EFFECTS OF MECHANICAL ACTIVATION ON THE CARBOTHERMAL REDUCTION OF CHROMITE WITH METALLURGICAL COKE

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ABSTRACT

The carbothermal reduction of mechanically activated chromite with metallurgical coke under an argon atmosphere was investigated at temperatures between 1100 and 1400°C and the effects of the mechanical activation on chromite structure were analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM). An increase in specific surface area resulted in more contact points. The activation procedure led to amorphization and structural disordering in chromite and accelerated the degree of reduction and metalization in the mixture of chromite and metallurgical coke. Carbothermal reduction products were analzed by using scanning electron microscopy (SEM/EDS).

Keywords: carbothermal reduction, chromite, ferrochromium, mechanical activation

KROMİTİN METALURJİK KOKLA KARBOTERMAL REDÜKSİYONUNA MEKANİK AKTİVASYONUN ETKİSİ

ÖZET

Mekanik aktive edilmiş kromitin argon atmosferi altında metalurjik kokla karbotermal redüksiyonu 1100 – 1400°C sıcaklık aralığında incelenmiş ve kromit yapısına mekanik aktivasyonun etkisi X-ışını difraksiyonu (XRD) ve taramalı elektron mikroskobisi (SEM) ile analiz edilmiştir. Yüzey alanındaki artış daha fazla temas noktasının oluşmasına neden olmuştur. Aktivasyon prosedürü kromitte amorflaşma ve yapısal düzensizliğe neden olmuş ve kromit ile metalurjik kok karışımında redüksiyon derecesini ve metalleşmeyi hızlandırmıştır. Karbotermal redüksiyon ürünleri taramalı elektron mikroskobisi (SEM/EDS) ile analiz edilmiştir.

Anahtar Kelimeler: karbotermal redüksiyon, kromit, ferrokrom, mekanik aktivasyon

I. INTRODUCTION

Chromite is the only mineral composed of metallic chromium, chromium compounds and other chemicals. Chromites comprise a wide range of composition in the spinel group of minerals. They can be expressed as (Mg, Fe^{2+})O.(Cr, Al, Fe^{3+})$_2$O$_3$ [1-3].

Ferrochromium is one of the most important alloying materials for the production of stainless and high-alloy ferritic steels. High-carbon ferrochromium is currently produced in submerged-arc furnaces. Disadvantages of this process are the limited use of chrome ore fines and friable chrome ores as well as its dependence on both expensive metallurgical coke and electrical energy. To improve cost effectiveness, solid-state carbothermal prereduction has grown in importance [4,5].

The carbothermal reduction of complex chromite and natural chromite ores has been investigated by many researchers to determine the reduction kinetics and reaction mechanisms. In these studies, it was reported that the carbothermic reduction of chromite is a complex procedure, and it depends on the origin of the ore, particle size, reaction temperature and time, reducing materials and morphology, etc. [6-12]. Soykan et al.[10,11] developed a generalized rate model based on an ionic diffusion mechanism and proposed a mechanism consisting of a four-stage reduction of the chromite spinel phase:

(1) A $Fe^{3+} \rightarrow Fe^{2+}$ transformation on the surface of the chromite followed soon after by the reduction of Cr^{3+} cations to Cr^{2+}
(2) The reduction of Fe^{3+} settled under the surface (diffusion to the center of the particle)
(3) The diffusion of Fe^{2+} cations to the surface and their reduction to the metallic state

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

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 [13,14]. High-energy ball milling can induce -at room temperature- some chemical reactions that normally occur at very high temperatures. However, some other reactions do not occur directly during milling at room temperatures but do occur with a higher reaction rate during the subsequent low temperature annealing process [15].

In this study, the reduction of Turkish chromite with metallurgical coke in the temperature range of 1100° to 1400°C under an argon atmosphere as well as the effects of mechanical activation on the chromite structure and reduction process were investigated.

II. MATERIALS AND METHOD

2.1. Materials

The chromite used in the experiments was obtained from Turkish chromite ore (Mugla region). After crushing and grinding, samples were screened under 100 µm. The chemical analysis of the chromite spinel is given in Table 1. Metallurgical coke (Erdemir) was used as the reducing agent.

