INVESTIGATION OF CARBOTHERMAL REDUCTION OF MECHANICALLY ACTIVATED CHROMITE WITH THERMAL ANALYSIS

Fatih APAYDIN[a], Kenan YILDIZ[b]

[a] *Bartin University, Metallurgy & Materials Engineering, Bartin, Turkey, fapaydin@bartin.edu.tr*
[b] *Sakarya University, Metallurgy & Materials Engineering, Sakarya, Turkey, kenyil@sakarya.edu.tr*

Abstract

Ferrochromium is one of the important alloying materials used in the production of stainless and high-alloy ferritic steels. The carbothermal reduction of chromite with graphite under argon atmosphere was studied by differential thermal analysis up to 1350 °C and the effects of mechanical activation on the chromite structure was investigated using of X-ray diffraction analysis and scanning electron microscopy. The results showed that the carbothermal reduction temperatures of reducible oxides in the chromite spinel were decreased after mechanical activation, due to structural disordering in chromite spinel.

Keywords: Chromite, ferrochromium, mechanical activation, carbothermal reduction

1. INTRODUCTION

Chromite is an oxide of iron and chromium having chemical composition $FeO{\cdot}Cr_2O_3$ and belonging to the spinel group. But in nature, the ferrous iron is generally replaced partially by magnesium and the chromium by ferric iron or aluminium. Thus, its compositions is represented by the generalized formula $(Mg, Fe^{2+})O{\cdot}(Cr, Al, Fe^{3+})_2O_3$ [1, 2].

Carbothermic reduction of complex chromite and natural chromite ores was investigated by many researchers to determine reduction kinetics and mechanisms of reactions. In these studies, it was reported that the carbothermic reduction process of the chromite is complex procedure and depends on origin of ore, particle size, reaction temperature and time, reducing materials, reduction atmospheres and morphology, etc. [3-10]. Soykan et al. [6] developed a generalized rate model based on an ionic diffusion mechanism and proposed a mechanism consisting of four stages for the reduction of chromite spinel phase:

(1) $Fe^{3+} \rightarrow Fe^{2+}$ transformation on the surface of chromite and soon after the reduction of Cr^{3+} cations to Cr^{2+}

(2) The reduction of Fe^{3+} settled under the surface (diffusion to the centre of particle)

(3) Diffusion of Fe^{2+} cations to the surface and reduction of them to the metallic state

(4) The reduction of Cr^{3+} cations, transformation of Cr^{2+} to Cr after the completion of iron reduction and finally, the formation of $MgAl_2O_4$ spinel.

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, to an increase surface area and to further phenomena. Mechanical activation by high-energy milling is an innovative procedure, that improves the efficiency of mineral processing via several factors, most importantly due to the formation of new surfaces and the creation of lattice defects. High energy ball milling can realise at room temperature some chemical reactions which normally take place at very high temperatures but some other reactions do not occur directly during milling at room temperatures, but occur with a higher reaction rate during the subsequent low temperature annealing process [11-13].

In this study, the carbothermal reduction of Turkish chromite with graphite with thermal analysis (TG/DTA) up to 1350 °C under argon atmosphere and the effects of mechanical activation on the chromite structure and the reduction process were investigated.

2. EXPERIMENTAL METHODS AND MATERIALS

The chromite used in the experiments was obtained from Mugla region, south-west of Turkey. The ore was ground to a size of <100 μm. The chemical analysis of the chromite spinel is given in **Table 1**. Graphite consisting of more than 98 % carbon was used as the reductant.

Table 1 Chemical analysis of chromite spinel

	Reducible oxides			Non-reducible oxides					
Oxides	Cr_2O_3	FeO	Fe_2O_3	MgO	Al_2O_3	SiO_2	CaO	LOI*	Total
Content (wt.%)	46.72	13.33	1.82	15.20	15.30	5.57	0.21	1.87	100

*Loss on Ignition

Mechanical activation of chromite was performed in a Planetary Mono Mill Pulverisette 6 under 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, 30 and 60 min; the speed of the main disc 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 Kα radiation. A JEOL 6060 LV scanning electron microscope was used to observe the phase transformations in the products after reduction. Thermal analysis (TG/DTA) of chromite + graphite mixing was performed by TA Instruments SDT

Q 600 at heating rate of 10 °C/min under argon atmosphere.

