

Carbothermal reduction of calcined and mechanically activated manganese carbonate ore

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Abstract: The carbothermal reduction of calcined and mechanically activated manganese carbonate ore with graphite under an argon atmosphere was investigated at temperatures between 1100 and 1300°C and the effects of mechanical activation on the ore structure were analysed by X-ray diffraction, scanning electron microscopy and particle size analysis. The activation procedure led to amorphisation in the ore and accelerated the degree of reduction in the mixture of the calcined ore and graphite.

Key words: carbothermal reduction, mechanical activation, ferromanganese

Introduction

Manganese is an element which has numerous applications in industry. Roughly 95% of all manganese units are used in iron and steel production nowadays and the remaining parts are used for the production of dry cell batteries and for certain chemical aims. The first utilization of it can be traced back to ancient times. Spartans used the presence of manganese in the iron ore to make their steel weapons superior to their opponents. Ancient Egyptians and Romans used it to control the color of glass and to glaze the surface of pottery in brown and this had been the main use for manganese until the 18th century (Elyutin, 1961).

Manganese is used as an alloying element for its beneficial properties such as strength, hardenability, toughness and workability of ferrous products and it is also essential to iron and steel production by virtue of its sulphur-fixing, deoxidizing, and alloying properties. Most of the manganese used in iron and steel industry are in the form of ferromanganese and silicomanganese. The addition of manganese can be in the form of its ore during the ironmaking or as ferromanganese alloy in the steelmaking stage (Akıl, 2006).

Akdogan & Eric (1994) studied characteristics of carbothermic reduction of manganese ores by classical thermogravimetric techniques in the temperature range 1100°C and 1350°C. They stated that a two stage mechanism has been proposed. First stage includes the reduction of higher oxides to their lower states by carbon and carbon monoxide. During this rapid initial stage the products were porous to varying degrees. In this stage rate control appears to be mixed, both inward diffusion of carbon monoxide and outward diffusion of carbon dioxide across the product layer and the reaction of carbon monoxide on the pore walls of oxide phase play important roles. During the second stage, the reaction is limited to the interface between manganese oxide and a mixed carbide of iron and manganese. The chemical reaction between the oxide and carbon appears to be the rate controlling mechanism.

Welham (2002) studied the effect of extended milling on the carbothermic reduction of a manganese ore using a combination of thermal analysis and X-ray diffraction (XRD). Thermodynamic modelling indicated that reduction of MnO_2 to MnO was possible at 25 °C, although no reaction was found to occur during milling of the ore with graphite for up to 10 h. For a physical mixture, cryptomelane, KMn_8O_{16} , reduced at 500 °C and braunite, Mn_7SiO_{12} , at 700 °C after 10 h milling these temperatures were reduced by 200 °C. The initial product was Mn_3O_4 , although in the 10-h-milled powder, the reduction of braunite may have been directly to MnO . Reduction at 600 °C only formed Mn_3O_4 in the unmilled powder but the major product in the 10-h-milled powder was MnO . The increased extent of reaction after premilling may allow current processing plants to expand their throughput without increasing the size of reduction kiln.

Eric & Burucu (1992) studied the kinetics of reduction of the manganese ore from Mamatwan mine in South Africa. They observed that the rate and degree of reduction increased with increasing temperature and decreasing particle size. In the early stages of reduction, up to about 4 minutes of reaction time corresponding to about 30% reduction, reduction of higher oxides of manganese and iron (Mn_2O_3 and Fe_2O_3) to MnO and FeO, respectively, was observed. This stage was possibly controlled by diffusional process across the boundary layer between the solid phases. An apparent activation energy of 61.03 kJ was calculated for this diffusional process. Metallization started as random nucleation of iron, which subsequently was carburized around MnO grains inside the particle. Also, after about 30% reduction, the formation of a silicate phase was observed. Up to 70% reduction at 1350°C, reduction rate was possibly controlled by chemical reaction between the oxide and gaseous phases for which an activation energy of 153.32 kJ was calculated. The later part of the process proceeded by the reduction of MnO, covered by either the carbide or silicate phase, by carbon dissolved in the carbide phase $(Mn, Fe)_5C_2$. Diffusion of Mn^{2+} ions in the oxide phase is the most likely rate determining step for this stage for which an apparent activation energy of 310.4 kJ was found.

The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering that the thermal activation may be omitted entirely. In this process, the complex influence of surface and bulk properties occurs. The mineral activation leads to a positive influence on the reaction kinetics, an increase in surface area and further phenomena. Mechanical activation by high energy milling is an innovative procedure that improves the efficiency of mineral processing because of several factors, most importantly the formation of new surfaces and the creation of lattice defects (Balaz, 2008).

