In-situ Investigation on the Reduction of Magnesiochromite with Ferrosilicon between 1 373–1 573 K

Xuan WANG,^{1,2)*} Tom Van GERVEN,²⁾ Bart BLANPAIN¹⁾ and Muxing GUO^{1)*}

1) Department of Materials Engineering, K.U.Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium.

2) Department of Chemical Engineering, K.U.Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium.

(Received on March 21, 2015; accepted on July 15, 2015)

Certain amount of the chromium in slags exists in the form of magnesiochromite (MgCr_2O_4) during the decarbonisation of stainless refining. It is mainly recovered through high temperature reduction. In this study, an interface of ferrosilicon and synthetic MgCr_2O_4 is made and the reduction behaviour is *in-situ* observed by confocal scanning laser microscope (CSLM) between 1 373–1 573 K. The samples were analysed afterwards through electron probe micro analyser (EPMA). Reduction of MgCr_2O_4 can already initiate at 1 373 K within around 30 min. The heat generated from the reaction between Si and Cr_2O_3 can increase the local temperature of the area surrounding the reaction zone. This makes the liquefaction of Fe–Si alloy possible even at measured bulk temperatures lower than its melting point. Although Fe does not participate in the reduction of Cr, it can diffuse into the reaction zone to form a Fe–Cr–Si alloy phase, together with the reduced Cr metal and residual Si. The liquid Fe–Cr–Si alloy can act as a transfer medium for Si to promote the reduction.

KEY WORDS: magnesiochromite reduction; ferrosilicon; CSLM; chromium recovery.

1. Introduction

Certain amount of the chromium in slags is chemically bound as oxides (mainly magnesiochromite, MgCr_2O_4).¹⁾ Although chromium is mainly immobilized in stable spinel phases and at its non-hazardous trivalent state, it can still be gradually oxidized to its highly soluble and carcinogenic hexavalent state in atmospheric environment.^{3–5)} Besides the potential risk to the environment, the effective recovery of chromium from slags also has economical importance due to the constantly rising demand of chromium in metallurgy.⁶⁾ Pyrometallurgical treatments of chromium containing slags have been applied to recover the chemically bound chromium. Although a multitude of laboratory and industrial studies have been performed on this subject,^{2,6–12)} there is still a lack of close investigation of the reaction between the reductant and the spinel phase, which is the major chromium bearing component in slags.

Ferrosilicon is commonly used to control chromium content in slags during the charging of furnace,^{2,13)} as well as to recover chromium from slags.^{6,11)} Silicon is the only component with reducing ability in ferrosilicon. Ferrosilicon is reported to have the ability to accelerate the carbothermic reduction of spinel phases.^{14–16)} The application of ferrosilicon enables the reduction of spinel at relatively low temperature and high reaction rate, which makes the reduction more economically feasible.¹⁵⁾

In this study, an interface of ferrosilicon and magnesiochromite is made and the reduction behaviour is *in-situ* observed by confocal scanning laser microscope (CSLM) and analysed afterwards. CSLM has been successfully applied in many metallurgical fields,¹⁷⁾ such as inclusion behaviours^{18,19)} and slag carburization^{20,21)} in steel making. It can provide *in-situ* observation of reduction behaviour of magnesiochromite, which generates more information comparing to post mortem methods used in the previous studies of slag reduction. Thereby, further understanding of the reduction behaviour of magnesiochromite can be achieved.

2. Experimental and Characterization

2.1. Synthesis of Magnesiochromite

The synthetic magnesiochromite is made from Cr_2O_3 (99.9 wt%) powder and MgO powder. MgO was heated in oven at 1 273 K for 1 h before mixing to release water and CO_2 , which was absorbed from ambient air. The two powders were weighted according to the mole ratio of 1:1 and mixed. 100 g of the mixed power was then brought in a plastic bottle together with 500 g ZrO_2 milling balls ($\varnothing=5$ mm) and 500 ml ethanol. The mixing was carried out through a Turbula mixer for 12 h. The obtained slurry was dried in a vacuum dryer and heated in the oven (363 K) for 12 hours. The obtained dry powder was then pressed by a mechanical presser in a cylindrical mould at a pressure of 20 MPa to form a disc of 12.5 mm diameter. The disc was then pressed again under pressure of 3 000 bar (300 MPa) by a hydraulic presser. Then the pressed discs were loaded in an alumina crucible with ZrO_2 milling balls as insulator

* Corresponding author: E-mail: xuanw1985@gmail.com,
muxing.guo@mtm.kuleuven.be
DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2015-126>

between each other and the wall of crucible. The sample was then heated in the furnace up to 1 873 K for 12 h in air atmosphere with both heating and cooling rate of 10 K/min.