3. RESULTS AND DISCUSSION

The X-ray diffraction analysis of non-activated and activated (30 and 60 min) chromite is given in **Fig. 1**. Comparing the peak, which is the highest diffraction peak of chromite, between 34 and 38° (2θ) showed that the height of the chromite peak decreased after mechanical activation. This result reflects the partial amorphization and structural disordering in chromite. Tromans & Meech [14, 15] 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, since extended milling causes X-ray diffraction peaks to show line broadening or to disappear altogether.

The differential thermal analysis (DTA) of non-activated chromite and activated (60 min) chromite with graphite under argon atmosphere was given in **Fig. 2**. The reduction of chromite with graphite is an endothermic reaction and reaction rate increases with increasing temperature. The iron content of chromite starts to reduce over 950°C, which is seen a broaden endothermic peak. In the early stage under 1200 °C, transformation of Fe^{3+} to Fe^{2+} and metallic iron formation, as given in Eqs. (1 & 2) are completed.

$$(Fe^{2+},Mg^{2+})(Fe^{3+},Cr^{3+},Al^{3+})_2O_4 \rightarrow (Fe^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \quad (1)$$

$$(Fe^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \rightarrow Fe + (Fe^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \quad (2)$$

In the stage over 1200 °C, transformation of chromite spinel and formation of $MgAl_2O_4$ phase, as given in Eqs. (3 & 4) are actualized.

$$Fe + (Fe^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \rightarrow (Fe+Cr) + (Cr^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \quad (3)$$

$$(Fe+Cr) + (Cr^{2+}, Mg^{2+})(Cr^{3+},Al^{3+})_2O_4 \rightarrow (Fe+Cr) + MgAl_2O_4 \quad (4)$$

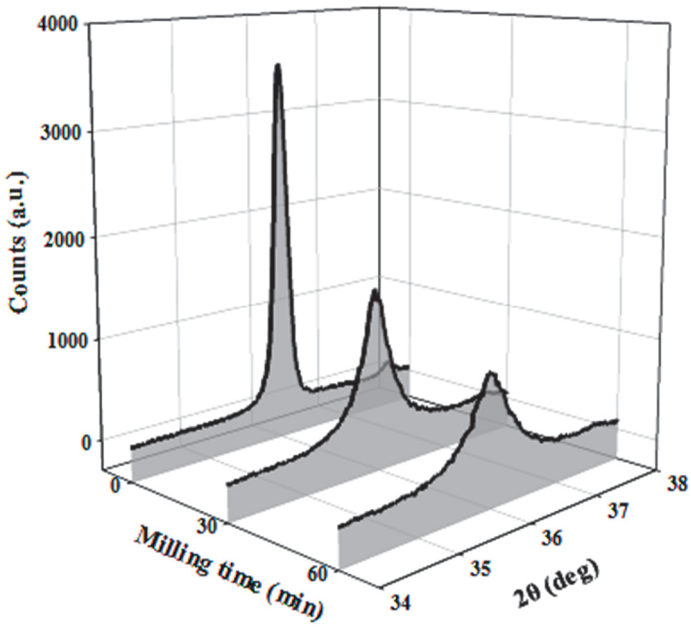

Fig. 1 X-ray diffraction analysis of non-activated and activated chromite samples