In this study, manganese carbonate ore was calcined and then activated mechanically in a planetary mill. The amorphization in the ore was calculated by using of X-ray diffraction data. The carbothermal reduction of the non-activated and activated (60 min) ore were studied between 1100°C and 1300°C, the effect of mechanical activation on the carbothermal reduction was studied.

Materials and Method

Manganese carbonate ore used in the experiments was obtained from Denizli-Tavas region in Turkey. The ore was ground to a size of <100 μm and calcined at 1000°C for 2 h. Manganese and iron contents in the ore was 39.69% and 5.45%, respectively. Graphite consisting of more than 98% carbon was used as the reductant.

The mechanical activation of the calcined ore was performed in a Planetary Mono Mill Pulverisette 6 under the following conditions: the weight of the sample was 10 g; the weight and diameter of tungsten carbide (WC) balls were 200 g and 10 mm respectively; the grinding bowl was 250 mL WC; the grinding times were 0, 15, 30, 60, 90 and 120 min; the speed of the main disk was 600 $rev\ min^{-1}$; the grinding process was dry.

X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu $K\alpha$ radiation. A JEOL 6060 LV scanning electron microscope was used for both the morphological analysis of the calcined ore after mechanical activation.

Reduction experiments were carried out in a horizontal furnace in the temperature range of 1100–1300°C under an argon atmosphere. Calcined manganese ore (2 g) and graphite (2 g) were thoroughly mixed, fed to an alumina crucible and placed inside the furnace. The furnace was heated to the reduction temperature under an argon atmosphere. The argon flow rate was 150 $mL\ min^{-1}$. At the end of the reduction time, samples were cooled in an argon flow. The reduction temperatures (1100, 1200 and 1300°C), reduction times (1, 3 and 5 h) and milling times (0, 15, 30 and 60 min) were investigated as parameters.

The degree of amorphization (A) of the mechanically activated manganese ore was calculated from equation (1),

$$A\% = \left(1 - \frac{B_0 I_X}{B_X I_0}\right) \times 100 \quad (1)$$

where I_0 is the integral intensity of the diffraction peak for non-activated manganese ore, B_0 is the background of the diffraction peak for non-activated manganese ore, and I_X and B_X are the equivalent values for the activated manganese ore.

Reduction degrees is calculated using equation (2), assuming that CO is the only gaseous element generated during reduction reactions.

$$R(\%) = \frac{^{16}/_{28}CO_{Evolved}}{RO_{Total}} \quad (2)$$

where $R\%$ is reduction degree, $CO_{Evolved}$ is the total weight of CO generated from the mixture of the ore and graphite and RO_{Total} is the total weight of the removable in the mixture from reducible oxides in the ore.

Results and Discussion

The X-ray diffraction analysis of non-activated and activated manganese ore is given in Fig. 1. Comparing the peaks in the six diffraction patterns between 20 and 60° shows that the height of the diffraction peaks decreases after mechanical activation. This result reflects the partial amorphisation and structural disordering in the ore. Mechanical activation has already been reported to amorphise mineral particles (Balaz, 2008). Tromans and Meech (2001) found that mechanical activation results in a large number of dislocations and associated strain fields, which may lead to an overall decrease in long range lattice periodicity. This may be interpreted as the formation of a metastable amorphous phase because extended milling causes X-ray diffraction peaks to exhibit line broadening or disappear altogether. The degree of amorphisation of manganese ore as a function of mechanical activation time was calculated by equation (1) and the degree was 68.72% for Mn_2O_3 and 87.28% for Mn_3O_4 after 15 min of activation. These values increased to 78.6% for Mn_2O_3 and 94.38% for Mn_3O_4 after 120 min of activation. Disordering in the bulk of the manganese ore increased with the time of mechanical activation.

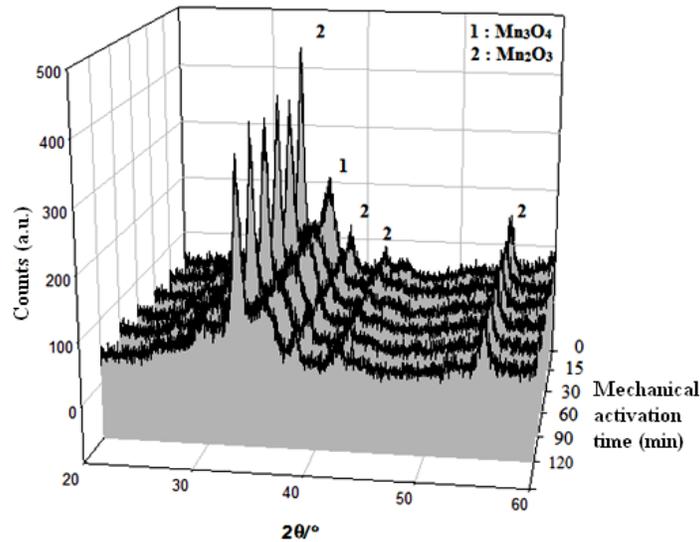


Figure 1: X-ray diffraction patterns of non-activated and activated manganese ore

D_{10} , D_{50} and D_{90} sizes corresponding to the particle sizes at the 10%, 50% and 90% points on the cumulative distribution for the non-activated and activated samples are shown in Table 1. Figure 2 shows the particle size distribution of the non-activated and activated (1 h) ore.