2.2. Reduction Couple

The set-up of the reduction couple is demonstrated in **Fig. 1**. The obtained synthetic magnesiochromite, as well as ferrosilicon (Si 86.52 wt%, Fe 13.04 wt%, Al 0.18 wt%, Ca 0.06 wt%),²²⁾ were cut and polished into a small rod with size about $2 \times 2 \times 5$ mm. Afterwards, the ferrosilicon and magnesiochromite rods were embedded in resin (Technovit 4004, Heraeus Kulzer). The embedded sample was then ground (with Streurs P320, P800, P1200 and P400, representing SiC grain diameters of, respectively, 46, 22, 14 and 6 μm) and polished with 3 μm diamond suspensions until mirror-like smooth surfaces are obtained. Subsequently, the ground specimen was dipped in acetone to dissolve the resin. After the removal of resin, the rods were cleaned and pressed against each other (on the polished surfaces) and mounted into a small alumina crucible ($\varnothing = 5$ mm) with alumina cement as supporting material. When the cement was totally solidified after 12 h of aging, the specimen was embedded in the resin again. The same grinding and polishing procedure followed by resin dissolution, as described before, was performed again to obtain the final reduction couple with mirror-polished surface on the top side.

2.3. Experimental Procedure

The experiments were performed with varying temperature and reaction time (**Table 1**) under Ar atmosphere, which is purified by flowing Ar through a magnesium particle bed at 773 K. The temperatures are chosen to be below the melting point (1 653 K) of ferrosilicon in order to observe a clear reaction interface, yet reduction can still initiate.⁵⁾ A thermal couple is placed under the sample to measure the temperature. A thin titanium wire is also put around the reduction couple to further avoid oxidation of the specimen. The heating and cooling rates are both set at 200 K/min. The behaviours of the sample are *in-situ* observed and recorded from the top of the reduction couple during heating, holding and cooling at a frame rate of 15 frame/s.

Fig. 1. Set up of the reduction couple.

Table 1. Experimental conditions.

Experimental factor	Value
Temperature (K)	1 373, 1 423, 1 473, 1 523, 1 573
Time (min)	10, 30, 60

After cooling, a cross-section was made by polishing the top of the reduction couple and subjected to characterizations with microscopes.

2.4. Characterization

The specimens after reduction experiments were polished and coated with Pt–Pd (1 nm thickness). The microstructure and elemental composition of the specimen were characterized with electron probe micro analyser (EPMA, JXA-8530F), using an acceleration voltage of 15 kV and a probe current of 15 nA. The thermodynamic calculation in this work was performed with FactSage 6.4 (database: FToxide and FSstel), which is a fully integrated computing system in chemical thermodynamics. It enables the user to access a series of information, database and manipulation modules to perform a wide variety of thermochemical calculations.²³⁾

3. Results and Discussions

3.1. In-situ Observation of the Ferrosilicon/spinel Reaction

The reduction process of sample heated at 1 473 K for 60 min was recorded through the camera equipped on CSLM and shown in **Fig. 2**, as an example to demonstrate the reaction behaviour of the ferrosilicon/magnesiochromite couple at high temperature. As shown in the figure, the ferrosilicon block is placed in the left part of the image and the magnesiochromite block in the right part. This configuration is also applied in the following reduction couple images. After heating, when temperature reached 1 473 K, part of the ferrosilicon block became liquefied (**Fig. 2(a)**). The approximate boundaries between liquid and solid phases are indicated by white dashed lines in the figures. According to the Fe–Si phase diagram (**Fig. 3**), the liquid phase of the applied ferrosilicon initiates at around 1 473 K (the vertical dash line), which is in line with the *in-situ* observation. The solid phase is assumed to be the silicon particle, which has higher melting point, while the liquid phase is considered to be the Fe–Si alloy (**Fig. 2(a)**). As the reduction proceeded, the liquid zone in the ferrosilicon block increased in volume and contacted the spinel block (**Fig. 2(b)**). The silicon par-

Fig. 2. Images of sample observed through CSLM at 1 473 K for: (a) 0 min; (b) 15 min; (c) 45 min and (d) 60 min. Long white dash line indicates the boundary between liquid and solid phase and short white dash line indicates the original ferrosilicon/spinel boundary. (b), (c) and (d) are the images of the same location at different reaction time.

ticle was shrinking (Fig. 2(c)) and dissolving into the liquid phase. This process may be because silicon was consumed during the reduction of spinel, which shifted the local composition of the ferrosilicon block towards the eutectic point (indicated by the arrow in Fig. 3). Therefore, the liquid phase volume increases.