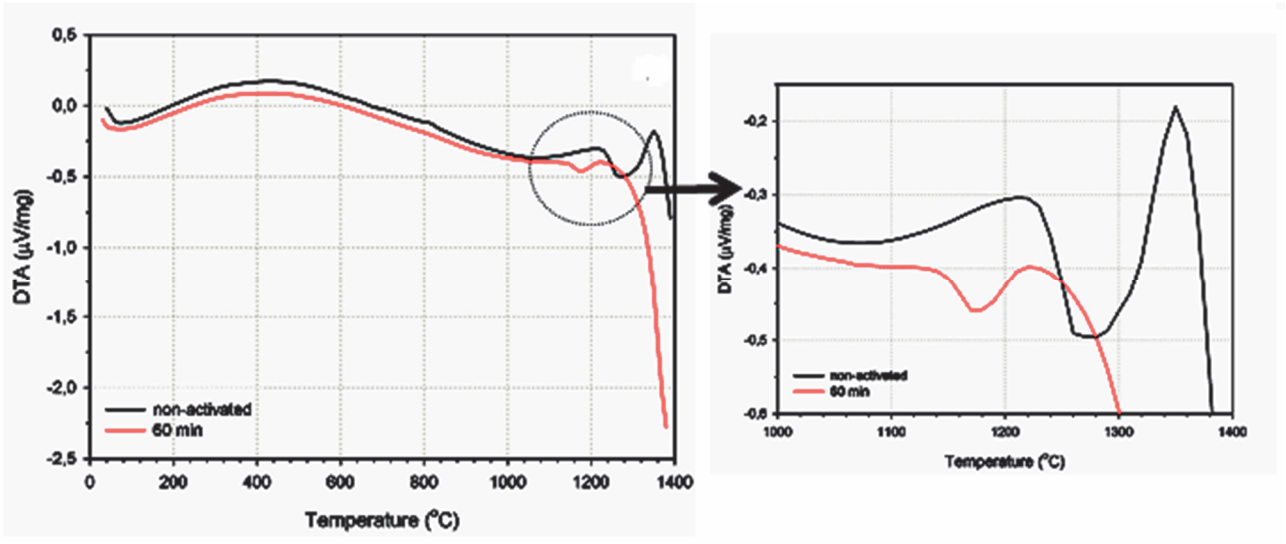

Fig. 2 Differential thermal analysis of non-activated and activated (60 min) chromite + graphite samples

The reduction region of chromite with graphite in the DTA is given in detail on the right of the **Fig. 2**. As seen from the figure, the reduction peak of chromium oxide is an endothermic peak at 1280 °C for non-activated chromite. After mechanical activation for 60 min, this peak temperature is decreased to 1170 °C and the reduction of chromium oxide started after 1140 °C. In our previous study [16] the reduction degrees for non-activated chromite were obtained as 11.5 % at 1100 °C and 38.2 % at 1250 °C for 1 h reduction time. These values for 60 min activated chromite under same conditions were 16.7 % at 1100 °C and 60.3 % at 1250 °C. It was reported that the higher reduction degrees were obtained at lower temperatures. As seen from DTA graphs, temperature peaks of endothermic reduction of chromite were decreased with mechanical activation.

Scanning electron micrographs of the reduced samples was presented in **Figs. 3a, 3b** for non-activated sample (a) and 60 min activated sample (b). As seen from these figures, there are some differences between the samples on the microstructure. White zone in micrographs (No. 1) represents metallic beads, the grey areas show the affected zone or the spinel structure (No. 2) and the dark area is indicating the original, unreacted chromite structure (No. 3). Generally chromite particles contain a variety of defects such as dislocations, inclusions, silicate veins, porosities and fractures. The polished section of the reduced non-activated chromite sample presents a quite large of rounded, spherical and lath of metallic beads along the imperfection or near the edge of the particle.

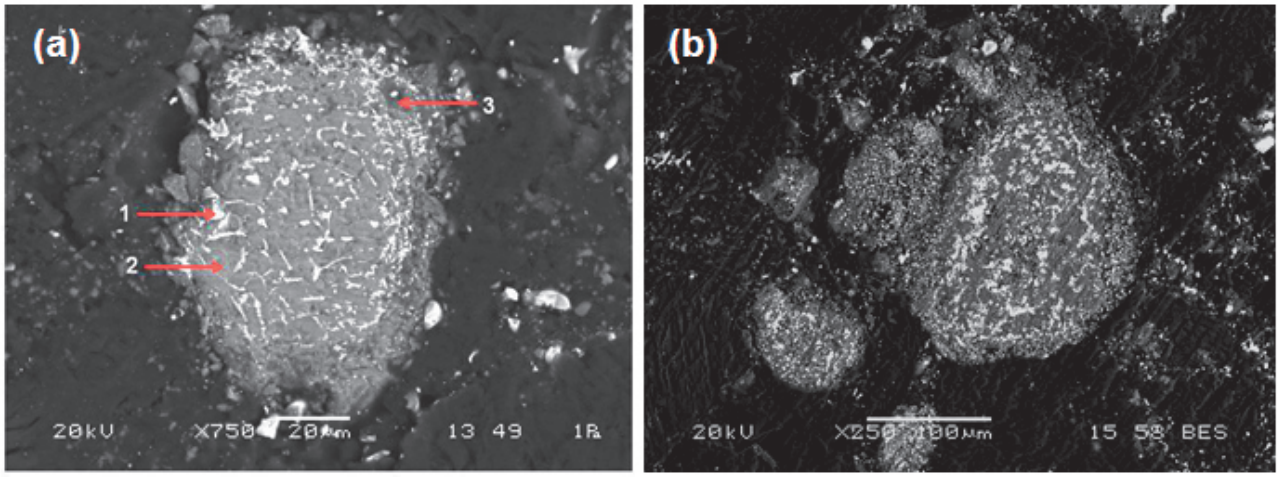

Fig. 3 Scanning electron micrographs of reduced samples at 1250 °C for non-activated (a) and 60 min activated sample (b)

In the scanning electron micrograph of the activated sample, the two zones are metallic beads in white colour and the affected areas in grey colour. The metallic beads are more regular spherical shapes and homogenously distributed in the activated sample than the non-activated sample. There are also common features between two samples. There are increase in size and amount of the metallised part in the both samples with increase in time and temperature. As a result of the fine particle size, the generalised three zones may not seen in the activated samples. The homogenous distribution of the metallic beads in the activated sample could be resulted because of the more contact points between chromite and graphite particles. The reduction in the particle size of the chromite may decrease the imperfections of the sample The amount of metallic beads and the degree of reduction are higher in the activated sample than the non-activated one.

