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Reduction behavior of medium grade manganese ore from Karangnunggal during a sintering process in methane gas

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Abstract. In this investigation, manganese has been produced from medium grade manganese ore from Karangnunggal mine (West Java, Indonesia). The effects of keeping it at a temperature of 1200°C in methane gas on the structural properties have been studied. The material's properties have been characterized on the basis of the experimental data obtained using X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared (FTIR) spectroscopy. It has been found that MnO₂ is reduced to hausmannite (Mn₃O₄), manganosite (MnO) and manganese carbide (Mn₇C₃). An increase of the keeping time up to 45 minutes during the sintering process leads to an increase of the MnO concentration, while at 90 minutes, the concentration decreases. The analysis based on the interpretation of both XRD patterns and FTIR spectrum allows one to explain the blockage in the particle surface of the ore by an increase of the carbon deposition.

1. Introduction

The manganese is one of the most abundant minerals in nature and important engineering material. It is well-known that in the industrial processes and technical devices, the manganese is an environmentally friendly and cheap material. It has a long history as an electrode material for energy storage systems with high energy and power density. Many studies have been carried out in order to investigate the properties of manganese and to estimate its applicability to various energy storage systems e.g. fuel cells, electrochemical capacitors, and lithium-ion batteries. A promising and actively studied variety of the latter are namely the lithium batteries. The manganese has a porous microsphere morphology composed of MnO and Mn₃O₄ nanoparticles, which is very appropriate for its use as appropriate anode materials for lithium-ion batteries that exhibit a reversible capacity of 757 mAh/g [1]. When its morphology changes from microsphere to sponge-like porous, its capacity increases to 869 mAh/g [2]. From these studies, it has been found that the lithium batteries can reach an energy density up to 800 mAh/g and power density of 340 W/kg. Such technological and economic benefits (high number of charge-discharge cycles; faster charge-discharge; absence of disposable parts and environmentally harmful components; high efficiency up to 90%; low thermal load; safety and reliability) make this material a promising energy storage media for many modern electronic devices, such as digital cameras, cell phones, MP3 players and high-tech toys.

The rapid progress in the development and commercialization of battery systems in consumer electronics market of the modern society drives increasing demand for production of manganese. In order to meet the requirements of a rapid development of the electrical storage power industry and especially to provide an electrode material for batteries, the utilization of medium-grade manganese ore has become increasingly important. The manganese is usually obtained by reducing manganese oxide in manganese ores using a variety of different methods. In this respect, a promising approach is to introduce an appropriate gas medium in which the ore is immersed during the sintering process. In such a way, the manganese ore can be reduced to ferromanganese carbide keeping the sintering temperature of 1200°C for 45 minutes and exposing it to CH₄-H₂-Ar gas mixtures [3]. Sorensen et al., have studied the phase composition of the ore sintered at 800 – 1200°C in different media [4]. It has been found that MnO₂ in air is reduced to Mn₂O₃ and Mn₃O₄, in hydrogen is reduced to MnO₂ and MnO and iron oxides to metallic iron, while in CO gas it is reduced only to MnO. Furthermore, it has been found that in methane gas the manganese MnO₂ phase of the ore decomposes to form Mn₂O₃ phase and then transits to Mn₃O₄ at temperatures above 850°C and to MnO at 950°C [5]. Recently, by heating in the same medium, the manganese ore has been reduced to carbide Mn₇C₃ and Mn₅C₂ at temperatures under and above 1200°C, respectively [6]. From these studies, it has been found that manganese ores of different origin have different mineralogy which affects their reduction properties. In this paper, we present the results of our study on the structural properties of the medium grade manganese ore of Karangnunggal sintered at a temperature of 1200°C and exposed to the methane gas.

