Reduction mechanism of chromite spinel with carbon

A.B. Hazar-Yoruç
Assistant Professor, Yildiz Technical University, Department of Metallurgical and Materials Engineering, Istanbul, Turkey

Abstract

Ferrochromium produced by smelting chromite ores is an important alloying component in the steel industry. Ore, coke and fluxes are mixed and reacted in an arc furnace for a smelting process of ferrochromium. In addition to this process, pre-reduction of chromite ore with carbon is an important industrial process. In all these processes, the mechanism and kinetics of reduction of chromite with carbon play an important role. In this study, the reduction of Turkish chromite ore with carbon was investigated. Chromite and carbon were ground to three different particle size groups. Chromite was mixed with carbon in stoichiometric and excess ratios. The samples were reduced under argon atmosphere at temperatures between 1,200° and 1,350°C. The formed phases and alloy compositions of reduced chromite samples were analyzed by optical microscopy, scanning electron microscope (SEM) with EDAX and X-ray diffraction analysis (XRD). Experimental results showed that the degree of reduction and the reduction rate increased with increasing temperature and decreasing particle size. The highest degree of reduction, 61.4%, was obtained at 1,350°C. The reduction took place in three stages: Stage 1: transformation of Fe^{3+} to Fe^{2+} and formation of metallic nuclei, Stage 2: formation of metallic crust around the particles and Stage 3: growth of the metallic crust and coalescence of the metallic phase.

Key words: Chromium ore, Coke, Carbothermic reduction, Ferrochromium, Reduction mechanism.

Introduction

Ferrochromium, which is a mixture of chromium and iron with varying amounts of other chemical constituents, is the most important ferroalloy in the metallurgical industry. Ferrochromium is further classified by its carbon content as high-, medium- or low-carbon ferrochromium. By far, the largest production of ferrochromium is the high-carbon variety. It is the major source of chromium for the production of steel alloys.

Ferrochromium production is a reduction process. The reductants used in ferrochromium production are C, Si and Al. Carbon is preferred as a reductant in high-carbon ferrochromium production. Chromite ore is blended with coal and with fluxes, fed into an electric-arc furnace and smelted. The smelting process uses electrical energy. Carbothermic reduction of complex chromite and natural chromite ores have been investigated by many researchers to determine reduction kinetics and the mechanisms of the reactions (Barcza et al., 1972; Bibb and Ossin, 1977; Nafziger et al., 1979; Barnes et al., 1983; Algie and Finn, 1984; Healy, 1988; Yoruç and Küçükkaragöz, 1990). In these studies, the effects of temperature, types and amounts of reductants and particle size of raw materials on the reduction rate and reduction mechanism of chromite ore were investigated.

Barnes et al. (1983) proved that the relation of metallization and reduction was not linear. Algie and Finn (1984) determined three stages for the reduction of chromite. In the first step, Fe^{3+} is reduced to Fe^{2+}. In the second step, Fe^{2+} is reduced to metallic Fe with a reduction ratio of 4% to 5%. When iron reduction was attained to about 50%, the transformation of Cr^{3+} to Cr^{0} was observed. After iron reduction was completed, 60% reduction of Cr could be achieved.

Soykan et al. (1991a, 1991b) 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:

- $Fe^{3+} \rightarrow Fe^{2+}$ transformation on the surface of chromite and soon after the reduction of Cr^{3+} cations to Cr^{2+}.
- The reduction of Fe^{3+} settled under the surface (diffusion to the center of particle).
- Diffusion of Fe^{2+} cations to the surface and reduction of them to the metallic state.
- 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.

Paper number MMP-06-010. Original manuscript submitted online February 2006. Revised manuscript received and accepted for publication December 2006. Discussion of this peer-reviewed and approved paper is invited and must be submitted to SME Publications Dept. prior to Nov. 30, 2007. Copyright 2007, *Society for Mining, Metallurgy, and Exploration, Inc.*

Table 1 — Chemical analysis of chromite spinel.