Another effect which may cause the volume increase of the liquid phase is that large amount of heat is released from the reduction of Cr in spinel with Si, as described in Eq. (1):¹⁶⁾

In order to highlight the heating effect of the reducing reaction, an adiabatic temperature calculation is performed with various ferrosilicon doses through dedicated module in FactSage, during which ΔH is set as zero. During the calculation, all the heat generated from the reduction is assumed to be utilized in the liquefaction of materials and heating up of the system, without heat exchange with the surroundings ($\Delta H = 0$). The initial temperature of the system is set as 1 473 K and the calculated temperature is plotted in Fig. 4. As shown in the figure, under adiabatic conditions, the materials could theoretically be heated up to as high as 2 003 K (with 73 mole% of applied ferrosilicon and 27 mole% spinel). At this temperature, ferrosilicon is completely in the liquid state (as indicated by solid line in Fig. 3). Although it was not an ideally closed system during

Fig. 3. Fe-Si phase diagram (calculated with FactSage 6.4). The red dash line indicates the composition of the ferrosilicon applied in this work.

Fig. 4. Calculated temperature of the reduction system with various spinel/ferrosilicon ratio (adiabatic system, $\Delta H = 0$).

the experiments and part of the generated heat was transferred into the surroundings, no significant temperature rise of the whole sample was observed during the experiments. It can be assumed that due to the poor thermal conductivity of oxides, only the reaction zone and its adjacent area are heated up above the bulk temperature of 1 473 K. In conclusion, the enlargement of the liquid zone can be the result of the combination of both silicon consumption and heat released from the reduction process.

The morphology of the spinel block also changed during the reaction, from smooth to wrinkled (Figs. 2(a)→2(b)→2(c)). This change of morphology may be due to the volume change caused by the newly formed reaction product. At the later stage of the reaction (after 40 min), liquid phase started to appear in the spinel side (Figs. 2(c) and 2(d)). This liquid phase is considered to be the reduced metal product alloyed with iron and residual silicon, which was confirmed by the EPMA analysis of the sample after the CLSM study (see section 3.2).

The images of samples reacted for 30 min at various temperatures are shown in Fig. 5. At 1 373 K, no liquid phase appeared in both ferrosilicon and spinel blocks (Fig. 5(a)). The surface of spinel block stayed unaltered. With increasing temperature to 1 423 K, liquid phase was observed in the ferrosilicon near the ferrosilicon/spinel boundary (Fig. 5(b)). Since the melting point of the Fe-Si alloy is higher than 1 423 K (Fig. 3), this localized alloy melting may be due to the extra heat released from the reduction process that occurred at the ferrosilicon/spinel interface as identified by FactSage calculation (Fig. 4). Part of the liquid phase also appeared inside the spinel block. In the sample at 1 523 K, extensive liquid phase can be observed on the spinel block. This may be caused by the infiltration of the formed liquid metal phase, which transported silicon further into the spinel block through pores inside the spinel or/and voids generated during reduction. The liquid metal acted both a transporting medium for silicon and an absorbing matrix for chromium. Larger liquid volumes of the sample at higher temperature indicated it was further reduced than the samples at lower temperatures.

During the tests performed at 1 573 K, the ferrosilicon

Fig. 5. Images of sample observed through CSLM at: (a) 1 373 K; (b) 1 423 K; (c) 1 473 K and (d) 1 523 K for 30 min. Long white dash line indicates the boundary between liquid and solid phase and short white dash line indicates the original ferrosilicon/spinel boundary.

block was almost fully melted within 10 min. As shown in **Fig. 6**, the surface of liquid ferrosilicon was lower than the surface of spinel block, since there was no barrier to hold the liquid, and therefore out of focus. The surface of the spinel block was metalized rapidly. After 60 min, the surface was almost fully metalized. However, the metalization was not accompanied with liquid phase generation in the spinel block.