2. Experimental procedure

2.1 Preparation of manganese ore powder

The manganese ores were obtained from the artisanal mining area in Karangnunggal, Tasikmalaya, Indonesia. The materials for the samples were selected manually, cleaned by washing with water, and then dried in the sun. The dried manganese ores were crushed into small pieces with an area of approximately 1 cm². Then, they were ground using a jar mill to pass through a 150 mesh sieve. The manganese ore powder was stored in a desiccator for further treatment.

2.2 Annealing the manganese ore

The powder samples were placed into a porcelain crucible and then inserted into a horizontal furnace. The powders were sintered with a controlled heating rate of 2°C/min up to the temperature of 1200°C in the air. Then the temperature was kept constant at 1200°C for 15, 30, 45 and 90 minutes in methane gas flow at a speed of 1000 mL/min. The cooling was performed by natural convection after turning off the electric furnace and leaving the samples inside.

2.3 The method used for characterizing the manganese ore

The XRF measurements were carried out on a Philips PW2400 wavelength dispersive spectrometer. The calibration was performed following the prescribed standard procedure. In addition, some correction factors for determining the influences of other elements were calculated. The measurement conditions were 24 kV – 100 mA, collimator mask 27 mm and Rh-X ray tube as an excitation source. A gas flow detector was used for controlling the rate of the gas flow. Furthermore, XRD was used to determine the change of the crystalline phase for samples sintered at 1200°C for 15, 30, 45 and 90 minutes and it was performed using a Smartlab X-ray diffractometer with filtered Cu K α radiation at a wavelength of 0.15418 nm. The intensity of the diffracted X-ray was measured as a function of the diffraction angle 2θ ranging from 10 to 90 degree. We used scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) in order to study the small scale relationships between textures and to measure the elemental distributions and abundances. The images were taken at a magnification of 5000 x at 20 kV. The Fourier transform infrared spectroscopy (FTIR) was performed on a SHIMADZU-FTS 8400 FTIR using KBr pellet techniques in the 400 – 4000 cm⁻¹ wavenumber range. The resolution and number of scans used in FTIR collection were 2.0 cm⁻¹ and 16, respectively.

2 Result and discussion

Table 1 shows the chemical composition of oxide contents and the loss on ignition for medium-grade of Karangnunggal manganese ore. The ore contains MnO as the main constituents at about 46.80 wt.%. The content of such magnitude is classified as a medium-grade ore [7]. It is also accompanied by a significant amount of SiO₂, CaO, Fe₂O₃, and Al₂O₃. It can also be seen that the ore contains small amount of MnO. The loss on ignition is associated with the presence of hydroxides, organic matter and volatile components.

Table 1. Chemical composition for medium-grade manganese ore of Karangnunggal.

Chemical composition	Medium-grade manganese ore of Karangnunggal (wt.%)
MnO ₂	46.80
SiO ₂	7.29
CaO	5.95
Fe ₂ O ₃	3.61
Al ₂ O ₃	2.71
MgO	2.46
BaO	1.54
Na ₂ O	1.07
P ₂ O ₅	0.80
SrO	0.66
K ₂ O	0.368
CuO	0.108
TiO ₂	0.0777
Cl	0.0561
V ₂ O ₅	0.0485
Co ₃ O ₄	0.0256
SO ₃	0.0207
Cr ₂ O ₃	0.0178
NiO	0.0144
Y ₂ O ₃	0.0057
ZnO	0.0051
Ga ₂ O ₃	0.0027
LOI	26.07