Component	Weight %	Component	Weight %
Cr_2O_3	49.05	Al_2O_3	10.35
Fe_2O_3	4.10	SiO_2	2.78
FeO	11.70	CaO	0.18
MgO	14.90	TiO_2	0.15

Lekatou and Walker (1995a; 1995b) reached the maximum metallization of iron and chromium at 91% and 67%, respectively. Also, they suggested the six-stage mechanism for the reduction of chromite concentrate in the temperature range of 1,100° to 1,470°C. Kekkonen (2000) found that preoxidation of iron promotes reduction and chromium metallization. Low-temperature reduction of chromite ores with carbon was studied by Reddy et al. (1998). Reddy et al. (1998) suggested that the overall rate of FeO reduction is controlled by the oxidation of carbon. Arvanitidis et al. (1996) studied the kinetics of reduction of iron chromate ($FeCr_2O_4$) by hydrogen. Below 1,646°C, $FeCr_2O_4$ was found to be the first compound reduced to iron and chromium oxide before further reduction to chromium. At higher temperatures, the reduction of Cr_2O_3 appeared to occur before the full recovery of iron. Experimental studies on the carbothermic reduction of composite chromite pellets made from graphite-chromite mixtures have been carried out by many researchers (Nafziger et al., 1979; Ding and Warner, 1996; Ding and Warner, 1997a, 1997b). The effects of silica and lime on the reduction kinetics were also studied (Neuschütz, 1992; Ding et al., 1997; Lekatou and Walker, 1997; Duong and Johnston, 2000).

In this study, the reduction of Turkish chromite ores with carbon was investigated in the temperature range of 950° to 1,350°C under argon atmosphere. The effects of various parameters were examined and the reduction mechanism was determined.

Experimental procedure

Materials. Chromite spinels used in the experiments was obtained from Turkish chromite ores. After crushing, grinding, screening, magnetic separation and secondary screening operations, samples were separated into three groups: -106+75, -75+53 and -53+38 μm. The chemical analysis of the produced chromite spinel is given in Table 1. Graphite consisting of more than 98% carbon was used as the reducing agent.

The laboratory setup for the reduction experiments consisted of two main parts: the reduction furnace unit and the cleaning unit of the reduction gas. The reduction furnace was a 37-mm-inner-diameter, 490-mm-long alumina tube, and it was heated by Mo resistance. In the gas cleaning system, argon was first passed through an H_2SO_4 solution and then $CaCl_2$ before transferring to the furnace. Secondly, it was passed through the deoxidation furnace. After the gas flow rate was fixed, the gas was sent to the reduction furnace.

Method. Reduction experiments (mainly isothermal) were carried out in a horizontal furnace in the temperature range of 1,100° to 1,350°C under argon atmosphere. Chromite (3.2 g) and graphite (0.8 g) with the same particle size were thoroughly mixed and placed in an alumina crucible. After the furnace was heated to reduction temperature under an argon atmosphere, the crucible was put into the furnace and the reduction time was commenced. The argon flow rate was 150 mL/min. At the end of the reduction time, samples were cooled in argon flow. Temperature, time, particle size and variations of carbon addition were investigated as parameters. The reduction degree was calculated according to the change of the weight of the sample and the stoichiometric amount of removable oxygen in chromite.

The characterization of metallization was investigated by micrographs, chemical analysis and EDX analysis. A Jeol, Model JSM 5410 LV, scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDAX) were used to determine phases. Concentration profiles of Fe, Mg, Cr and Al elements were obtained by EDAX. Compositions of the obtained alloy phases were revealed by chemical analysis using a wet chemical method and an atomic absorption spectrometer.

Results

In the chromite spinel, the reducible oxides were FeO, Fe_2O_3 and Cr_2O_3. These oxides were reduced with C to metallic phase involving gaseous intermediates, CO, according to the following reactions:

$$Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)} \quad (1)$$

$$FeO_{(s)} + C_{(s)} \rightarrow Fe_{(s)} + CO_{(g)} \quad (2)$$

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

The CO created was the reason of the weight loss. The degree of reduction was calculated by the following reaction, supposing that CO was the only gaseous element that occurred during the reduction reactions:

$$Degree\ of\ reduction,\ \% = \frac{Mass\ loss\ (as\ CO)}{Total\ probable\ mass\ loss\ (as\ CO)} \cdot 100 \quad (4)$$

The effects of temperature and time on the reduction degree are given in Fig. 1. The degree of reduction of chromite spinel by graphite was found to increase with increasing temperature and time. The temperature dependence of the reduction rate at higher temperatures was significantly greater than that at lower temperatures. At higher temperatures (>1,200°C), the reduction rate slowed after 80 minutes. The rate and the degree of reduction were insufficient at relatively lower (<1,200°C) temperatures. The maximum reduction degree was obtained as 61.40% at 1,350°C for 180 min.

The effect of the three different particle sizes on the reduction rate is shown in Fig. 2. For the first 60 minutes, the particle size of the chromite spinel didn't affect the reduction rate. But after 60 minutes the reduction rate increased with decreasing particle size. The best result was obtained with particle size of -53+38 μm.