3.2. Microstructure of the Interaction Zone and the Reduction Process

Only optical information of the reduction process could be recorded by CSLM, which could not provide information on the generated phases. In order to further study the phases generated during reduction and understand the reduction process, the samples were analyzed through EPMA after

quenching. The microstructure of the reduced samples and the formation of various reduced products are discussed below.

The Cr_2O_3 is considered as the only reducible component in magnesiochromite under present experimental conditions. The obtained SiO_2 intends to react with the MgO left in the spinel structure to form enstatite (MgSiO_3):

Combining Eqs. (1) and (2), the overall reaction equation can be written as:

The microstructures of reduction couple holding at 1 373 K for 30 min are demonstrated in **Fig. 7**. The identification of various phase observed in the figure (indicated by point number) are based on the EPMA compositional analysis

Fig. 6. Images of sample observed through CSLM at 1 573 K for: (a) 10 min and (b) 30 min.

Fig. 7. BSE images of sample that was treated at 1 373 K for 30 min: (a) $\times 500$ magnification; (b) $\times 2\,000$ magnification. Ferrosilicon block is on the left side of the image and spinel block is on the right side of the image.

Table 2. Chemical composition of various phases in sample kept at 1 373 K for 30 min analyzed through EPMA.

Point No.	wt%					mol%				
	O	Cr	Mg	Si	Fe	O	Cr	Mg	Si	Fe
1	0.01	0.21	0.00	99.78	0.00	0.02	0.18	0.00	99.80	0.00
2	0.00	1.17	0.03	54.84	43.96	0.00	0.81	0.05	70.77	27.97
3	33.48	51.40	14.51	0.08	0.00	56.85	26.85	16.22	0.08	0.00
4	0.96	97.28	0.05	0.76	0.94	2.99	92.78	0.11	1.34	0.83
5	47.48	14.18	16.25	22.06	0.02	63.21	5.81	14.24	16.73	0.01
6	48.36	11.04	17.23	24.19	0.05	62.90	4.42	14.75	17.92	0.02
7	37.00	46.19	12.89	3.90	0.02	59.75	22.95	13.70	3.59	0.01
8	52.21	8.01	4.35	35.39	0.04	67.19	3.17	3.69	25.94	0.01
9	1.73	96.32	0.10	1.04	0.79	5.39	91.86	0.21	1.84	0.70

listed in **Table 2**. As discussed in the previous section, the ferrosilicon employed in this work is a mixture of pure Si phase and Fe_3Si_7 phase in the temperature range of 1 273 to 1 473 K (Fig. 3). According to the composition analysis with the sample after the CLSM observations, the two phases in the ferrosilicon block are proven to be Si and Fe_3Si_7 (point 1 and 2 in Table 2).

According to Fig. 7(a), two new layers formed between the original ferrosilicon block (point 1 and 2) and spinel block (point 3), indicated by A and B. In both layers, chromium particles (Fig. 7(b), point 4 and 9), as reduction product, can be observed. The light gray particles (point 7) in the layer B are unreduced MgCr_2O_4 . The darker phase in layer A (point 8), is SiO_2 generated from the reduction, with a minor quantity of MgO dissolved inside. The gray phase in layer A (point 6) is MgSiO_3 , located between SiO_2 and spinel. This phase also filled up the space between the unreduced MgCr_2O_4 phase. The metallic Cr is mainly located at the Fe–Si alloy/layer A interface and at the layer A/layer B boundary, respectively. Cr can also be observed inside layer B (Fig. 7(b)). This may be due to the entrapped reduced Cr metal and/or unreduced MgCr_2O_4 , which are predicted to coexist with MgSiO_3 and SiO_2 at the locations close to the spinel block (point 8 in Fig. 7(b)). Figure 7 demonstrates the distribution of various elements in the sample treated at 1 273 K for 30 min. Layer A and B can be differentiated based on their different Si concentration. The former can be considered as the highly reduced zone, while the latter is the less reduced zone.

