

REACTION MECHANISM STUDY ON CARBOTHERMAL REDUCTION OF CHROMITE

Fei WANG^{1,2,3*}, Bin YANG^{2,3}, Annelies MALFLIET¹, Bart BLANPAIN¹, Muxing GUO¹

¹ Department of Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

² State Key Laboratory of Complex Nonferrous Metal Resources Clear Utilization in Yunnan Province, Kunming 650093, P. R. China

³ Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, P. R. China

fayerswing@hotmail.com

Introduction

Chromium is the most important element in manufacturing of stainless steels ¹. After the stainless steelmaking, a certain amount of chromium remains in the slag in the form of chromite, resulting in considerable chromium losses. Many efforts have been attempted to recover the Cr from the stainless steel slag through high temperature reduction². Numerous studies have been carried out on the reduction of chromite and chromium oxide³⁻⁷ either through direct interaction between solid carbon and chromite particles or through gas/solid reaction. The information dealing with the enhancement of chromite reduction and the different reaction mechanisms is incomplete. In this paper, the carbothermal reduction mechanism of chromite has been investigated by post-mortem assessment of the sample after the reduction. The result provides a fundamental understanding of recovering Cr from chromite-containing stainless steel slag.

Experimental

The chromite was prepared by using magnesium oxide (MgO, $\geq 98\%$ purity, CAS:1309-48-4) and chromium(III) oxide (Cr₂O₃, $\geq 99\%$, CAS:1308-38-9) in a molar proportion corresponding to MgO·Cr₂O₃. After drying at 1000°C in air, the powders were mixed for 20 h in ethanol in a rotary mill, with zirconia balls with a ball/powder weight ratio of 3:1. The obtained slurry was dried at 80°C and then heated in bottom loading furnace at 1550°C for 12 hours. After sieving in a centrifugal mill (Retsch ZM100) the chromite powders were obtained with diameters around 40 μm . Carbon black (Grade: special black, Brand: degussa, Size: 25 nm) were used as reductant due to its large surface area.

The reduction experiments were carried out in a vertical furnace in the temperature range from 1100°C to 1500°C, at an argon flow rate of 400 mL/min. Chromite and carbon were thoroughly mixed and placed in an alumina crucible. The heating rate and

cooling rate were both 5°C/min and the dwell time at the temperature of interest was 60 min.

The reduced samples were examined with X-ray powder diffraction (XRD; Seifert 3003-TT, Ahrensburg) using Cu K α (40 kV, 40 mA) radiation to analyse the phase composition and thereby evaluating the reduction degree at different temperatures. Analysis of the microstructure and the elemental composition of the phases of the reduced samples was performed by scanning electron microscopy (SEM; XL 30 FEG, Philips) at 10 kV.

Results and Discussion

XRD semi-quantitative analyses of the compositions of the reduced samples are listed in Table 1. The remaining MgCr₂O₄ decreased with increasing temperature. Chromite converts to Cr₃C₂, Cr₇C₃, Cr₂₃C₆ and Cr, for which the carbides with the higher Cr content were formed at the higher temperatures. At the temperature of 1500°C, chromite was completely reduced to metallic chromium and Cr₂₃C₆.

Table 1: XRD Semi-quantitative analysis of the samples (wt%)

Temperature (°C)	MgCrO ₄	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₂₃ C ₆	Cr	MgO
1100	86.6	13.4	-	-	-	-
1200	33.1	19.2	18.9	-	-	28.8
1300	24.5	-	46.4	-	-	29.1
1400	20.4	-	30.6	2.8	19.3	27.0
1500	-	-	-	36.4	6.7	56.9

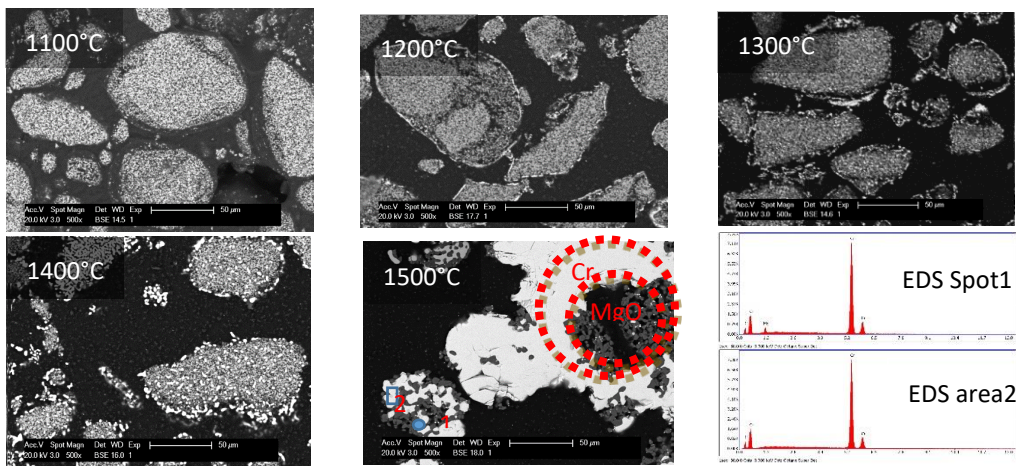
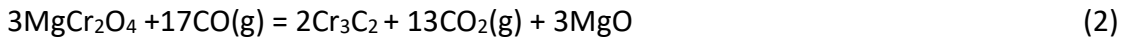
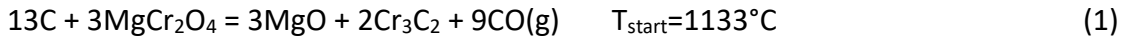


