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# DIRECT CHROMIUM ALLOYING BY CHROMITE ORE WITH THE PRESENCE OF METALLIC IRON

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#### Abstract

Direct chromium alloying by chromite ore in EAF operation is a promising process in stainless steel production, which has the advantage of resource-saving, energy-saving, and environment-friendly. In the present investigation, iron, carbon, and chromite ore mixture  $(Fe+C+FeCr_2O_4)$  were chosen as the precursor for direct chromium alloying. Thermogravimetric Analysis (TGA) experiments were carried out to investigate the effect of iron content on the reduction kinetics, and the results show that the presence of metallic iron in the precursor will increase the reduction rate of chromite. Up-scaling experiments (100 g and 500 g scale) have been carried out in the induction furnace to further test the effectiveness of using industrial chromite ore for direct chromium alloying. The induction furnace tests confirmed the necessity of adjusting composition of the slags to ensure high yield of chromium in the final products; and chromium yield can reach 90%.

Key words: Direct alloying; Chromite ore; Stainless steel; Thermogravimetric analysis.

# 1. Introduction

Chromium is an important and expensive alloying element, which is intentionally added to steel to increase its corrosion-resistance, hardness and strength. During steelmaking process, chromium is added to the steel bath mainly in the form of ferrochrome (FeCr). In 2010 the worldwide ferrochrome consumption is more than 8 million tons [1]. Production of FeCr requires a large amount of electricity power, viz. 2.4-4.8 MWh/ton [2]. Further, during the producing process, nearly 20% of chromium is lost to the slag phase [3]. Since FeCr usually contains high amount of carbon, the excess of carbon in the melt, obtained after FeCr is charged into EAF, needs to be removed by oxygen blowing in the melting units (for example, EAF or AOD converter), during which more chromium would get oxidized and enter the slag phase, even though a part of it could be recovered by the addition of expensive ferrosilicon. The dumping of Cr-containing slags can pose significant environmental problems when considering the carcinogenic property of Cr6+. Hence, both from economic and environmental points of view, it is necessary to retain as much as chromium in the steel during any part of chromium cycle.

Direct alloying by using oxide-bearing ore, concentrate or even alloying-element-containing slags offers a promising technology in future steelmaking process; the application of this technology has the

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advantages of saving of raw materials, saving of electric energy, high alloying elements yield, as well as alleviating environmental problems. A direct alloying operation can either be implemented in an arc furnace or in a ladle/converter by smelting reduction. In a review of the available literature, manganese, chromium, vanadium, and molybdenum are among the elements that raised more interest to researchers. Kologrivova et al [4] showed that primary manganese ore can be reduced by direct alloying steel; and up to 2% manganese can be alloyed; the quality of steel corresponded to that alloyed with manganese ferroalloys. Nokhrina et al [5] pointed out that silicon was the element that actually reduced manganese. These authors concluded that direct manganese alloying in electric arc furnace can reduce the consumption of manganese and silicon; the manganese assimilation in the steel can reach 90-95%. Further, these authors observed that there was no quality difference between traditional alloyed steel by manganese ferroalloys and direct alloyed steel by manganese ore. While, Bobkova et al [6] point out that, the main concerns of direct manganese alloying were the low recovery degree, the instability of operation parameters, and the presence of nonmetallic inclusions, and they also pointed out that, to ensure fast reduction, steel should be alloyed with eutectic type mixtures of oxides, which has a liquidus temperature lower than the finishing temperature of the molten steel. Dzhandieri et al [7] pointed out that