2.2. Method

The mechanical activation of chromite concentrate 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 time was 0, 15, 30, 60, 90 and 120 min; the speed of the main disk was 600 rpm; the grinding process was dry.

Table 1. Chemical analysis of chromite spinel

	Oxides	Weight %
Reducible oxides	Cr_2O_3	46.72
	FeO	13.33
	Fe_2O_3	1.82
Non-reducible oxides	MgO	15.20
	Al_2O_3	15.30
	SiO_2	5.57
	CaO	0.21
Loss on ignition		1.87

X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu Kα radiation. The surface area was determined by the low-temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA). A JEOL 6060 LV scanning electron microscope (SEM) was used for both the morphological analysis of chromite after mechanical activation and the phase formations in the products after reduction.

Reduction experiments were carried out in a horizontal furnace in the temperature range of 1100 to 1400°C under an argon atmosphere. Chromite (2 g) and metallurgical coke (2 g) were thoroughly mixed, placed in an alumina crucible and submitted to the furnace. The furnace was heated to the reduction temperature under an argon atmosphere. The argon flow rate was 150 mL/min. At the end of the reduction time samples were cooled in an argon flow. The reduction temperatures (1100, 1200, 1300 and 1400°C), reduction times (30, 60 and 120 min) and milling times (0, 30 and 60 min) were investigated as parameters.

The reducible oxides in the chromite spinel are FeO, Fe_2O_3 and Cr_2O_3. These oxides are reduced with C to their metallic phases with the generation of gaseous intermediates, CO, according to the following reactions:

$$Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)} \quad (2)$$
$$FeO_{(s)} + C_{(s)} \rightarrow Fe_{(s)} + CO_{(g)} \quad (3)$$
$$Cr_2O_{3(s)} + 3C_{(s)} \rightarrow 2Cr_{(s)} + 3CO_{(g)} \quad (4)$$

The CO gas generated is the reason for the observed weight loss. The degree of reduction is calculated by the following reaction, assuming that CO is the only gaseous element generated during the reduction reactions:

$$R_{\%} = \frac{\text{Mass of oxygen removed}}{\text{Mass of removable oxygen}} \times 100 \qquad (5a)$$

$$R_{\%} = \frac{{}^{16}\!/\!_{28}\,CO_{INVOLVED}}{RO_{TOTAL}} \times 100 \qquad (5b)$$

Where $R_{\%}$ is the degree of reduction, $CO_{INVOLVED}$ is the total weight of the carbon monoxide generated from the mixture of the chromite and the reductant, i.e. weight loss after the loss of any volatiles. RO_{TOTAL} is the total weight of the removable oxygen in the mixture from the reducible oxides in chromite [6].

III. RESULTS AND DISCUSSION

3.1. Structural changes

Scanning electron micrographs of the non-activated and activated (60 min) chromite are shown in Figure 1. The particle sizes of non-activated chromite were between 100 and 50 µm. After mechanical activation for 60 min the particle sizes were less than 50 µm.

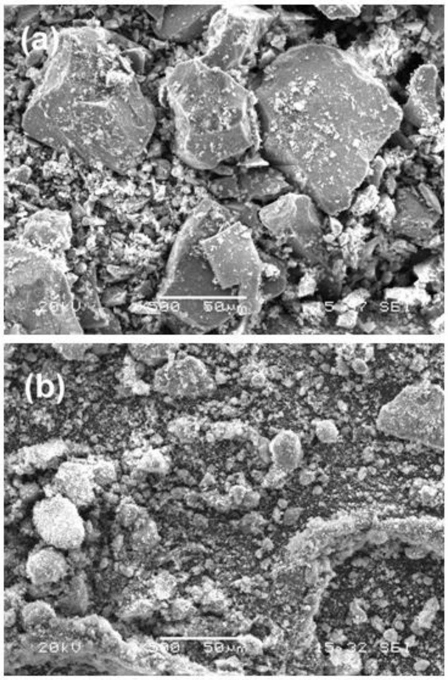

Figure 1. SEM micrographs of chromite: a) non-activated (X500) and b) activated for 60 min (X500)

The X-ray diffraction analysis of non-activated and activated chromite concentrate is given in Figure 2. Comparing the peaks in the six diffraction patterns between (2θ) 32° and 40° shows that the chromite diffraction peaks get shorter after mechanical activation. This result reflects the partial amorphization and structural disordering in chromite. Mechanical activation has already been reported to amorphize mineral particles[13,14]. Tromans & Meech [16,17] 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. Disordering in the bulk of the chromite increased with the time of mechanical activation.