The carbon ratio had a negligible effect on the degree of reduction of chromite spinel. A stoichiometric carbon ratio (20%) and excess carbon (50%) were used in the reduction experiments. However, an effect of carbon on the reduction degree was not observed. It can be stated that the stoichiometric carbon ratio was sufficient for reduction of the chromite spinel.

SEM micrographs of unreduced and reduced chromite spinels are given in Figs. 3 and 4. SEM micrographs of reduced chromite spinels showed that metallic Fe nuclei first formed on the chromite particle surface in the early stage of the reduction. Metallic nuclei grew with the progress of reduction. This situation continued up to a metallic crust formation on the chromite particle surface. In this stage, the metallic crust surrounded the chromite particle. This phenomenon was observed

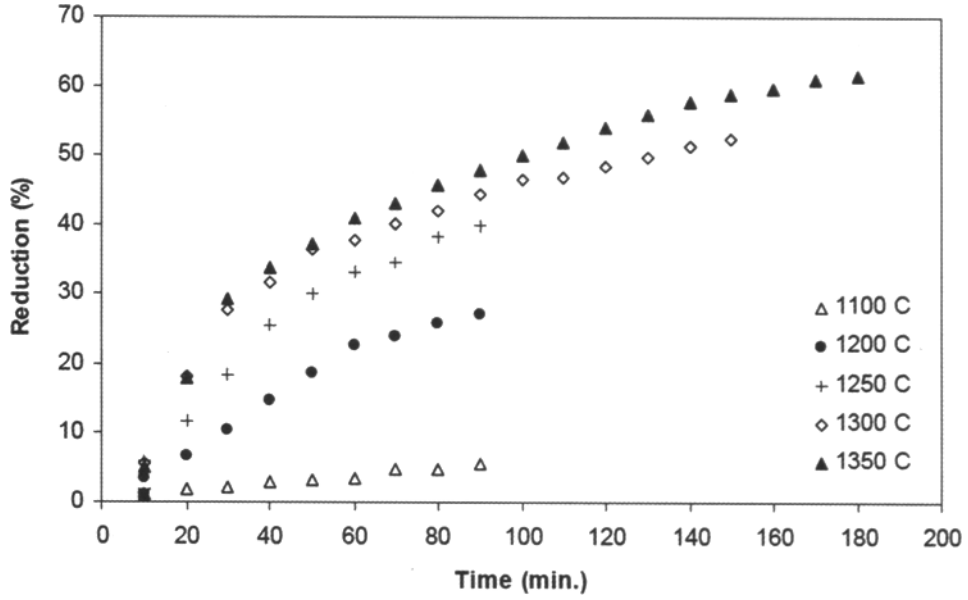


Figure 1 — Effect of time and temperature on the reduction degree of chromite spinel.

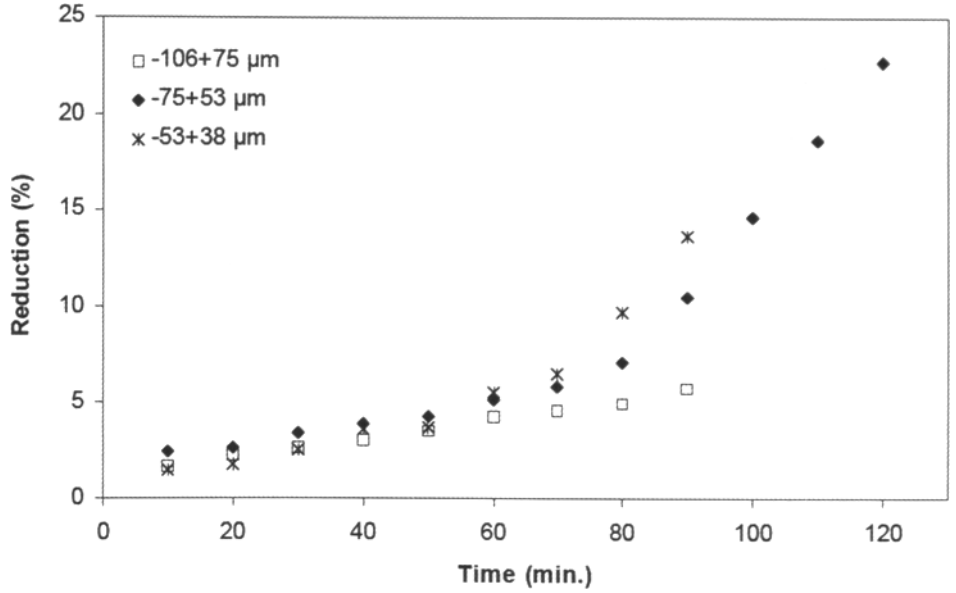


Figure 2 — Effect of particle size on the reduction degree of chromite spinel.

in the reduction range of 30% to 50%. Lately, thickness of the metallic crust increased and then broke down when it reached the higher degree of reduction.