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stochastic nature (for example, temperature of tapped melts) of the process and the density differences between briquettes and liquid melts disturbed stable implementation of the process; and they developed a structure model to control the process of direct alloying of alloys by manganese carbonate. Compared with manganese alloying, direct chromium alloying is more commonly implemented by smelting reduction in a converter. Kawakami et al [8] investigated the kinetics of the reduction process of bottom-injected chromite ore powder, and concluded that oxygen transport in the melt should be the rate-controlling step. Keizo et al [9] investigated the smelting reduction of top-charged chromite ore (pretreated and pelletized) into combined oxygen blowing converter, the results showed the improvement of productivity and energy cost for stainless steel. The pilot plant experiments carried out by Takeuchi et al [10] showed that both bottom and top oxygen blow injection of chromite ore can reach an almost same recovery ratio of 70-93%. Simbi et al [11] investigated the smelting reduction of chromite ore fines in the CaO-FeO-Cr2O3-SiO2-Al2O3 slag system by carbon dissolved in the melt. These authors found that the reduction progressed preferentially by a zeroth order reduction of FeO and then a first order reduction of Cr<sub>2</sub>O<sub>3</sub> It was reported that increasing slag basicity can enhance the reduction by minimizing the formation of CrO, which is thermodynamically quite stable in the slags. The early work with respect to direct vanadium alloying was mostly carried out in the 1990s by Russia researchers [12, 13]; their results showed that, by using V-containing slags, the assimilation of vanadium in the micro alloyed steel amounted to 70-80% in the converter and 95-97.5% in electric-arc furnace, and the steel products qualified various kinds of vanadiummicro-alloyed steels. The most recent work done by Chinese researchers showed that, direct thermosilicon reduction of calcium vanadate and V<sub>2</sub>O<sub>5</sub> can result in a recovery ratio of vanadium more than 90% [14, 15]. For direct molybdenum alloying, Song et al [16] investigated the thermosilicon reduction of molybdenum oxide with the addition of CaO in an induction furnace, and they concluded that CaO can inhibit the volatilization of MoO<sub>2</sub>, and the molybdenum yield can reach 97%; Chychko et al [17] designed an alloying mixture (FeO<sub>x</sub> + MoO<sub>3</sub> + C), and Mo yield was found to be up to 98%. Direct alloving with respect to other alloying elements, such as nickel [18], was also reported in the literature, and the combination of the direct alloying of two or more elements also raised a lot of interests among researchers [19, 20].

By changing the present chromium alloying procedure, direct chromium alloying by chromite ore in EAF operation can be a promising alternative route to produce chromium containing steels. This method offers a choice of cheaper raw materials, better control of the carbon content and less number of unit processes (avoiding the process step, *viz.* the production of ferrochrome, at least partially). Thus, there is likely to be a reduction in the consumption of energy as well. This method may open up the possibilities of less chromium loss to the slag phase.

According to the materials and energy balance calculation in the EAF, the in-situ formation of Fe-Cr alloy by use of (Fe+FeCr<sub>2</sub>O<sub>4</sub>+C) mixture will reduce the carbon content in the EAF charge mix, lower the cost of raw materials significantly, and decrease the energy consumption (-70 kWh/ton of liquid steel, by taking account the energy consumption for FeCr production) as compared to FeCr alloy additions. In the present work, the reduction kinetics of synthetic iron chromite with the presence of metallic iron was investigated by thermogravimetric analyse (TGA); up-scaling experiments (from 100 g to 500 g scale) by using the mixture of iron (both the pure iron powder and industrial iron scrap were tested), industrial carbon, and chromite ore were carried out in an induction furnace to investigate the reduction effectiveness of the designed mixture and also to simulate the real EAF operation of stainless steelmaking. The results are expected to be confirmed by a 3-ton-scale industrial trial in the near future.

# 2. Experimental 2.1 Synthesis of FeCr<sub>2</sub>O<sub>4</sub>

Pure iron fine powder (purity≥99%, from Riedelde Haen, Germany), iron oxide powder (purity≥99%, size < 5 micron, from Sigma-Aldrich, Germany), and chromium oxide powder (purity≥99%, from KEBO Lab, Sweden) were well-mixed in an agate mortar in stoichiometric proportions, and sealed in a pure iron crucible by welding. The crucible with the sample was placed in a vertical furnace and heated up to a temperature of 1573 K under a protecting stream of argon gas and maintained at this temperature for 24 hours before quenching in water [21]. The product was analyzed by X-ray Diffraction (XRD). As can be seen from Fig. 1, the XRD spectrum confirmed the presence of FeCr<sub>2</sub>O<sub>4</sub>, while no iron, iron oxides, or chromium oxides were detected.

#### 2.2 Thermogravimetric Analysis (TGA)

Synthetic iron chromite, pure iron fine powder, graphite (graphite was used as the reducing agent due to its high purity) were well-mixed before conducting the thermogravimetric analysis. Five different mixtures with different ratios of iron chromite to iron were prepared. Stoichiometric amount of graphite needed to reduce all the iron chromite in the mixture with 20% excess according to the formula (1) was added.

$$FeCr_{2}O_{4} + 4C = Fe + 2Cr + 4CO$$
 ...(1)



Figure 1. XRD pattern for the synthetic iron chromite.