Another phenomenon which can be observed from Fig. 7(a) is that the boundary of the Si grain is not on the same level as the Fe–Si alloy/spinel boundary (Fig. 7(a)), which is the original ferrosilicon/spinel boundary. The iron in ferrosilicon does not participate in the reduction process and hinders the transport of silicon, which is due to the fact that energy is required to release silicon from ferroalloy.⁶⁾ The part of spinel block adjacent to the Fe_3Si_7 grain was less reduced, which was indicated by a thinner layer A and B compared to the part near the silicon grain (Fig. 7(a)). The approximate boundary between layer B and original spinel block is highlighted with white dashed line in Fig. 7(a). The layer A and B adjacent to Fe_3Si_7 grain is around 1 μm and 20 μm , while the thickness of both layers adjacent to silicon grain are around 10 μm and 40 μm , respectively. This indicates the different reducing abilities of Si and Fe–Si alloy, *i.e.* Si is a stronger reductant than Fe–Si alloy. With the reduction proceeded, Si was consumed and the volume of the silicon decreased. Therefore the edge of silicon grain moved away from the spinel block towards the ferrosilicon block. Meanwhile, the early stage reduction products (Eq. (1)), *i.e.* SiO_2 and Cr metal, filled the space between silicon grain and spinel block. The MgO , which was liberated from the spinel grain, reacts with SiO_2 forming MgSiO_3 in the original locations or in the SiO_2 layer after diffusing into it (Eq. (2)). Even after this thin SiO_2 layer has formed, Si could still be transported to the spinel block by diffusion through this layer. As the Fe–Si alloy has lower reducing ability, the consumption of Si in Fe–Si phase is slower.

Figure 8 demonstrates the microstructure of sample treated at 1 373 K for 60 min. Further reduction of the spinel can be observed through the thicker reaction layer A and

Fig. 8. BSE images of sample treated at 1 373 K for 60 min: (a) $\times 200$ magnification; (b) $\times 2\,000$ magnification (detailed image of the reaction zone).

B and extensive metallization of layer A (Fig. 8(a)). Large pores can be found between layer A and B. They are possibly generated during the decomposition of spinel grains and forming of reaction layers. Comparing with the sample after 30 min (Fig. 7), no contact boundary of silicon grain and reaction layer A can be observed in the sample after 60 min (Fig. 8(a)). A layer of Fe–Si alloy can be observed between the silicon grain and layer A (indicated by white frames in Fig. 8(a)). A possible mechanism can be assumed as follows: as mentioned earlier, during the reduction the boundary of the silicon grain kept on moving away from the spinel block, while Si was diffusing towards the spinel block through reaction layer A. Up to a certain moment, the silicon grain detached from layer A due to the slower growth rate of layer A and left a gap in between. The heat generated during reduction made the Fe–Si alloy liquefied and filled the gap between the silicon grain and reaction layer A. The diffusion of Si from the silicon grain would first move through the newly formed Fe–Si alloy layer, then reach reaction layer A. This assumption cannot be observed during the CSLM experiment at 1 273 K, which was possibly due to the fact that this phenomenon is not obvious at macro scale and the newly formed layer of Fe–Si alloy is relatively thin (around 10 μm) (Fig. 8). However, it is supported by the phenomena observed during the experiment at 1 473 K (Fig. 2), where size reduction of the silicon grain and movement of Fe–Si alloy were recorded.

Compared to the reduced metal particles in Fig. 7(b), the reduced metal particles in Fig. 8(b) are larger and demonstrate a mesh-like structure. The chemical composition of the phases indicated in Fig. 8(b) is listed in **Table 3**. Besides pure Cr metal particles (point 2), which are mostly associated with unreduced spinel particles, Cr–Si alloy (point 1)

Table 3. Chemical composition of various phases in sample treated at 1 373 K for 60 min analyzed through EPMA.

No.	wt%					mol%				
	O	Cr	Mg	Si	Fe	O	Cr	Mg	Si	Fe
1	0.45	48.52	0.02	50.69	0.33	1.01	33.66	0.02	65.09	0.22
2	0.83	98.03	0.02	0.95	0.17	2.63	95.46	0.05	1.71	0.16
3	0.50	47.52	0.04	34.01	17.93	1.26	36.87	0.06	48.85	12.96
4	0.00	0.99	0.03	55.15	43.87	0.00	0.52	0.03	71.21	28.23