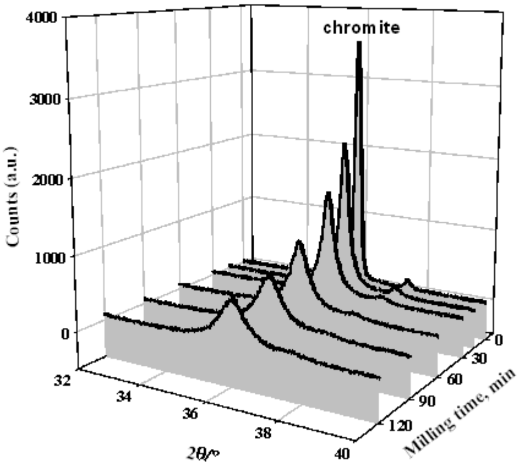

Figure 2. X-ray diffraction analysis of non-activated and activated chromite samples

3.2. Effect of milling on the reduction of chromite

The reduction of chromite with metallurgical coke is an endothermic reaction and the reaction rate increases with increasing temperature. The iron content within chromite is reduced at temperatures starting at 1100°C. In the early stage of the process under 1200°C, the transformation of Fe^{3+} to Fe^{2+} and metallic iron formation are actualized. In the stage over 1250°C, the transformation of chromite spinel and formation of the $MgAl_2O_4$ phase are actualized.

Table 2. Degrees of reduction for non-activated and activated chromite (A0: non-activated chromite, A30: activated for 30 min, A60: activated for 60 min)

Temperature (°C)	Time (min)	Reduction Degree, %		
		A0	A30	A60
1100	30	15,59	19,85	21,51
	60	16,57	20,63	23,83

	120	17,82	23,95	26,16
1200	30	34,50	38,88	39,70
	60	43,89	49,68	52,57
	120	51,51	58,84	60,61
1300	30	57,83	63,40	64,46
	60	62,86	71,40	73,49
	120	71,04	74,13	76,66
1400	30	77,49	80,38	82,44
	60	79,42	82,71	85,62
	120	92,25	95,91	96,62

The degrees of reduction of chromite with metallurgical coke, depending on the milling time, reduction temperature and time, are listed in Table 2. In the reduction of the non-activated chromite (A0), the degrees of reduction are 16,57% at 1100°C and 79,42% at 1400°C for a reduction time of 60 min. In the reduction of the activated (60 min) chromite (A60), the degrees of reduction are 23,83% at 1100°C and 85,62% at 1400°C for a reduction time of 60 min.

The degrees of reduction are increased by mechanical activation due to structural disordering in the chromite. The Highest reduction degrees were obtained at the highest reduction temperatures and time at highest activated time.

Scanning electron micrographs of the reduced samples are presented in Figure 3 for the non-activated chromite+coke mixture and in Figure 4 for the activated chromite+coke mixture. As seen in these figures, there are some differences in the microstructure of the samples. It was reported in the literature [18] that this effect depends on the experimental parameters of time, temperature, particle size and reducing materials. In the non-activated chromite, three zones can be observed on the polished section of the reduced sample (Figure 3). These zones are highly distinguishable from each other. The generally white zone represents metallic beads, the dark areas show the affected zone or the spinel structure, and the grey area is the original, unreacted chromite structure.