The TGA experiments were carried out in the SETARAM TG-24 double-furnace unit with 0.001 mg detection limit. A schematic diagram of the unit is presented in Figure 2. Approximately 100 mg mixture was placed in a pure alumina crucible with inner diameter 8 mm, and height 8 mm. The crucible with the mixture was hung at one end of the balance beam, while a pure alumina crucible with alumina pieces was hung at the other end of the balance beam as reference. Argon gas (purity  $\geq$  99.999%, supplied by AGA gas, Stockholm) was used as the protecting gas during the experiments. The argon gas was further purified by passing through columns of silica gel, ascarite, copper turnings (maintained at 873 K), and magnesium chips (maintained at 773 K), to decrease the traces of moisture and CO<sub>2</sub> impurities present in the argon gas, and also to lower the partial pressure of oxygen. During the experiments, the furnace was



Figure 2. Schematic diagram of the TG-24 unit: 1-beam balance; 2-platinum wire; 3- carrier gas inlet; 4graphite heating elements; 5-alumina crucible with sample; 6- thermocouple; 7-carrier gas outlet; 8-alumina crucible with alumina pieces; 9-doulbe furnace.

flushed with argon gas for 6 hours and then the sample was heated according to the temperature program which can be seen from the TGA curves discussed below. After the heating process, the sample was cooled down at a cooling rate of 40 K/min to room temperature. The crucible with the mixture was carefully weighed on an analytical balance before and after each experiment. It was found that the mass loss matched accurately with that monitored by the TGA apparatus. Selected experiments were also repeated in order to confirm the reproducibility of the experiments.

## 2.3 Induction furnace experiments

In the induction furnace experiments, industrial chromite ore (particle size < 1 mm, with mean diameter 50% = 0.13 mm, from Outokumpu, Finland) was used as alloying precursor instead of the synthetic iron chromite; industrial carbon (purity≥99.3%) was crushed into small particles (particle size <0.25 mm) and used as the reducing agent. Industrial iron scrap (<30 mm in dimension, and <5 mm in thickness) or pure iron fine powder (<20 mess, purity  $\geq$ 99%) was used as the base metal for chromium alloying. A typical chemical analysis of the chromite ore is shown in Table 1 and the chemical analysis of the scrap is shown in Table 2. The experiments were carried out in three steps. In the first step, only chromite ore, carbon, and iron powder were mixed together; and in step two, a slag phase was added, either by mixing well with alloying mixture or positioning on the upper side of the mixture. In step three, a slag phase was added, after complete reduction was perceived. All the samples were placed in an alumina crucible and the sample in the crucible was protected from oxidation by a graphite lid and also argon gas. The schematic diagram of induction furnace setup is shown in Fig. 3. The mixture compositions used in the induction furnace experiments as well as temperature program for each step are shown in Table 3.

 
 Table 1. Typical composition analysis of chromite ore used in the induction furnace experiments (%)

Cr <sub>2</sub> O <sub>3</sub>	Fe	Fe <sup>2+</sup>	Fe <sup>2+</sup> /Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO
44	18	15	0.8	4	12	11
CaO	V	Na <sub>2</sub> O	K <sub>2</sub> O	С	S	Volatiles
0.6	0.1	< 0.1	< 0.1	0.6	< 0.05	3

 
 Table 2. Typical composition analysis of the iron scrap used in the induction furnace experiments (%)

С	Si	Mn	Cr	Мо	Ni	Р
0.1	0.2	0.7	0.1	0.015	0.07	0.012

			Chromite	Industrial	Base	metal	Slag addition				
	Number Scale		ore carbon		Iron powder	Iron scrap	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO		
	N1-1	100	85.1	14.9	-	-	-	-	-		
G( 1	N1-2	100	62.2	10.9	26.9	-	-	-	-		
Step 1	N1-3	100	26.5	4.7	68.8	-	-	-	-		
	10-15 K/min to 1873-1883 K, and held on for 45 minutes, then cooled down to room temperature.										
	N2-1	100	20.5	3.6	53.3	-	1.8	9.6	11.2		
	N2-2	100	20.5	3.6	53.3	-	1.8	9.6	11.2		
	N2-3	500	102.7	18	-	266.4	8.9	48.1	55.9		
Step 2	N2-4	500	102.7	18	-	266.4	8.9	48.1	55.9		
	10-15 K/min to 1773-1783 K, and held on for 30 minutes, then heated up to 1873-1883 K, and then cooled down to room temperature. For N2-1 and N2-3, slags were placed on the upper layer of the alloying mixture; while for N2-2 and N2-4, slags were well mixed with alloying mixture.										
	N3	500	102.7	18	-	266.4	8.9	41.1	55.9		
Step 3	10-15 K/min to 1773-1783 K, and held on for 30 minutes, then heat up to 1873-1883 K, and then cool down to 1573 K, at this moment slags were introduced into the crucible; the sample with slags were reheated to 1873-1883 K and held on for 15 minutes, then cooled down to room temperature.										

