Reduction mechanism of indonesian limonite ore by solid reducing agents

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Abstract. Limonite ore from Sulawesi Island (Indonesia) was reduced isothermally at 900 – 1200°C by pulverized coal and charcoal to produce ferronickel. XRD and XRF analyses were used to characterize the samples. The influence of reductive conditions on the reduction and metallization degree of the samples, including reduction temperature, reduction time and reducing agent types were studied. Results have shown that both the reduction and metallization degrees increase as temperature and time increase. The reduction reactions will be more completed at higher reduction temperature. It could be seen from XRD results that magnetite and Fe-Ni peaks increased at higher temperature reduction. This could be mean that the rate of reduction reaction is faster at higher temperature. The losses of samples weight also happen faster at higher temperature. It was also found that the reduction behaviors using coal differed from those using wood charcoal due to the differences in proximate content. From this study, it could be concluded that fixed carbon content in the reducing agent did not always be the most important aspect of choosing a reducing agent. The sample which has been reduced with coal and charcoal showed an almost exactly same pattern even they both had different characteristics. The relatively higher volatile matter content in charcoal gave a significant contribution to the reduction process.

1. Introduction

Nickel is one of the most important metal in the world. Mostly, nickel is used as a raw material in the stainless steel making process which accounted for 62% of nickel consumption [1]. One of the sources of nickel is nickel laterite ore. Nickel laterite ore is the primary raw material in the process of making nickel pig iron (NPI) and ferronickel. NPI or ferronickel is usually produced in the blast furnace using coal or coke as a fuel. In recent years, the rapid rise in stainless steel demand has dramatically increased the production of nickel metal by approximately 4.7% per year [2]. Therefore, the recovery of nickel from laterite ores using pyrometallurgy has been extensively investigated [2].

Indonesia is one of the largest producers of nickel ore in the world and has approximately 16% of total global nickel resources. These are in the form of lateritic ores; they are widely distributed and spread among the islands of Kalimantan, Sulawesi, Halmahera, Gag, and Papua [3]. Nickel pig iron (NPI) production is a new promising process, although it was firstly developed about 50 years ago but it has not...
been commercially used until some Chinese pig iron producers changed their production methods into NPI production. Chinese NPI production was firstly started in blast furnaces using low-grade laterite ores imported from Indonesia, Philippines and New Guinea [2]. The process is almost same as pig iron production processes. The only difference is that the ore contains more nickel. Not only as a fuel, coal or coke also act as a solid reducing agent in the nickel laterite reduction. The use of coal or coke as solid reducing agent can be substituted by other carbon sources such as charcoal and other biomass. However, the use of charcoal for reducing laterite ores has not been studied more particularly in term of reduction mechanism.

In this study, therefore, the reduction of nickel from a low-grade limonite ore was performed using different solid reducing agents i.e. coal and charcoal in order to compare the reduction mechanism of those reducing agents. The effects of reduction temperature and time on the reduction process were also investigated. Moreover, the reduction mechanisms of nickel were analyzed based on the change of mineral phase during the reduction process. The present study aims to provide a basis for the utilization of low-grade limonite ore from Indonesia especially using pyrometallurgical method.

2. Materials and methods

2.1. Materials

A low-grade limonite ore from Indonesia (Sulawesi Island) was used in this experiment. The samples were mineralogically and chemically characterized. X-ray fluorescence (XRF) was used to determine the chemical compositions of the sample. The mineral phases of the raw ore sample were identified by X-ray diffraction (XRD), using CuKα radiation, in the 2θ range 5° to 80°. The accelerating voltage and applied current were 40 kV and 40 mA, respectively, with a scanning speed of 2°/min and a scanning step of 0.02°. Thermogravimetric-differential thermal analysis (TG-DTA; 2000SA, Bruker, Billerica, MA, USA) of the ores samples was performed from room temperature to 1250 °C at a heating rate of 10°C/min to clarify the mineral contents of each sample. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS; VE-9800 SEM, Keyence, Osaka, Japan, and EDAX Genesis, Ametek, NJ, USA) was used to determine the nickel contents of the different minerals by metal mapping. The selected reducing agents are coal and charcoal. The proximate analysis of the reducing agents is listed in table 1. Bentonite was also used as a binder in the pellet making. In addition, limestone was also applied in the pellet composition as a flux in the pellet when reduction process conducted. All raw materials were ground and sieved to get the particle size of -100 mesh. The mixtures of all raw materials in certain composition i.e. limonite ore (80 wt%), reductant (15 wt%), limestone (3 wt%), bentonite (2 wt%) and some water were pelletized in order to obtain the composite pellets with a diameter of pellet approximately 1 cm.

| Reducing Agents | Total Moisture (%) | Volatile Matter (%) | Ash (%) | Fixed Carbon (%) |
|-----------------|-------------------|---------------------|---------|------------------|
| Coal            | 7,01              | 29,50               | 2,79    | 60,70            |
| Charcoal        | 7,69              | 51,74               | 7,24    | 30,66            |

2.2. Reduction methods

Reduction process was carried out in the laboratory using muffle furnace. The dried composite pellet was placed in a ceramic crucible, which was then placed in the muffle furnace when the temperature of furnace reached the reduction temperature. Once the reduction experiments were finished, the samples were taken out of the furnace and cooled to room temperature. The reduced product was dried for weighing and XRD analysis. Thermodynamic analysis using Ellingham diagram shows that the lowest temperature for a complete iron reduction was about 720°C [4]. Based on that analysis, the temperature used in this research was 800 - 1200°C. The reduction time used in this research was 15, 30, 60, 120, and 240 minutes.
3. Results and discussion