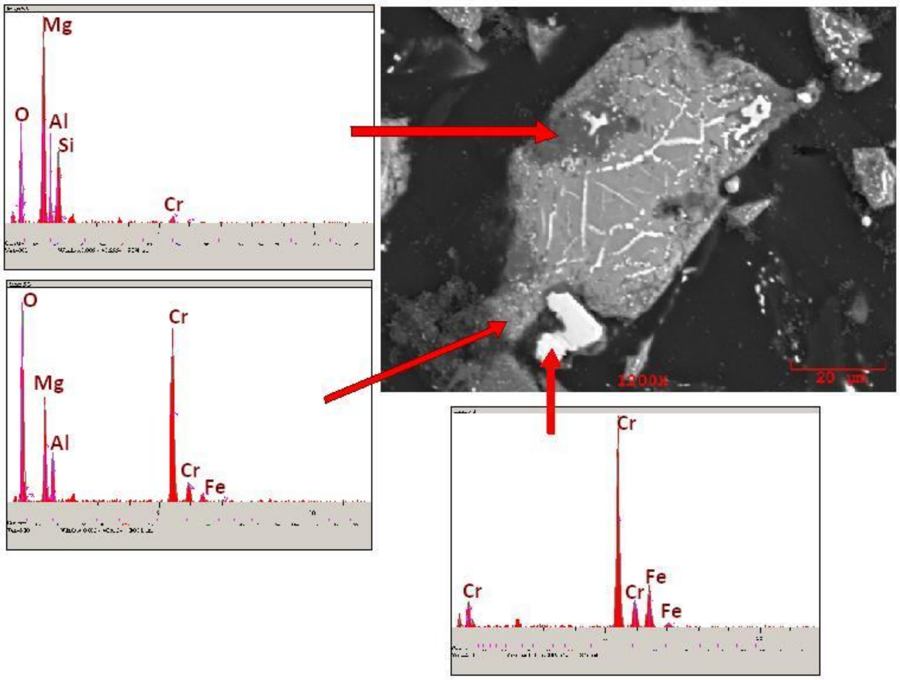

Figure 3. Scanning electron micrograph and EDS analysis of reduced non-activated chromite (1350°C, 30 min)

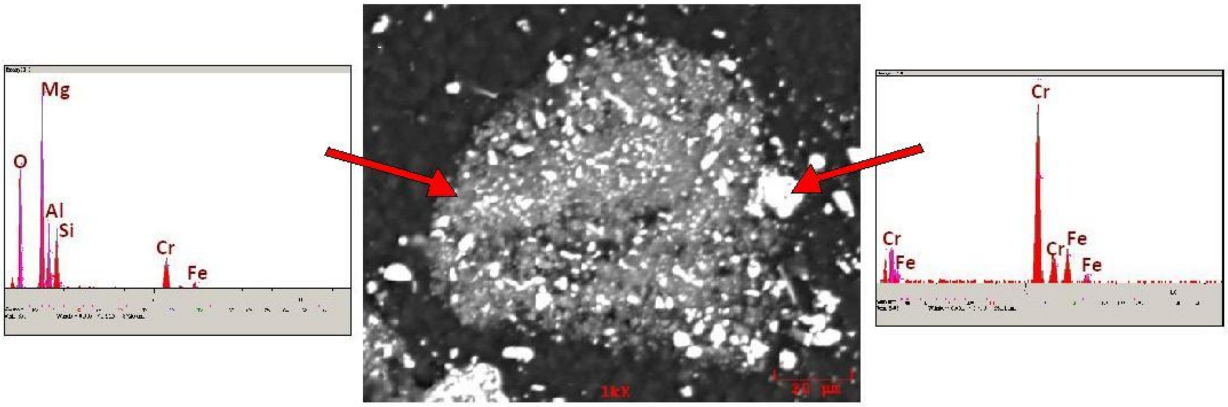

Figure 4. Scanning electron micrograph and EDS analysis of reduced activated (30 min) chromite (1350°C, 30 min)

Chromite particles generally contain a variety of defects such as dislocations, inclusions, silicate veins, porosities and fractures. There are a number of metalization areas around these imperfections. The polished section of the reduced, non-activated chromite sample contains quite large rounded, spherical and lath metallic beads along the imperfection or near the edge of the particle. The Fe-Cr alloys that form close to the surface are commonly in the shape of round beads, but laths range in width from 1-3 µm in length and 5-50 µm laths are common along veins. Alloys are irregular shapes found on the surface or near the edge of the reduced sample. In the scanning electron micrograph and EDS analysis of the activated sample (Figure 4) the two zones observed are the metallic beads (in white) and the affected areas (dark area). There are some differences between Figures 3 and 4. The metallic beads are more regular spherical shapes and more homogenously distributed in the activated sample than in the non-activated sample. There are also common features between the two samples. There is an increase in the size and amount of metalized components in both samples as time and temperature increase. As a result of the fine particle size, the generalized three zones may not be seen in the activated sample. The homogenous distribution of the metallic beads in the activated sample could be a result of the greater number of contact points between the chromite and coke particles. The reduction in the particle size of the chromite may decrease the imperfections of the sample. By comparing the number of metallic beads between the two samples there are also good agreements in the degrees of reduction of the non-activated and activated chromite samples. The number of metallic beads and degree of reduction are higher in the activated sample than in the non-activated one.