*Table 3.* Composition of Cr alloying precursor used in each step of induction furnace experiments and temperature program for each step (in gram)



Figure 3. Schematic diagram of induction furnace experiments: 1-refractory; 2-graphite lid; 3thermocouple; 4-alumina crucible; 5-graphite crucible; 6-mixture of industrial carbon and ore; 7-iron scrap; 8-gas tube for argon gas; 9induciton coil.

# 3. Results

## 3.1 Thermogravimetric analysis

In the TGA experiments, the weight loss of the sample was used to derive the reducibility of the ore. The percentage of reduction degree of iron chromite was defined as:

R = (mass loss of the sample / mass loss expected if all the iron chromite in the sample was reduced by graphite to form CO) × 100 The percentage chromium yield (the reduced chromium entrapped in the slag was not taken into account) in the final droplets or ingots was defined as:

 $Cr_{yield} = (mass of chromium dissolved in the droplets or ingots) / (calculated mass of chromium element in the mixture) × 100$ 

The non-isothermal reduction curves and isothermal reduction curves (at 1523 K) of five samples derived from TGA are shown in Fig. 4.

It can be seen from figure 4 that the presence of metallic iron in the alloying mixture is favorable for the reduction especially at high temperatures. The reduction rate increased with increase of the iron added. The reduction grade was higher as can be noticed in the final stage of reduction. The results were also confirmed by analyzing the droplets formed after TGA. This can be explained in the following way: as chromium was formed by reduction, it was dissolved in the iron by diffusion; this would lower the activity of chromium in the FeCr<sub>2</sub>O<sub>4</sub>-C interface and promote further reduction reaction as shown in equation (1). Since the diffusion between iron and chromium was sensitive to temperature, higher reduction rate can be reached at higher temperature.

The typical SEM micrographs of the droplets formed at 1773 K (for sample S5 at 1823 K) in the TGA experiments are shown in Fig. 5; while Table 4 shows the composition analysis of five droplets by EDS. Generally, the droplets formed consisted of two phases: one with lower chromium content (phase 1, light grey phase), another one with higher (phase 2,



Figure 4. Non-isothermal reduction curves (a) and isothermal reduction curves (b) derived from TGA: for the nonisothermal curves, the heating program was 5K/min to 1773 K (for sample S5, to 1823 K); for the isothermal curves, the heating program was 40K/min, and then held on 120 min at 1523 K.

dark grey phase), and the chromium content of both phases decreased with the increase of iron addition in the mixture. It can be seen from Table 4 that, in all cases, chromium yield could be as high as ca. 95%, except S5. The irregularity of S5 was due to the oxidation of chromium at the final stage of reduction when almost all the graphite was consumed. This was confirmed by the decreasing trend in the reduction percentage of non-isothermal and isothermal reduction curves of S5 shown in Fig. 4. This is corroborated by the surface colour of reaction product, which corresponded to that of  $Cr_2O_2$ . In fact, a slight oxidation of the reaction product at final stage was also observed in S2, S3, S4; so the actually reduction curves should show a slightly higher reduction degree than that indicated in Fig. 4. Thus, the real chromium yield should be higher than that indicated in Table 4.

 Table 4.
 Composition analysis of the droplets obtained after reduction of sample S1, S2, S3, S4, S5 on TGA experiments by SEM-EDS

	Element / %	Phase 1	Phase 2	Area Scanning	Calculated value	Cr yield	
S1	Cr	56.7	82.7	62.5	65	06.1	
51	Fe	43.3	17.3	37.5	35	90.1	
52	Cr	31.4	68.1	45.4	48.2	04.2	
52	Fe	68.7	31.9	54.6	51.9	JT.J	
52	Cr	26.5	69.5	31.7	33.6	04.2	
35	Fe	73.5	30.5	68.3	66.4	94.2	
54	Cr			19.9	21	05.1	
54	Fe			79.8	79	93.1	
85	Cr			7.7	9.9	78 /	
35	Fe			92.3	90.2	/0.4	



Figure 5. SEM micrographs of the droplets obtained after reduction of sample S1, S2, S3, S4, S5 on TGA experiments.