Figure 1: SEM images of reduced sample at different temperature

The SEM images of the reduced samples at different temperatures are shown in Figure 1. At 1100°C, most of the chromite was not reduced, and only a small amount of chromium carbide particles can be seen. With increasing temperature up to 1400°C, the amount of carbides increases, and they form especially on the rim of the chromite particles, leaving some unreduced chromite embedded in it. At 1500°C, all of the chromite converted into metallic chromium and a small amount of magnesia and chromium carbides (Cr_{23}C_6) as confirmed by SEM-EDS (Figure 1). This analysis shows that during the reduction of chromite, intermediate chromium carbides form. These carbides form layers around the original chromite particles with the chromium content in these carbides increasing toward the outer layer.

Standard free energies of the reactions during chromite reduction were calculated with the HSC software and the starting temperatures of the respective reactions are given. Chromium easily binds with carbon to form chromium carbide because there is a metastable eutectic point under 1490°C⁸. From these results, carbothermal reduction of magnesiachromite can be considered as follows: at first, direct reduction by solid carbon (Reaction(1)) takes place, producing Cr_3C_2 , CO and MgO above 1133°C.



The reduction of chromite is dependent on the temperature and the ratio of $P_{\text{CO}_2}/P_{\text{CO}}$. As expressed by Reactions (2) and (3), CO generated in Reaction 1 will further reduce MgCr_2O_4 , generating CO_2 . When the ratio of $P_{\text{CO}}/P_{\text{CO}_2} > 28$, the starting temperature of Reaction (2) will be 1000°C. The higher $P_{\text{CO}}/P_{\text{CO}_2}$ ratio favours the reaction. However, as the reaction proceeds, the ratio of $P_{\text{CO}}/P_{\text{CO}_2}$ decreases due to CO consumption and CO_2 generation until the Reactions (2) and (3) ceases. Then CO_2 could react with chromium carbide (Cr_3C_2) to produce Cr_7C_3 , Cr_{23}C_6 and Cr. The chromium carbide oxidation by CO_2 and the calculated starting temperatures are represented as follows:



Based on the present experimental observation and thermodynamic calculation, the following steps of the solid - gas reaction taking place inside the carbon containing chromite particle during the reduction process can be proposed (Figure 2): (1) Reaction between chromite and carbon at the point of contact leading to formation of CO and chromium carbides. (2) Reduction of chromite by generating CO to form CO_2 with the transfer of CO from the carbon surface to proximate chromite *via* voids based

on higher ratio of P_{CO}/P_{CO_2} . (3) Diffusion of the gaseous product (CO_2) through the porous product layer of the particle to the outer reaction interface through voids. (4) Conversion from the carbide with lower Cr content to the carbide with higher content until the production of pure metallic chromium by CO_2 transfer from the reaction surface to the boundary layer, as shown in Figure 2. The diffusion of the gaseous products through the product layer is the rate controlling step which was experimentally proved and will be not discussed in this paper.

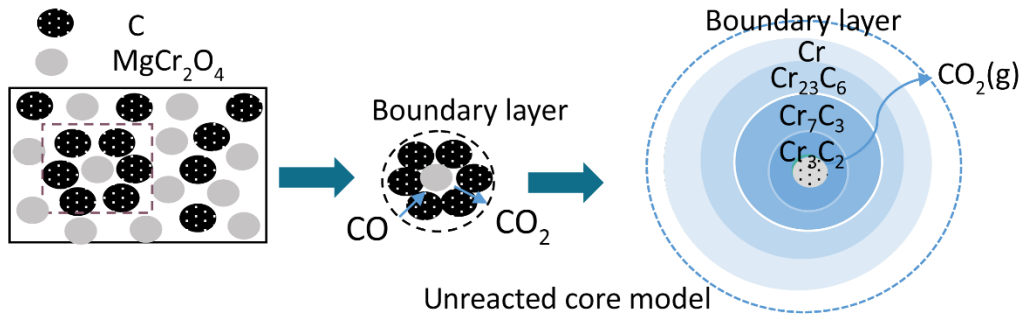


Figure 2: Schematic representation of the carbothermal reaction mechanism of $MgCr_2O_4$

Conclusions

Carbothermal reduction of synthetic chromite was carried out under argon atmosphere. Chromite is gradually reduced by carbon through the consecutive formation of low chromium content carbides as intermediate phase, which then react with CO_2 to form carbides with higher Cr content, which are then finally reduced to metallic chromium. The reaction mechanism is proposed based on the experimental results and thermodynamic calculation.

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