X-ray analysis of the unreduced chromite spinel indicated that the chromite spinel had the structure of $(Fe,Mg)(Fe,Cr,Al)_2O_4$. After approximately 15% reduction, $(Fe,Cr)_7C_3$ and Fe_7C_3 carbides appeared. Concentration profiles of Fe, Cr, Al and Mg elements in the alloy and oxide phase in the reduced samples were determined by SEM micrographs and EDAX analysis (Figs. 5 through 7).

In the analysis of samples reduced at 1,200°, 1,250° and 1,350°C, Fe and Cr were found in the metal phase and Fe, Cr, Mg and Al in the oxide phase. While Fe ratio in the metal phase increased with increasing reduction degree, Fe ratio in the oxide phase decreased. In other words, the amounts of Fe and Cr diffusing from oxide phase to alloy phase increased with increasing temperature. The concentration distributions of Mg and Al in oxide phase were homogeneous in each reduction temperature. In all reduction stages, the alloy phase had the highest iron concentration. Diffusion of Fe and Cr continue till concentration of Fe and Cr in alloy-oxide interface is equal to the concentration in the center of oxide phase.

Discussion

Effect of temperature. The degree of reduction was a function of temperature and time (Fig. 1), because, the reduction of chromite with carbon is an endothermic reaction and reaction rate increases with increasing temperature. In the early stage of the reduction, temperature elevation accelerated the $Fe^{3+} \rightarrow Fe^{2+}$ transformation and later increased the formation of nuclei. In