# 3.2 Induction furnace experiments

Fig. 6 shows the samples obtained after induction furnace experiments. It can be seen that, for sample N1-1 (chromite ore + carbon), no visible metallic droplets were formed; for sample N1-2 (chromite ore + carbon + iron powder, the ratio of nominal  $FeCr_2O_4$ in the chromite ore to iron powder is 3:2), the droplets formed had an average diameter of 1-2 mm; for sample N1-3 (chromite ore + carbon + iron powder, the ratio of nominal  $FeCr_2O_4$  in the chromite ore to iron powder is 1:4), both ingot and droplets were formed; N2-4 showed a typical image that can represent all the experiments in step two and three that the ingots were well separated from slags. The typical SEM micrographs and composition analysis of the droplets formed in N1-2, the ingot formed in N1-3, the droplets embedded in the slags in N1-3s, and the ingots formed in steps two and three are shown in Fig. 7 and Table 5, respectively. In step one, N1-2 in Fig. 7 corresponded to that of S3 in the Fig. 5 (they have almost same ratio of iron to chromite), and in this case, the chromium yield was 87.2%. For sample N1-3, the average chromium content in the ingots was 1.6%, which is far lower than the theoretical value. However, high content of chromium (54.5%) was found to be alloyed in the droplets which were closely embedded in and between the slags. A possible reason for this could be that, during the heating process, the iron in the mixture melted down before all the ore was reduced. The small trace of iron left in the slags

experiments									
	Element	Phase 1	Phase 2	Area	Cr				
	/%	i nuse i	T Huse 2	scanning	yield				
N1-2	Cr	21.4	72.17	29.3	87.2				
	Fe	78.6	27.83	70.7					
N1-3	Cr	1	4.14	1.6					
	Fe	99	95.9	98.4					
N1-3s*	Cr	84.7		54.5					
	Fe	15.4		45.5					
NO 1	Cr	5.3	28.7	9.1	92.4				
112-1	Fe	94.7	64.2	90.9	<i>)</i> 2. <del>,</del>				
N2_2	Cr	4.7	28.7	8.5	863				
182-2	Fe	95.3	71.3	91.5	80.5				
N/2 2	Cr	6.9	40.9	7.8	70.6				
112-3	Fe	93.1	50.1	92.2	79.0				
N2 4	Cr	5	35.8	5.8	58.0				
1NZ-4	Fe	95	64.2	94.2	36.7				
N3	Cr	7.3	53.3	8.8	80.4				
	Fe	92.7	46.7	91.2	07.4				
*For N1-3s, the metallic phase embedded in the slags was analyzed									

Table 5. SEM-EDS composition analysis of the droplets/ingots obtained from induction furnace experiments





Figure 6. Samples (N1-1, N1-2, N1-3, N2-4) obtained after induction furnace experiments.



Figure 7. SEM micrographs of the ingots/droplets obtained after induction furnace experiments.

assimilated the chromium, but failed to coalesce to form a big droplets or ingots, probably because of the high viscosity of slags in the mixture. After experiments, samples N1-1, N1-2, and N1-3 were sieved and separated by magnet in order to remove the entrapped iron alloys and get the slags with relatively higher purity. The XRD results of these slags showed that the main phase in the slags was MgAl<sub>2</sub>O<sub>4</sub> spinel phase, while no chromite ore or chromium oxide was detected. This confirmed the reasoning that the chromium oxide in the ore mixture was almost completely reduced. In step two, some slags were added in the alloying mixture and a higher Cr yield was obtained both for using iron powder and iron scrap; however, it seems that it is more advantageous if slag phase was added on the upper layer rather than being mixed with alloying mixtures. Iron powder was found to be more effective than iron scrap. In step three, the slag phase was added into the mixture at around 1573 K after complete reduction of the mixture, and then heated up to 1873 K for 15 minutes; in this case, Cr yield, by using iron scrap, reached almost 90%.

The ingots and final slags obtained from sample N2-3, N3 were also analysed at Uddeholms AB, Sweden. The results are shown in Table 6. These results show good consistency with the results from SEM/EDS analysis, with respect to Cr and Fe; and the mass balance of Cr and Fe in ingots and slags shows good agreement with that from chromite ore and iron scarp. The inconsistency of  $Al_2O_3$  was due to the slight dissolution of alumina crucible in which the samples were contained.