CONCLUSION

The effect of mechanical activation on the carbothermal reduction of chromite with graphite was investigated by differential thermal analysis and the results were showed that the high-energy ball milling is effective on the reduction of chromite with graphite. Increase in surface areas by reducing particle size results in more contact points in the mixture of the activated chromite with graphite. Decrease in the imperfections of the chromite particle has also resulted more homogenous and larger metallisation all around the activated chromite. The mechanical activation was decreased the reduction temperatures of reducible oxides in the chromite spinel, due to structural disordering in the chromite structure.

REFERENCES

[1] CHATTERJEE, K.K. *Uses of metals and metallic minerals*. New Age International Ltd. Pub., New Delhi, 2007.

[2] YARKADAS, K., YILDIZ, K. Effects of mechanical activation on the soda roasting of chromite. *Canadian Metallurgical Quarterly*, 2009, Vol. 48, No. 1, p. 69.

[3] BARNES, A.R., FINN, C.W.P., ALGIE, S.H. The reduction and smelting of chromite concentrate of low chromium-to-iron ratio. *Journal of South African Institute of Minerals and Metallurgy*, 1983, Vol. 83, No. 3, p. 49.

[4] HEALY, G.W. Carbon reduction of chromites in Bird River and other ores and concentrates at 1200 - 1700 °C. *Canadian Metallurgical Quarterly*, 1988, Vol. 27, No. 4, p. 281.

[5] NAFZIGER, R.H., TRESS, J.E., PAIGE, J.I. Carbothermic reduction of domestic chromites. *Metallurgical Transactions B*, 1979, Vol. 10B, No. 1, p. 5.

[6] SOYKAN, O., ERIC, R.H., KING, R.P. Kinetics of the reduction of Bushveld complex chromite ore at 1416 °C. *Metallurgical Transactions B*, 1991, Vol. 22, No. 6, p. 801.

[7] HAZAR-YORUC, A.B. Reduction mechanism of chromite spinel with carbon, *Minerals and Metallurgical Processing*, 2007, Vol. 24, No. 2, p. 115.

[8] WEBER, P., ERIC, R.H. The reduction mechanism of chromite in the presence of silica flux. *Metallurgical Transactions B*, 1993, Vol. 24B, No. 6, p. 987.

[9] CHAKRABORTY, D., RANGANATHAN, S., SINHA, S.N. Investigations on the carbothermic reduction of chromite ores. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science,* 2005, Vol. 36, No. 4, p. 437.

[10] CHAKRABORTY, D., RANGANATHAN, S., SINHA, S.N. Carbothermic reduction of chromite ore under different flow rates of inert gas. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science,* 2010, Vol. 41, No. 1, p. 10.

[11] BALAZ, P. *Mechanochemistry in Nanoscience and Minerals Engineering*, Springer-Verlag, Berlin, 2008.

[12] TUNÇ, T., APAYDIN, F., YILDIZ, K. Effects of mechanical activation on the structure of nickeliferous laterite. *Acta Physica Polonica A*, 2013, Vol. 123, No. 2, p. 319.

[13] CHEN, Y., HWANG, T., MARSH, M., WILLIAMS, J.S. Study on mechanism of mechanical activation. *Materials Science and Engineering A*, 1997, Vol. A226-228, p. 95.

[14] TROMANS, D., MEECH, J.A. Enhanced dissolution of minerals: microtopography and mechanical activation. *Minerals Engineering*, 1999, Vol. 12, No. 6, p. 609.

[15] TROMANS, D., MEECH, J.A. Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation. *Minerals Engineering*, 2001, Vol. 14, No. 11, p. 1359.

[16] APAYDIN, F., ATASOY, A., YILDIZ, K. Effect of mechanical activation on carbothermal reduction of chromite with graphite. *Canadian Metallurgical Quarterly*, 2011, Vol. 50, No. 2, p. 113.