Fig. 9. BSE image of samples treated for 60 min at: (a) 1 373 K; (b) 1 423 K; (c) 1 473 K; (d) 1 523 K. Ferrosilicon block is on the left side of the image and spinel block is on the right side of the image. **Fig. 10.** BSE image of samples kept at 1 573 K for: (a) 10 min; (b) 10 min (area indicated by white frame in (a)); (c) 30 min; (d) 60 min. Ferrosilicon block is on the left side of the image and spinel block is on the right side of the image.

and Cr–Si–Fe alloy (point 3) also formed. Although Fe in Fe–Si alloy (point 4) does not participate in the reduction of spinel, it also diffused into the reaction layer, probably together with Si, to form an alloy phase with Si and Cr. This eutectic alloy system has a lower melting point and exists as liquid phase with high fluidability, as demonstrated during CSLM observations. This liquefied alloy can promote the formation of the mesh structure of the metal phase.

As can be observed from **Fig. 9**, with increasing temperature, further reduction of spinel can be achieved. The two reaction layers A and B can still be recognized, however, the boundary between each other becomes less clear. The approximate boundary between layer A and B is indicated by the white dashed line. The thickness of reaction layer A varies at different locations. The cracks and holes (Figs. 9(c) and 9(d)) generated by the decomposition of spinel and formation of new minerals may also affect the transport of Si and the formation of the layers. On the other hand, pores and cracks can provide transport pathways for liquid Fe–Si alloy to flow into reaction layers and transport silicon to promote the reduction and/or forming alloys. In general, qualitatively speaking, a thicker reaction layer A formed at higher temperatures. The size of the formed metal particles also increases with increasing temperature. This is in line with the phenomena observed from CSLM: at higher temperature, the volume of liquid metal in the reaction zone increases (Fig. 5). Iron acts as matrix material in alloying of Fe–Cr–Si alloy and further lowers the melting temperature of the metal phase and increases its mobility. When

the reduction proceeds the temperature increases and the reduced metal develops from small particles (Fig. 7) into mesh structures or large metal particles (Fig. 9).

As observed during *in-situ* observations, at 1 573 K ferrosilicon was almost fully liquefied and the spinel surface was extensively metalized, which is different from the reduction process in other samples. In the sample kept at 1 573 K for 10 min, large Fe–Cr–Si alloy particles can be observed not only at the interface between the ferrosilicon block and the spinel block, but also in the middle of the spinel block (**Fig. 10(a)**). No clear reaction layer A and B can be observed. Large pieces of Fe–Cr–Si metal appeared in the middle of the spinel block. This may be because, at this temperature, it is possible for the liquid ferrosilicon to penetrate into the spinel block through the small pores between spinel grains very fast. In this case, Si was transferred much faster, compared with solid stated diffusion, and resulted in rapid reduction of spinel phase. Hence, liquid Fe–Si alloy can be considered as a carrying medium to improve the transport of Si, as well as an absorber of reduced chromium. The rapid decomposition of the spinel block and intrusion of the ferrosilicon can be observed in Figs. 10(c) and 10(d).

3.3. Thermodynamic Calculation

Thermodynamic calculations were carried out with respect to the ferrosilicon/spinel reduction couple. The composition of ferrosilicon applied in the calculation was set as the same as the one used in the presented CLSM experiment. The calculated temperatures and major phases

Fig. 11. (a) Calculated temperature of the reduction system with various spinel/ferrosilicon ratio (adiabatic system, $\Delta H = 0$) and (b) calculated phase distribution during the reduction of magnesiochromite by ferrosilicon at 1473 K under adiabatic conditions.

Fig. 12. Calculated phase distribution during the reduction of magnesiochromite by ferrosilicon at 1473 K under isothermal conditions.

are plotted in Figs. 11 and 12, in both adiabatic ($\Delta H = 0$) and isothermal systems, respectively. The listed phases are in solid form, unless indicated as “liquid”. The actual reduction process situates between these two systems. And the

reaction layers A and B are composed with phases situate between ferrosilicon block (left boundary) and spinel block (right boundary) in Figs. 11(b) and 12.