Table 1: Particle size analysis of the non activated and activated manganese ore samples

Samples	Particle size (μm)		
	$D_{10}(\mu\text{m})$	$D_{50}(\mu\text{m})$	$D_{90}(\mu\text{m})$
Non-activated ore	1,090	3,320	56,97
Activated ore (15 min)	0,625	1,121	8,97
Activated ore (30 min)	0,651	1,302	9,14
Activated ore (60 min)	0,668	1,351	8,27
Activated ore (90 min)	0,674	1,361	8,20
Activated ore (120 min)	0,671	1,345	7,49

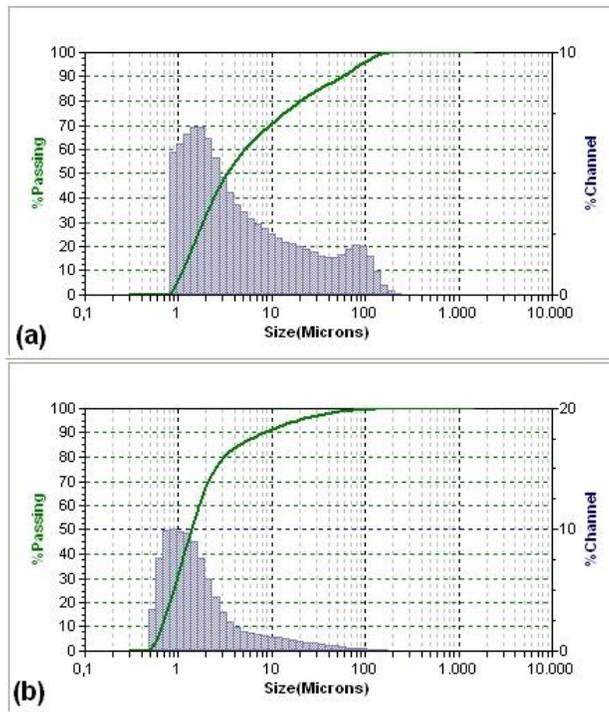


Figure 2: Particle size analysis of non-activated and activated (60 min) manganese ore

Reducible oxides such as Fe_2O_3 , Mn_2O_3 and Mn_3O_4 in the ore are reacted with graphite under argon atmosphere to form carbides according to following reactions. Reduction degrees for the non-activated and activated (60 min) manganese ore are given in Table 2.

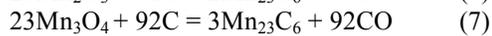
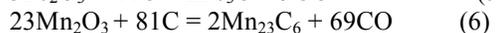
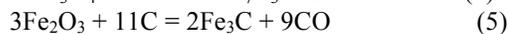
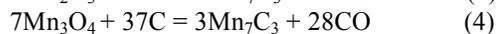
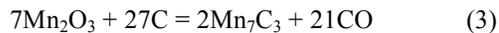


Table 2: Effect of reduction temperature and time on carbothermal reduction degree of non-activated and activated (60 min) manganese ore

Reduction temperature (°C)	Reduction time (h)	Reduction degree (%)	
		Non-activated ore	Activated (60 min) ore
1100	1	34,29	41,70
	3	43,97	50,89
	5	51,14	57,10
1200	1	55,11	70,43
	3	70,55	80,30
	5	79,43	89,17
1300	1	71,77	76,31
	3	79,98	84,58
	5	84,82	90,03

The reduction of manganese ore with graphite is an endothermic reaction and the reaction rate increases with increasing temperature. In the reduction of the non-activated ore, the degrees of reduction are 34.29% at 1100°C and 71.77% at 1300°C for a reduction time of 1 h. In the reduction of the activated (60 min) ore, the degrees of reduction are 41.70% at 1100°C and 76.31% at 1300°C for a reduction time of 1 h. The degrees of reduction are increased by mechanical activation due to structural disordering in the ore. Higher degrees of reduction were obtained at lower temperatures. Ferromanganese formation in high percent, up to 90%, was obtained for the activated ore at 1200°C for 5 h and this value was about 80% for the non-activated ore at the same reduction conditions.