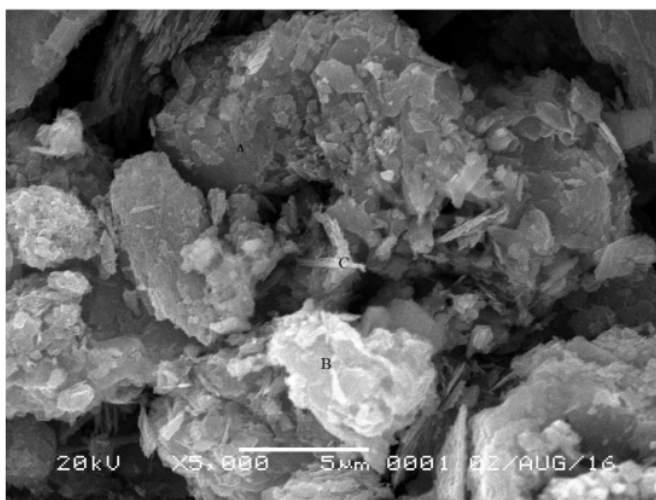


Figure 1. SEM image of medium-grade manganese ores from Karangnunggal.

Figure 1 shows SEM image of medium-grade manganese ores from Karangnunggal. It can be observed that the ore particles are agglomerated forming dense grains with different texture and morphology. The EDS reveals that the irregular-shaped grains with dark contrast marked as A are associated with the presence of manganese [8]. The large brighter grains marked as B are associated with the presence of calcium, while the relatively smaller grains with bright texture and smooth surfaces marked as C are quartz [9].

Figure 2 shows some representative XRD patterns for the raw material samples of medium-grade manganese ore from Karangnunggal and samples sintered at a temperature of 1200°C with varying keeping time in methane gas. It is clear from figure 1 that the raw material sample consists of manganese oxide mainly in the form of pyrolusite (MnO_2) and quartz (SiO_2). For the sample sintered for 15 minutes, MnO_2 disappears and is replaced by three new phases, namely hausmannite (Mn_3O_4), manganosite (MnO) and manganese carbide (Mn_7C_3). The hausmannite (peak 1) appears at $2\theta = 18.31^\circ, 32.59^\circ, 38.29^\circ, 56.37^\circ$ and 58.78° (JCPDS 24-0734), manganosite (peak 4) at $2\theta = 36.39^\circ, 40.69^\circ, 60.33^\circ,$ and 74.61° (JCPDS 00-001-1206), and manganese carbide (peak 5) at $2\theta = 44.47^\circ, 51.18^\circ,$ and 54.12° (PDF 01-075-1498). At a temperature of 1200°C the keeping time does not have any effect on the formation of crystals and the crystalline phases remain almost unchanged in the time range from 15 to 90 minutes. The intensity of MnO at $2\theta = 36.39^\circ$ increases with the rise of the keeping time up to 45 minutes. The increase in the intensity can be explained by an increase of the degree of crystallinity of MnO. This crystallization affects significantly the grain growth and the sintering process provides energy, which is necessary for bonding the particles together and removing the porosity simultaneously [10]. For the sample sintered for 90 minutes, the intensity of MnO is reduced. At longer keeping times the excess reaction of the methane gas and manganese oxide in the ore causes an increase of carbon deposition [3]. As a result, it blocks the particle surface and then hinders the reduction process of manganese oxide.

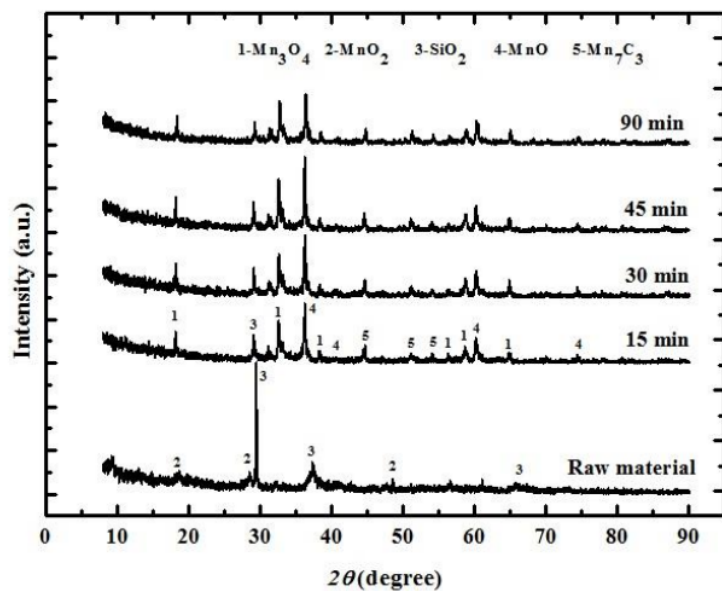


Figure 2. XRD patterns for medium-grade manganese ore from Karangnunggal with varying the keeping time at a temperature of 1200°C in methane gas.