In the adiabatic system (Figs. 11(a) and 11(b)), liquid alloy, containing unreacted Si, Fe and reduced Cr, appears immediately after the reduction starts and grows in mole fraction, accompanied with temperature increase of about 353 K. This is in line with the phenomena observed through CSLM (Fig. 2(a)), that liquid phase was generated at the very beginning of the reduction carried out at 1473 K. When solid Si is depleted through melting and consumption due to reduction, the temperature of the system increases sharply from around 1573 K to the maximum of 2003 K, where the mole fraction of spinel in the system is up to 26%. According to Fig. 11(b), the system is composed with fully liquid alloy (Si, Fe and Cr) and slag (MgO , SiO_2 and CrO) when the mole fraction of spinel is between 25% and 35%. The vast amount of liquid phase, which has been observed during *in-situ* observation, is considered to be the mixture of liquid alloy and liquid slag. And the liquid slag, generated due to the disintegration of the spinel block, accumulates and moves, generating pores as shown in Figs. 9 and 10. With increasing amount of spinel, the liquid alloy starts to solidify rapidly, accompanied with certain heat release indicated by a small temperature peak in Fig. 11(a), as indicated by the red arrow. When more spinel is introduced into the system (> 42 mole%), the temperature of the system and the amount of liquid slag decreases, while unreacted MgCr_2O_4 starts to appear in the system. The adiabatic system can be applied to interpret the phenomena observed by CSLM at high temperatures, since the released heat is taken into account.

In the isothermal system (Fig. 12), less amount of liquid alloy and no liquid slag are generated. More CrSi_2 is produced than in the adiabatic system and Si also exists as alloys, such as CrSi , Cr_5Si_3 , Cr_3Si and FeSi . These products compose the Fe–Cr–Si alloy observed in the samples after cooling. This is supported by the chemical analysis of different metal phases listed in Table 3. Instead of liquid slag, the oxidised Si appears in the forms of MgSiO_3 and SiO_2 , which were also observed in the obtained samples (Fig. 7). The isothermal system can be applied to identify the reduction products after cooling.

3.4. Reduction Mechanism

Based on the previously mentioned observations and discussions, the reduction mechanism of magnesiochromite by ferrosilicon is proposed, as demonstrated schematically in Fig. 13.

At the first stage of reduction (Fig. 13(b)), both silicon grains and Fe–Si alloy grains participate in the reduction. Two layers (named A and B) of materials form during reduction. According to the chemical analysis results, the reaction layer A is mainly composed of SiO_2 with MgSiO_3 and large Cr metal particles, while the reaction layer B is mainly composed of unreduced MgCr_2O_4 , surrounded by SiO_2 , MgSiO_3 and Cr metal. Silicon has a stronger reducing ability than Fe–Si alloy, therefore the reaction layer A is first generated at the locations in contact with the silicon grain. Reaction layer B is generated across the whole interaction surface. In the later stage of reduction (Fig. 13(c)), the sili-

Fig. 13. Schematic representation of the proposed reduction process of magnesiochromite by ferrosilicon.

con grain detaches from the reaction layer and only Fe–Si alloy participates in the reduction. However, when liquefaction of ferrosilicon alloy is extensively achieved, the solid silicon particle can float and move into the liquid bath (Fig. 2(d)) where it comes in contact with the reaction layer (Figs. 9(b) and 9(c)). Si diffuses through reaction layer A and reduces spinel in reaction layer B, thereby increasing the thickness of reaction layer A. During the diffusion, Si can also be captured by reduced Cr metal to form Cr–Si alloy. Fe, although it does not participate in the reduction process, transports Si, in the form of a liquid Fe–Si alloy, into reaction layer A and forms there the Fe–Cr–Si alloy phase.

4. Conclusions

The reduction of magnesiochromite by ferrosilicon, at 1 373 to 1 573 K, was studied by *in-situ* observations carried out using CSLM. The obtained samples were characterized by EPMA. Based on the previous discussions, some conclusions can be drawn as follows:

(1) Reduction of magnesiochromite can already initiate at 1 373 K within a relatively short time (around 30 min).

(2) Ferrosilicon block is composed of silicon grain and Fe–Si alloy grain. Silicon has a stronger reducing ability than Fe–Si alloy. When the reduction proceeds, Si in the silicon grain is consumed and the size of silicon grain

decreases. The silicon grain detaches from the reaction zone and the gap in-between is filled with liquid Fe–Si alloy. This layer of Fe–Si alloy can act as transfer medium for Si from the silicon grain to the reaction zone.

(3) The reaction zone can be divided into two reaction layers: A and B. Layer A is mainly composed of SiO_2 , MgSiO_3 and large Cr metal particles, while the layer B is mainly composed of unreduced MgCr_2O_4 , surrounded by SiO_2 , MgSiO_3 and small Cr metal particles.