### 4. Discussions

Generally, the present chromium alloying process consisted of two sequential steps: (a) the reduction of chromite ore; (b) the dissolving of the iron-chromium in the steel melt. Step (a) can be reached by appropriate thermal and kinetic conditions, *viz*. temperature, particle size, the presence of iron, etc. The TG experiments and induction furnace experiments described in present paper confirmed the

kinetic possibility of using iron, ore, and carbon as mixture for the chromium alloying. Step (b) can be realized when temperature is high enough, time is long enough, and the composition of the slag is appropriate to get the final liquid slag which has lower viscosity and good wettability to ensure the coalescence of the slag droplets. Assuming that all the chromite can be reduced in every case in step one, the final composition of slags should be around 43.5% of Al<sub>2</sub>O<sub>2</sub>, MgO of 39.9%, 14.5% SiO<sub>2</sub>, and 2.2% of CaO. The melting point of this slag is around 2273 K (2000 degree Celsius), by referring to the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram [22] in Fig. 8. So, it is quite necessary to adjust the composition of the slags to ensure high Cr yield in the final products. In step two, by adding some CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> in the mixture, the melting point of slag could be lowered to around 1573 K (1300 degree Celsius), and finally the Cr yield could be increased to some extent, but still, a lot of chromite was lost to the slag phase. This is attributed to the following factors:

- during the reduction process, the presence of the



**Figure 8.** MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram[22]: the estimated slag composition (mainly MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) after complete reduction of chromite ore was circled in the figure.

Table 6. Composition analysis of the slags and droplets for sample N2-3 and N3 by Uddeholms AB, Sweden

	Composition analysis of slags (%)											
	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	SiO <sub>2</sub>	FeO	Cr <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	S
N2-3	24	33	6.16	30.5	1.4	5.18	<0.5	1.41	< 0.02	0.12	0.34	0.004
N3	35	27.7	6.95	26.1	0.62	2.73	<0.5	0.98	< 0.02	0.05	0.35	0.01
	Composition analysis of the ingots (%)											
	C Si Mn P S Cr Ni Mo W Nb V											
N2-3	1.68	0.1	0.18	0.02	0.0057	7.55	0.08	< 0.01	< 0.01	< 0.01	0.02	
N3	0.97	0.22	0.14	0.02	0.0058	8.89	0.06	< 0.01	< 0.01	< 0.01	0.04	

slag disseminated between the chromite ore and carbon reduced the contact area of the two, thus kinetically lowered down the reaction, though the presence of CaO may work as a catalyst for the reaction [23];

- some chromite may dissolve in the slags, and in this case the reduction will be retarded because, on one hand, the reduction was progressed slowly between the interface of carbon and slags at low temperature or at high temperature between the interface of melts and slags by carbon dissolved in the melts; and on the other hand, the dissolving of chromite into slags can lower the activity of chromite, then also slow down the reduction. This was corroborated by the phenomena that Cr yield was higher if the slag phase was placed on the upper layer of the alloying mixture than mixed with the mixture.

And it is also easy to understand that iron powder seems to be more effective than iron scrap, since the former has more active surface area than iron scrap and can be homogenously disseminated between the chromite ore; when chromite is reduced, chromium can be instantly be dissolved in the iron. This explanation is corroborated by the TGA curves discussed earlier. In step three, there is still some chromium left in the slag phase, though the Cr yield in the ingots is already very high. The possible reason for this can be that, during the addition of slag builders, some oxygen (from the air) might have been introduced to the reduced sample, and the chromium was re-oxidized and entered the slags. So, in a better controlled atmosphere during slag addition, a higher chromium yield can be expected.

With respect to direct Cr alloying by chromite ore, the high MgO content in the ore seems to limit the maximum value of chromite ore addition in the alloying process, because it may need to consume a lot of lime and silica to get a proper content of MgO in the slag which is normally around 6-10%; however the presence of MgO and lime in the ore can also be an added advantage which can reduce the consumption of these slag builder materials. The negative effect of sulphur impurity getting introduced in this process through the chromite ore has been considered in the present work. However, sulphur content can be lowered by the addition of lime in the EAF and an additional desulphurization step can be introduced in the down-stream refining process.