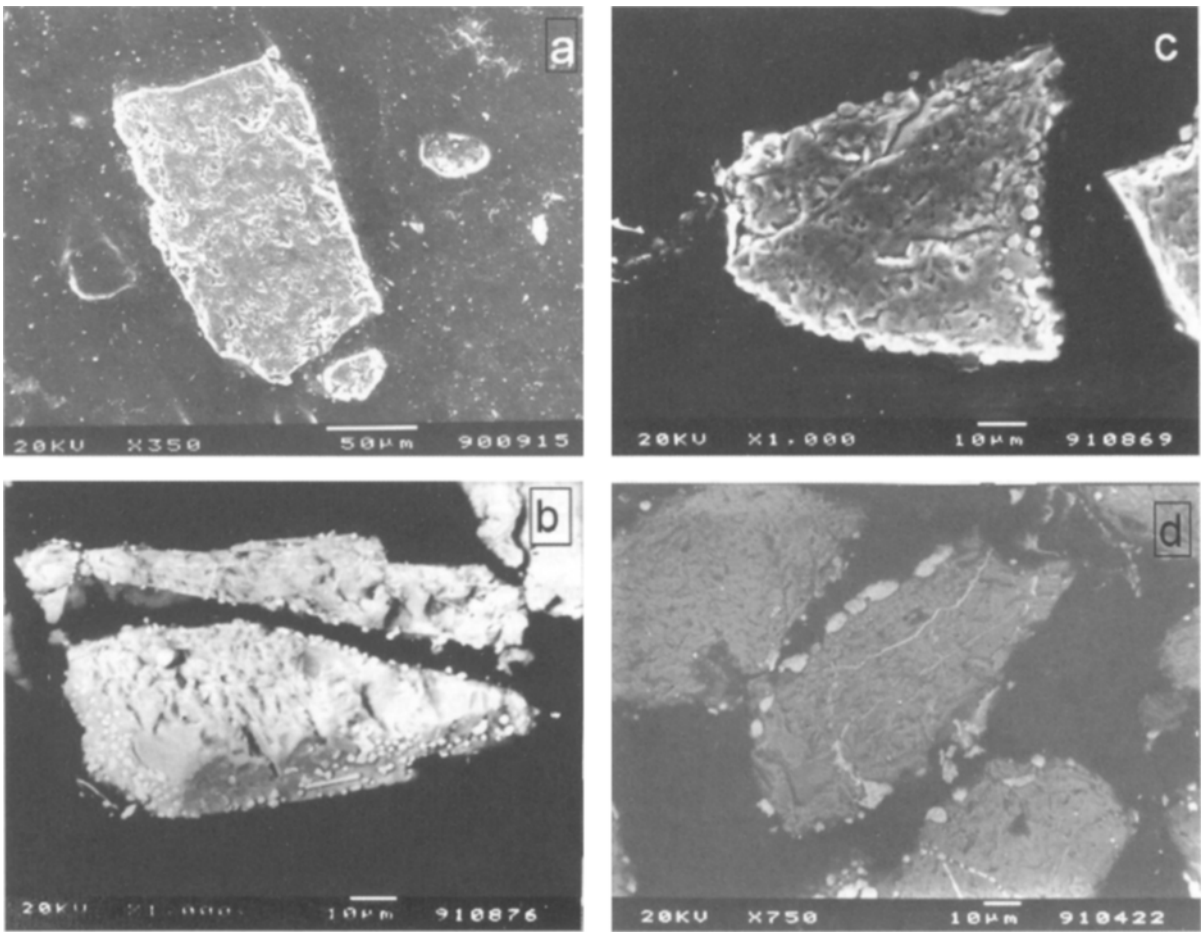


Figure 3 — SEM micrographs of unreduced and reduced chromite spinels at 1,200°C: (a) unreduced chromite spinel; (b) 14.68% reduction (40 min.); (c) 25.80% reduction (80 min.); and (d) 34.52% reduction (160 min).

the advanced stages of the reduction, interface reactions and transportation of Cr^{3+} and O^{2-} ions took place rapidly because of the elevation in temperature.

Effect of particle size. The degree of reduction and the rate of the reduction increased with decreasing particle size (Fig. 2). Chromite-carbon contact points increased, and more surface area reacted with decreasing particle size. Also, there were shorter diffusion paths for Cr^{3+} and O^{2-} ions with relatively small particle sizes.

Effect of reducing agent. There was no effect when carbon addition was changed. In the early stages of the reduction, there was enough CO in the furnace atmosphere for both stoichiometric and excess carbon. In the later stages, reduction reactions progressed by solved C in the alloy. As there was sufficient saturated carbon present in the alloy, the carbon ratio didn't affect the reduction degree.

Metallographic analysis. According to the SEM micrographs and EDAX analysis, the metallization began on the surface of the chromite spinel by nucleation of iron (Figs. 3 and 4). Favorable nucleation regions were cracks, impure areas on the surface, dislocations and cavities/spaces.

After nucleation, the surface of the chromite particle was entirely covered with alloy phase (Fig 4 (d)). This phenomenon occurred by growing of the nuclei. In this stage the unreduced part of the spinel was observed to be a porous structure.

EDAX analysis showed that iron diffusion happened before chromium diffusion. Diffused iron and chromium combined in the alloy phase with developing reduction. Diffusion of iron and chromium from oxide phase to alloy phase increased with increasing temperature. The concentration distributions of Mg and Al in the oxide phase were homogeneous (Figs. 5 through 7)

Reduction kinetics. In accordance with the degree of reduction, SEM micrographs and EDAX analysis, it is possible to state that the reduction of chromite spinel with carbon was carried out in three stages:

First stage: Transformation of Fe^{3+} to Fe^{2+} and metallic iron formation (0% to 15% reduction):

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

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

It was accepted that first reduction began with carbon-chromite contact and CO appeared. In this stage, metallic nuclei content was 90% iron.