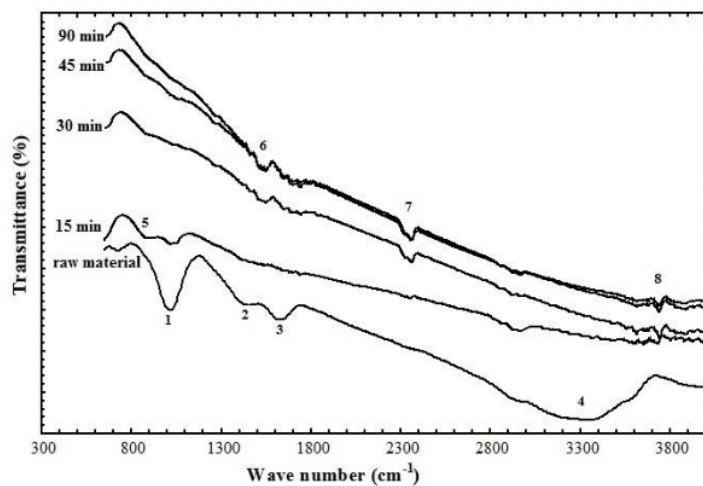


Figure 3. FTIR spectra for medium-grade manganese ore from Karangnunggal with varying the keeping time at a temperature of 1200°C in methane gas.

In figure 3, we show the Fourier transform infrared (FTIR) spectra for medium-grade manganese ore varying the keeping time at a temperature of 1200°C in methane gas. For the raw material sample, the band (1) identified at about 1020 cm^{-1} corresponds to pyrolusite (MnO_2). Additionally, the weak band

(2) at around 1450 cm^{-1} and the band (3) at 1640 cm^{-1} correspond to the existence of large numbers of residual hydroxyl groups, which imply the O-H vibrating mode of traces of adsorbed water [11-13]. In the sample sintered for 15 minutes, the characteristic bands of pyrolusite are gradually reduced as the keeping time increases and eventually disappear completely above time of 15 minutes. Then they are replaced by three new bands (5, 7 and 8) attributed to hausmannite [14], C=O stretching mode [15] and SiOH at about 895 cm^{-1} , 2370 cm^{-1} and 3750 cm^{-1} [16], respectively. The appearance of C=O stretching mode arises from absorption of atmospheric methane and manganese oxide of the ore. The intensity of this band increases with increasing the keeping time, indicating an increase of carbon deposition on the surface of manganese oxide. For the sample sintered from 30 to 90 minutes, there is an absorption band (6) at about 1552 cm^{-1} attributed to asymmetric O-C-O stretching [17].

4. Conclusion

Manganese ore was produced successfully from medium-grade ore of arangnunggal by controlling the keeping time in methane gas flow during the sintering process. The results presented in this study show that the existing phases in raw material are manganese oxide in the form of pyrolusite (MnO_2) and quartz (SiO_2). In the sample sintered at 1200°C for 15 – 90 minutes, the crystalline phases are hausmannite (Mn_3O_4), manganosite (MnO) and manganese carbide (Mn_7C_3). An interesting phenomenon has been observed analyzing the XRD pattern and FTIR spectra of the sample sintered for 90 minutes. It manifests itself in the finding that for long times of sintering in methane gas the reduction process for manganese oxide ore is considerably hindered.

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