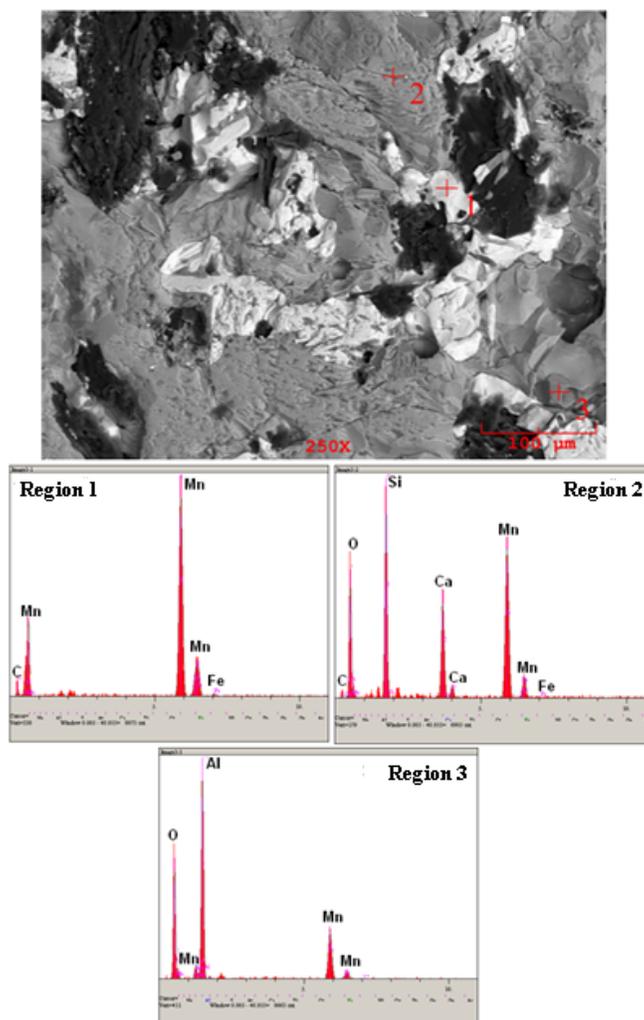


Figure 3: SEM/EDAX analysis for the activated and reduced ore (1300°C, 1 h)

Scanning electron micrographs of the activated and reduced sample are presented in Fig. 3. As seen in these figures, three zones can be observed on the polished sections of the reduced samples. The white zone (region 1) represents metallic beads, the grey area (region 2) is the original unreacted ore structure. Region 3 is the affected zone. The metallic portion of the sample is rich in manganese. Same regions are observed in SEM/EDAX analysis for the non-activated and reduced ore.

The XRD analysis of the activated and reduced manganese ore is given in Fig. 4. After carbothermal reduction, formation of manganese carbides (Mn_7C_3 and $Mn_{23}C_6$) and iron carbide (Fe_3C) was observed in the product. The other phases are carbon as graphite, calcium silicate (Ca_2SiO_4) and alumina (Al_2O_3).

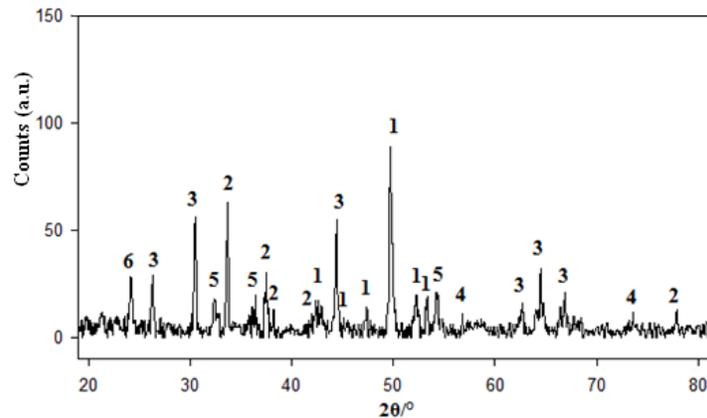


Figure 4: XRD analysis of the activated and reduced (1300°C, 1 h) ore.
(1- Mn_7C_3 , 2- $Mn_{23}C_6$, 3-C, 4- Fe_3C , 5- Al_2O_3 , 6- Ca_2SiO_4)

Conclusions

The non-activated and activated manganese ore were reduced at temperatures between 1100 and 1300°C in the presence of graphite. The results indicate that high energy ball milling is effective for the reduction of manganese ore with graphite. The mechanical activation process increased the degrees of reduction and metallisation in the ore due to structural disordering in the ore structure. The reduction degrees of activated ore were higher than those of non-activated ore at the same reduction temperatures and times.

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