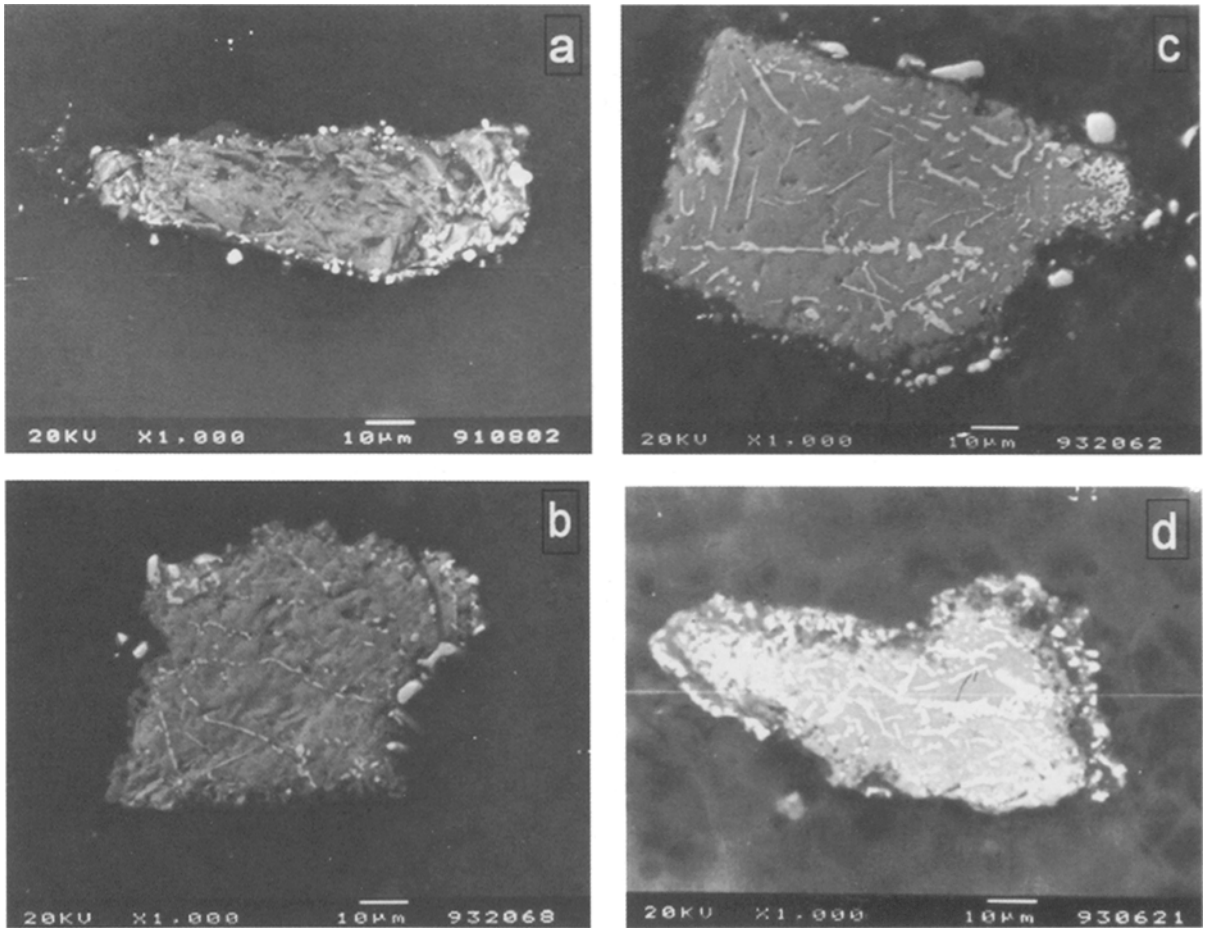


Figure 4 — SEM micrographs of reduced chromite spinels in different temperature and time: (a) 19.51% reduction (1,200°C, 60 min.); (b) 30.04% reduction (1,250°C, 60 min.); (c) 50.31% reduction (1,350°C, 90 min.); and (d) 61.40% reduction (1,350°C, 180 min).

Second stage: Transformation of chromite spinel (15% to 40% reduction):

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

This stage involved the level of nuclei formation in the critical dimension and the level of metallic phase formation in the form of crust covering the chromite spinel. Composition of the metallic crust was about 80% to 90% Fe and 10% to 20% Cr. On this occasion, about 70% of iron and 20% of chromium reduced and transformed to alloy phase.

Third stage: $MgAl_2O_4$ phase formation (>40% reduction):

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

In this stage, metallic crust developed and reached maximum thickness (average 9 µm). Metallic phase also contained $(Fe,Cr)_7C_3$. Because of the metallic crust, reduction was carried out by dissolved carbon in the alloy phase. Reduction rate was determined by diffusion of chromium, which was slower than diffusion of carbon ($D_{Cr} = 1 \cdot 10^{-10}$ to $1 \cdot 10^{-9}$ cm^2/s (Rankin, 1979), $D_{C\,in\,Cr} = 1{,}87 \cdot 10^{-6}$ and $D_{C\,in\,Fe} = 2.83 \cdot 10^{-6}$ cm^2/s (Weast, 1979)). The reduction finished after Cr diffusion completed at the alloy-oxide interface. The first stage of the reduction of the chromite spinel with carbon was carried out very fast, so that these stages couldn't affect the total reduction rate.

Conclusions

- In the reduction process of Turkish chromite spinel with carbon, the reduction rate and degree was a function of temperature. The maximum reduction rate (61.40%) was attained at the maximum temperature (1,350°C).
- The particle sizes of chromite spinel and carbon were important factors affecting the degree of reduction and the rate of reduction. The degree of reduction increased with decreasing particle sizes.
- There was no difference between reduction experiments carried out with 20% C (stoichiometric C) and 50% C.
- The reduction of chromite spinel with carbon was realized in four stages. The final product consisted of metallic Fe, metallic Cr and $MgAl_2O_4$.
- Reduction kinetics depended on diffusion of chromium in the spinel.

References

Algie, S.H., and Finn, C.W.P., 1984, "Reaction mechanisms in the reduction of Winterveld chrome spinel with graphite and carbon," *Mintek*, pp. 1-40.