#### 5. Summary and results

In present investigation, a mixture of iron (both fine powder and industrial scrap), carbon, chromite ore was used as precursor for direct chromium alloying. Thermogravimetric analysis experiments, using different mixtures (mixtures with different ratio of iron chromite to iron), were carried out in order to investigate the kinetics of reduction. The induction furnace experiments have been done to investigate the effectiveness of the designed mixture for direct chromium alloying. The conclusions can be summarized as follows:

The presence of metallic iron in the mixture was favourable for the chromite reduction;

It is feasible to use iron scrap, chromite ore and carbon mixture for direct chromium alloying, the Cr yield can reach 90%;

Iron powder is kinetically more advantageous than iron scrap with respect to chromium yield in the final product; the composition of the slags needs to be adjusted to ensure high Cr yield in the final product, while the dissolving of chromite into the slags and the oxidation of chromium during slags addition should be avoided.

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#### References

- [1] International Ferro Metals Limited, Annual report 2011, 2011.
- [2] J. Johnson, B.K. Reck, T. Wang, T.E. Graedel, Energy Policy, 36 (2008) 181-192.
- [3] J. Johnson, L. Schewel, T.E. Graedel, Environmental Science & Technology, 40 (2006) 7060-7069.
- [4] L.N. Kologrivova, A.Y. Nakonechnyi, Z.G. Trofimova, O.V. Nosochenko, N.N. Kulik, Metallurgist, 31 (1987) 123-124.
- [5] O.I. Nokhrina, V.P. Komshukov, V.I. Dmitrienko, Metallurgist, 48 (2004) 264-265.
- [6] O. Bobkova, V. Barsegyan, Metallurgist, 50 (2006) 463-468.
- [7] G.V. Dzhandieri, T.A. Surguladze, D.V. Robakidze, M.S. Shalamberidze, B.A. Shchukin, Met Sci Heat Treat, 51 (2009) 533-539.
- [8] M. Kawakami, Y. Kitajima, K. Hashimoto, K. Ito, J. Iron Steel Inst. Jpn., 73 (1987) 820-827.
- [9] K. Taoka, C. Tada, Z. Yamada, H. Nomura, M. Ohnishi, H. Bada, J. Iron Steel Inst. Jpn., 76 (1990) 1863-1870.
- [10] S. Takeuchi, H. Nakamura, T. Sakuraya, T. Fujii, T. Nozaki, J. Iron Steel Inst. Jpn., 76 (1990) 1847-1854.
- [11] D.J. Simbi, M.B.C. Tsomondo, Ironmaking & Steelmaking, 29 (2002) 271-275.
- [12] V.V. Mogil'nyi, V.F. Tsarev, N.A. Kozyev, A.L.

Nikulina, V.V. Gorkavenko, Steel Transl, 27 (1997) 65-67.

- [13] S.B. Batuev, V.V. Petrenev, A.V. Chernushevich, N.M. Milyutin, V.N. Zhirikov, Steel Transl, 25 (1995) 19-21.
- [14] Z.F. Yuan, W.L. Huang, S.Y. Zhu, D.H. Liao, H.F. Hu, Steel Res, 73 (2002) 428-432.
- [15] W.X. Wang, Z.L. Xue, S.Q. Song, P. Li, Z.C. Chen, Advanced Materials Research, 476-478 (2012) 164-169.
- [16] S.Q. Song, Z.L. Xue, W.X. Wang, P. Li, R.N. Liu, G.L. Metal Int, 17 (2012) 83-85.
- [17] A. Chychko, L. Teng, M. Nzotta, S. Seetharaman, Steel Res Int, 82 (2011) 886-897.
- [18] L. Cao, Y. Gao, M. Zhu, China Metallurgy, 05 (2009).
- [19] J. Li, J. Mao, Special Steel, 01 (1997).
- [20] Z. Li, P. Guo, G. Lin, H. Zhang, The Technology of Direct Reducing and Alloying the Concentrate of Tungsten, Molybdenum Oxide and Vanadium Slag, China Tunsten Industry, 01 (2000).
- [21] B.F. Naylor, Industrial & Engineering Chemistry, 36 (1944) 933-934.
- [22] Ernest M. Levin, Carl R. Robbins, Howard F. McMurdie, Phase Diagrams for Ceramists, The America Ceramic Society, Ohio, 1969, p. 264.
- [23] Y.L. Ding, N.A. Warner, Thermochimica Acta, 292 (1997) 85-94.