3.1. Ore characteristics

The chemical composition of the limonite ore by X-ray fluorescence (XRF) is given in Table 2. X-ray diffraction analysis (XRD) for limonite ore shows that goethite (FeOOH), olivine (MgNiO$_4$Si), and quartz (SiO$_2$) is the essential mineral in the limonite sample. The XRD pattern shows no independent peaks for nickel compounds. The SEM/EDS analysis is a simple method for element mapping and the data can be used to predict the minerals associated with nickel and other metals. Figure 1 shows the metal mapping for each sample, obtained using SEM/EDS analysis. The figure shows that nickel is associated with both magnesium- and silica-containing minerals such as olivine, and also iron-containing mineral i.e. goethite.

The result from DTA shows the temperatures at which thermal reactions such as phase transformation and thermal decomposition take place in a material when it is heated continuously to high temperature, and also the intensity and general characteristics (endothermic or exothermic) of such reactions [5]. The result from TGA shows the weight gain or loss of a material (e.g., a mineral) as a result of absorption or gas release as a function of temperature. The TG-DTA patterns of the sample figure 2 shows that there are three endothermic peaks, at 50, 250, and 1150 °C and one exothermic peak at 838 °C. The endothermic peaks at 50 and 250 °C are associated with moisture evaporation and goethite decomposition, respectively. The endothermic peak at 567 °C arises from dehydroxylation of olivine, whereas the exothermic peak at 805 °C is associated with recrystallization of forsterite (Mg$_2$SiO$_4$); these observations confirm the presence of olivine minerals [6, 7, 8]. The endothermic peak at 1165 °C is assigned to the dehydroxylation of talc sheets, accompanied by the formation of enstatite (Mg$_2$Si$_2$O$_6$) and silica.

Table 2. Chemical composition of nickel limonite ore (mass fraction, %).

| Ore samples | SiO$_2$ (wt%) | Fe | Ni | Co | Mg | Mn | Cr | Al |
|-------------|---------------|----|----|----|----|----|----|----|
| Limonite ore| 34.00         | 19.24 | 0.94 | 0.05 | 11.18 | 0.34 | 1.18 | 1.31 |

Figure 1. SEM/EDS metal mapping of limonite ore.
3.2. Reduction mechanism analysis

The reaction mechanism differences happened because the reactions which took place consist of various step such as carbon oxidation, reducing gas diffusion, and reduction reaction hence the reaction was very complex. From the analysis of the XRD results figure 3, the sample which has been reduced with coal and charcoal show an almost exactly same pattern with both had strong magnetite peaks although on the sample which has been reduced with charcoal had a slightly lower magnetite peak. However, Fe-Ni peaks on the sample which has been reduced with charcoal were higher compared to the sample which has been reduced with coal. It means that reduction reaction of the sample with charcoal as reducing agents proceed more complete because there was more magnetite which has been reduced to Fe. Based on that, it could be concluded that charcoal could be a promising substitute for coal in the reduction process of nickel laterite. From this study, it could be concluded that fixed carbon content in the reducing agents did not always be the most important aspect of choosing a reducing agent. The sample which has been reduced with coal and charcoal show an almost exactly same pattern even they both had different characteristics. The relatively higher volatile matter content in charcoal gave a significant contribution to the reduction process. This was also supported by XRD results of samples on 15 minutes reduction duration which shown that sample which has been reduced with charcoal had stronger magnetite peaks compared to the sample which has been reduced with another reducing agent. It could happen because the volatile matter on charcoal would evaporate on the early reduction stage. The changes of the fraction of reduction reaction also shows that in the early stage of the reduction process. The change of sample which has been reduced with charcoal was higher because of the volatile matter evaporation. Physical properties of the reductant also had an important role in the reduction process. The density of coal was 1.48 g/cm³ and charcoal was 0.72 g/cm³. The smaller density of charcoal than that of coal was indicated that samples which used charcoal as a reducing agent will be more porous.

Figure 2. TG-DTA pattern of limonite ore
3.3. The effect of reduction temperature and time on the reduction process

The reaction of iron and nickel reduction will be more completed on longer duration of the reduction process. The reduction reactions were also more completed at higher reduction temperature. It could be shown by the color changes of pellet composite during reduction process as depicted in figure 4. The color of the raw material is red and the color becomes black and grey after reduction process occurs. From figure 4, it can be seen that the color of pellet composite during reduction at temperature of 800°C and 900°C did not change. However, the color of pellet become black and gray at the reduction temperature of 1100°C. The changes of color at 1100°C was started on the 15 minutes of reduction time. This could be mean that the rate of reduction reaction is faster at higher temperature. The losses of samples weight also happen faster at the higher temperature.

Figure 3. XRD analysis of reduced limonite, (a) coal as reducing agent; (b) charcoal as reducing agent, at 1100°C and 15 minutes of reduction time.
Figure 4. The color changes of pellet composite during reduction process.

4. Conclusion
Charcoal performance as a reducing agent in the nickel laterite reduction process is well enough compared to coal. Reduction temperature and reduction time significantly influence the growth behavior of Fe-Ni metallic particles. The reduction degree of limonite ore increases with increasing reaction temperature and prolonging reaction time.

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