Arvanitidis, I., Artin, C., Claeson, P., Jacobsson, H., Johansson, P., Rassmus, J., and Swartling, D., 1996, "Study of the kinetics of reduction of iron chromate by hydrogen," *Scandinavian Journal of Metallurgy*, Vol. 25, No. 4, pp. 141-147.

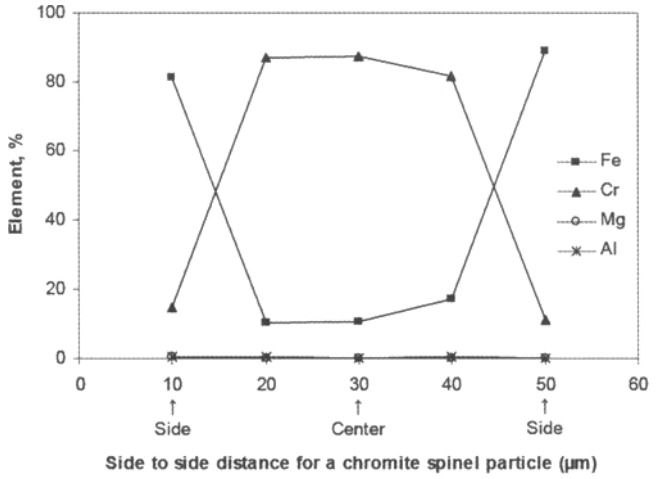


Figure 5 — Concentration profile of the particle of 14.68% reduced chromite spinel (1,200°C, 40 min).

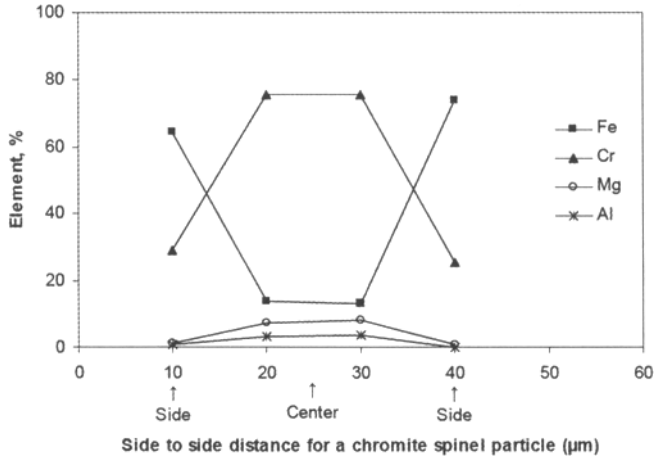


Figure 6 — Concentration profile of the particle of 38.30% reduced chromite spinel (1,250°C, 80 min).

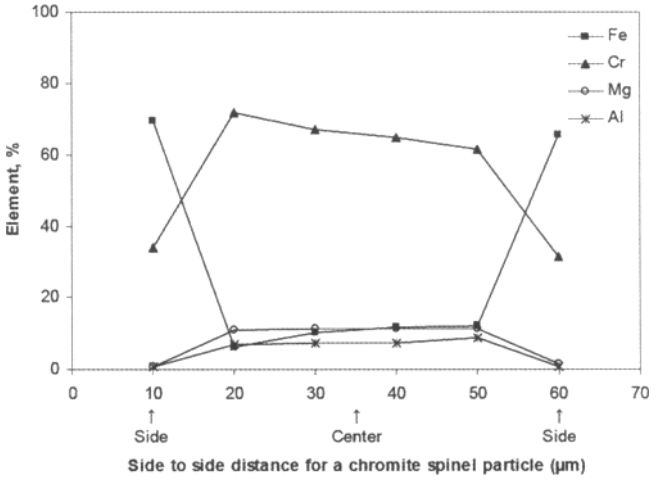


Figure 7 — Concentration profile of the particle of 61.40% reduced chromite spinel (1,350°C, 180 min).

Barcza, N.A., Jochens, P.R., and Howat, D.D., 1972, "The mechanism and kinetics of reduction of Transvaal chromite ores," *29th Electric Conference Proceedings*, Metallurgical Society of AIME, 1972, New York, pp. 88-93.

Barnes, A.R., Finn, C.W.P., and Algie, S.H., 1983, "Prereduction and smelting of chromite concentrate of low chromium-to-iron ratio," *Journal of the South African Inst. of Min. and Metall.*, Vol. 83, No. 3, pp. 49-54.

Bibb, M., and Ossin, D.I., 1977, "Low-Temperature Reduction of Chromite Ore by Carbon-Hydrogen Mixtures," National Institute for Metallurgy, Project No. 09076, Johannesburg.

