased. However, initial values for reduced iron of each reduction temperature are significantly different.

Kinetic studies on the effect of particle size to metallization during reduction process has in general indicated that the particle sizes influenced significantly the metallization for reduction temperatures especially at reduction temperatures of less than 1100 °C from which

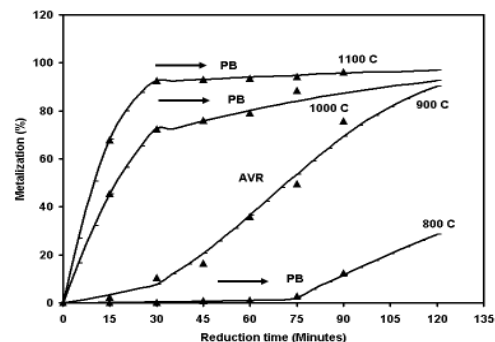


Figure 2. Experimental data for Metallization fitted with PB and AVR kinetics at various reduction temperatures

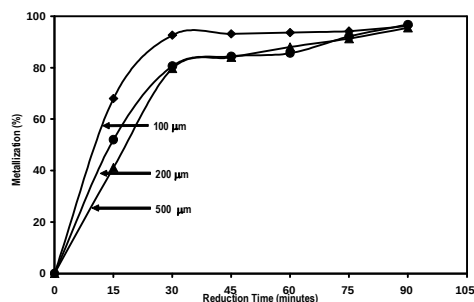


Figure 3. Experimental data for metallization reduced at 1100 °C with 3 different particle sizes

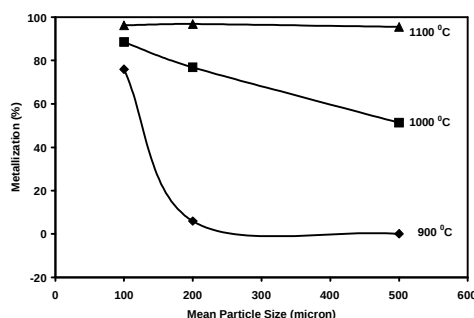


Figure 4. Metallization obtained at 90 minute reduction

values of metallization increased with decreasing in particle sizes due to increasing in specific surface area. It means that contact surface between the ore particles and the reductor is increased with reducing particle size, higher contact surface will enhance the reduction reaction. Figure 3 shows reduction kinetics of 3 different particle sizes at 1100 °C.

At the first 30 minutes reduction, both particle sizes of 200 µm and 500 µm have resulted in ~ 80 % metallization but particles of 100 µm resulted more than 90 %. A slower reduction rate after the first 30 minutes reduction seems applied to the three different particle sizes and they have achieved metallization of ~ 96 % after 90 minutes reduction time. This was not applicable to the lower reduction temperatures as it showed in Figure 4 in which metallization values obtained after 90 minutes reduction time were plotted against the particle size of composite.

It showed that particle size is one of the controlling factor in reduction of lateritic iron ore. Significant enhancement of reduction towards a high value for metallization may be obtained by a small particle size of 100 µm.

CONCLUSION

Lateritic iron ore can be reduced by anthracite, the metallization achieved was up to 96 %, means the reduced lateritic iron ore from metallization point of view can fulfill the standard metallization minimum for steel making raw material. Particle sizes determined lateritic iron ore reduction achievement, in this case the metallization. Metallization decreases with increasing particle size due to decreasing the contact surface area between iron ore and reductant particle. Particle size is one of the controlling factor in lateritic iron ore.

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