(4) The heat generated from the reaction between Si and Cr_2O_3 can increase the local temperature of the area surrounding the reaction zone. This makes the liquefaction of Fe–Si alloy possible even at measured bulk temperatures lower than its melting point.

(5) Although Fe does not participate in the reduction of Cr, it can diffuse into the reaction layers to form a Fe–Cr–Si alloy phase, together with the reduced Cr metal and residual Si. Fe can also act as carrying medium for Si to improve its transfer.

(6) During the experiments performed at 1 573 K, the ferrosilicon was totally liquefied and penetrates into the spinel block through the pores between the spinel grains. Rapid reduction of spinel was achieved due to the fast transfer of Si through the liquid phase.

REFERENCES

- 1) H. Shen, E. Forssberg and U. Nordstrom: *Resour. Conserv. Recycl.*, **40** (2004), 245.
- 2) T. Kho, D. Swinbourne, B. Blanpain, S. Arnout and D. Langberg: *Miner. Process. Extr. Metall.*, **119** (2010), 1.
- 3) A. L. Rowbotham, L. S. Levy and L. K. Shuker: *J. Toxicol. Environ. Health B*, **3** (2000), 145.
- 4) K. Pillay, H. von Blottnitz and J. Petersen: *Chemosphere*, **52** (2003), 1771.
- 5) P. Mostbauer: *Waste Manag.*, **23** (2003), 547.
- 6) B. Adamczyk, R. Brenneis, C. Adam and D. Madersbach: *Steel Res. Int.*, **81** (2010), 1078.
- 7) G. Ye, E. Burström, M. Kuhn and J. Piret: *Scand. J. Metall.*, **32** (2003), 7.
- 8) M. Divakar, M. Görnerup and A. Lahiri: *Ironmaking Steelmaking*, **29** (2002), 297.
- 9) M. Görnerup and A. Lahiri: *Ironmaking Steelmaking*, **25** (1998), 317.
- 10) N. Sano: Proc. 10th Int. Ferroalloys Cong., IFCA, Cape Town, South Africa, (2004), 670.
- 11) S. Lee, H. Song, H. Hwang, P. Rhee and O. Klevan: *Scand. J. Metall.*, **32** (2003), 247.
- 12) W. Rankin and A. Biswas: *Miner. Sci. Eng.*, **7** (1975), 89.
- 13) J. Björkvall, S. Ångström and L. Kallin: Proc. VII Int. Conf. on Molten Slags Fluxes and Salts, SAIMM, Johannesburg, (2004), 663.
- 14) T. Hu, X. Lv, C. Bai, Z. Lun and G. Qiu: *ISIJ Int.*, **53** (2013), 557.
- 15) A. Zambrano, C. Takano, M. Mourao, Y. Tagusagawa and Y. Iguchi: *ISIJ Int.*, **51** (2011), 1296.
- 16) R. Huang, X. Lv, C. Bai, K. Zhang and G. Qiu: *Steel Res. Int.*, **84** (2013), 892.
- 17) P. Jones, D. Desmet, M. Guo, D. Durinck, F. Verhaeghe, J. Van Dyck, J. Liu, B. Blanpain and P. Wollants: *J. Eur. Ceram. Soc.*, **27** (2007), 3497.
- 18) Y. Wang, S. Sridhar and M. Valdez: *Metall. Mater. Trans. B*, **33** (2002), 625.
- 19) S. Kimura, Y. Nabeshima, K. Nakajima and S. Mizoguchi: *Metall. Mater. Trans. B*, **31** (2000), 1013.
- 20) H. Kim, Y. Kang, J. Kim and Y. Sasaki: *ISIJ Int.*, **51** (2011), 166.
- 21) K. Ohno, T. Miki and M. Hino: *ISIJ Int.*, **44** (2004), 2033.
- 22) M. Pande, M. Guo, D. Geysen, S. Devisscher, B. Blanpain and P. Wollants: *Ironmaking Steelmaking*, **37** (2010), 502.
- 23) C. Bale, E. Bélisle, P. Chartrand, S. Decterov, G. Eriksson, K. Hack, I. Jung, Y. Kang, J. Melançon, A. Pelton, C. Robelin and S. Petersen: *Calphad*, **33** (2009), 295.