Ding, Y.L., and Warner, N.A., 1996, "Experimental study on the carbothermic reduction of composite chromite pellets," *Proceedings of The 1996 IChemE Research Event/Second European Conference for Young Researchers*, Leeds, UK, 2-3 April 1996, pp. 506-509.

Ding, Y.L., and Warner, N.A., 1997a, "The importance of heat transfer in the reduction of carbon-chromite composite pellets," *Proceedings of Institution of Chemical Engineers—The 1997 Jubilee Research Event*, Nottingham, UK, 8-9 April 1997, pp. 1281-1284.

Ding, Y.L., and Warner, N.A., 1997b, "Kinetics and mechanism of reduction of carbon-chromite composite pellets," *Ironmaking and Steelmaking*, Vol. 24, No. 3, pp. 224-229.

Ding, Y.L., Warner, N.A., and Merchant, A.J., 1997, "Reduction of chromite by graphite with CaO-SiO_2 fluxes," *Scandinavian Journal of Metallurgy*, Vol. 26, pp. 55-63.

Duong, H.V., and Johnston, R.F., 2000, "Kinetics of solid state silica fluxed reduction of chromite with coal," *Ironmaking and Steelmaking*, Vol. 27, No. 3, pp. 202-206.

Healy, G.W., 1988, "Carbon reduction of chromites in Bird River and other ores and concentrates at 1200-1700°C," *Canadian Metallurgical Quarterly*, Vol. 27, No. 4, pp. 281-285.

Kekkonen, M., 2000, "Kinetic study on solid state and smelting reduction of chromite ore," *Acta Polytechnica Scandinavica*, Chemical Technology Series, No. 276, pp. 5-96.

Lekatou, A., and Walker, R.D., 1995, "Solid state reduction of chromite concentrate: melting of prereduced chromite," *Ironmaking and Steelmaking*, Vol. 22, No. 5, pp. 378-392.

Lekatou, A., and Walker, R.D., 1995, "Mechanism of solid state reduction of chromite concentrate," *Ironmaking and Steelmaking*, Vol. 22, No. 5, pp. 393-404.

Lekatou, A., and Walker, R.D., 1997, "Effect of SiO_2 addition on solid state reduction of chromite concentrate," *Ironmaking and Steelmaking*, Vol. 24, No. 2, pp. 133-143.

Nafziger, R.H., Tress, J.E., and Paige, J.I., 1979, "Carbothermic reduction of domestic chromites," *Metallurgical Transactions B*, Vol. 10B, No. 1, pp. 5-12.

Neuschütz, D., 1992, "Kinetic aspects of chromite ore reduction with coal at 1200 to 1550°C," *Proceedings of INFACON 6*, 1992, Cape Town, pp. 65-70.

Rankin, W.J., 1979, "The composition and structure of chromite during reduction with carbon," *Arch. Eisenhüttenwes.*, Vol. 50, No. 9, pp. 373-378.

Weast, R.C., 1979, *CRC Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, B17-B18.

Reddy, R.G., Inturi, R.B., and Klein, M.V., 1998, "Low temperature reduction of chromite ores with carbon," *Proceedings of TMS Annual Meeting*, EPD Congress, Feb. 1998, San Antonio, Texas, pp. 697-715.

Shimoo, T., 1990, "Carbothermic reduction of synthetic complex chromite (Fe_xMg_{1-x}) Cr_2O_4 at high temperatures," *Journal of the Japan Institute of Metals*, Vol. 54, No.8, pp. 911-918.

Soykan, O., Eric, R.H., and King, R.P., 1991a, "Reduction mechanism of a natural chromite at 1416°C," *Metallurgical Transactions B*, Vol. 22, No. 1, pp. 53-63.

Soykan, O., Eric, R.H., and King, R.P., 1991b, "Kinetics of the reduction of Bushveld complex chromite ore at 1416°C," *Metallurgical Transactions B*, Vol. 22, No. 6, pp. 801-810.

Vazarlis, H.G., and Lekatou, A., 1993, "Pelletising-sintering, prereduction, and smelting of Greek chromite ores and concentrates," *Ironmaking and Steelmaking*, Vol. 20, No. 1, pp. 42-53.

Yoruç, A.B., and Küçükkaragöz, C.S., 1990, "Fethiye Kromit cevherlerinin karbon ile redüksiyonunun incelenmesi," *Proceedings of 6th Metallurgy Congress*, Chamber of Metallurgical Engineers (Turkey), Oct. 31- Nov. 04, 1990, Ankara, pp. 43-52.