IV. CONCLUSIONS

The non-activated and activated chromite samples were reduced at temperatures between 1100-1400°C in the presence of metallurgical coke. The results indicate that high-energy ball milling is effective for the reduction of chromite with metallurgical coke. The increase in surface area resulting from the reduction in particle size allows for more contact points in the mixture of the activated chromite and coke. A decrease in the imperfections of the chromite particle has also resulted in more homogenous and larger metalization around the activated chromite. The mechanical activation process increased the degrees of reduction and metalization in the chromite due to structural disordering in the chromite structure. The higher degrees of reduction were obtained at lower temperatures.

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REFERENCES

[1] H.M. Mikami, Industrial Minerals and Rocks, fifth ed., Vol.1, AIME, New York, 1983.
[2] K.K. Chatterjee, Uses of Metals and Metallic Minerals, New Age Int. Ltd Pub., New Delhi, 2007.
[3] G. Yarkadaş, K. Yildiz, Effects of mechanical activation on the soda roasting of chromite, Can. Metal. Quarterly 48(1), 69-72, 2009.
[4] P. Weber, R.H. Eric, The reduction of chromite in the presence of silica flux, Minerals Eng. 19, 318-324, 2006.
[5] Y.L. Ding, N.A. Warner, Catalytic reduction of carbon-chromite composite pellets by lime, Thermochimica Acta 292, 85-94, 1997.

[6] A. Atasoy, Mineral processing and reduction of Turkish chromite ore, PhD Thesis, UMIST, 2001.
[7] A.R. Barnes, C.W.P. Finn, S.H. Algie, Prereduction and smelting of chromite concentrate of low chromium to iron ratio, J. South African Inst. of Min. And Metal. 83(3), 49-54, 1983.
[8] G.W. Healy, Carbon reduction of chromites in Bird River and other ores and concentrates at 1200-1700°C, Can. Metal. Quarterly 27(4), 281-285, 1988.
[9] R.H. Nafziger, J.E. Tress, J.I. Paige, Carbothermic reduction of domestic chromites, Metallurgical Transactions B 10B(1), 5-12, 1979.
[10] O. Soykan, R.H. Eric, R.P. King, Reduction mechanism of a natural chromite at 1416°C, Metallurgical Transactions B 22(1), 53-63, 1991.
[11] O. Soykan, R.H. Eric, R.P. King, Kinetics of the reduction of Bushveld complex chromite ore at 1416°C, Metallurgical Transactions B 22(6), 801-810, 1991.
[12] A.B. Hazar-Yoruc, Reduction mechanism of chromite spinel with carbon, Minerals and Metal. Proces. 24(2), 115-120, 2007.
[13] P. Balaz, Extractive Metallurgy of Activated Minerals, Elsevier Science, Amsterdam, 2000.
[14] P. Balaz, Mechanochemistry in Nanoscience and Minerals Engineering, Springer Verlag, Berlin, 2008
[15] Y. Chen, T. Hwang, M. Marsh, J.S. Williams, Study on mechanism of mechanical activation, Materials Science and Engineering A 226-228, 95-98, 1997.
[16] D. Tromans, J.A. Meech, enhanced dissolution of minerals: stored energy, amorphism and mechanical activation, Minerals Engineering 14(11), 1359-1377, 2001.
[17] D. Tromans, J.A. Meech, Enhanced dissolution of minerals: microtopography and mechanical activation, Minerals Engineering 12(6), 609-625, 1999.
[18] A. Atasoy, F.R. Sale, An investigation on the solid state reduction of chromite concentrate, J. Solid State Phenomena 147-149, 752-757, 2009.