Innovations in Ferro Alloy Industry
INFACON XI
2007

IFAPA
THE INDIAN FERRO ALLOY PRODUCERS' ASSOCIATION

REDUCTION BEHAVIORS OF CHROMITE AND NIO IN LIQUID FE-C ALLOYS

T. Uzunoglu, B. Derin and O. Yücel

Istanbul Technical University, Metallurgical and Materials Eng. Department
Maslak, Istanbul, Turkey
E-mail: yucel@itu.edu.tr

ABSTRACT

In this study, reduction behaviours of Turkish chromite concentrate (48 % Cr_2O_3, 13.30 % FeO, 18.33 % MgO, 12.37 % Al_2O_3, 5.76 % SiO_2) and nickel oxide by Fe-C alloy in graphite crucible were investigated. In the first stage of experiments, steel scraps were melted in graphite crucibles and were saturated with carbon at 1600 °C and 30 min. In the second stage, mixtures of different amount of chromite concentrate, nickel oxide and flux additives (CaO,SiO_2 and CaF_2) were charged into the graphite crucible containing the Fe-C alloy and heated to 1600 °C for different reduction times (0-180 min) under argon gas. The highest Cr and Ni contents in alloys were found as 11.41 and 14.37 % and the highest Cr and Ni recoveries were found as 88 and 94 %, respectively at 180 min.

1. INTRODUCTION

Ferrochromium and nickel are both added to the hot steel as alloying materials to produce corrosion and heat resistant steels. Studies exist that investigate the direct usage of chromite ore, nickel oxide or nickel sulfide as an alternative way of using the cost intensive alloying materials in the low or high alloyed steel production [1-7] Eric *et al.* used rotating cylinder technique to study the reduction kinetic of chromite spinels in Fe-Cr-C-Si alloy at 1600 °C [1]. Dresler *et al* worked on the carbothermic reduction of chromite concentrates in the presence of nickel oxide or nickel sulfide with flux additions between 1550 and 1650 °C [2] Pei and Wijk studied on chromite ore smelting reduction through the CaO-SiO_2 and CaO-SiO_2-MgO-Al_2O_3 slags by a solid carbon or a carbon saturated iron melt above 1600°C [3-5]. Ding *et al.* investigated the reduction of chromite by graphite in the presence of a CaO-SiO_2 slag or under CO atmosphere at different temperatures [6,7].

In the present study, the reduction of Turkish chromite concentrate and nickel oxide in a carbon saturated iron alloy was studied with flux additions in a carbon crucible at 1600 °C. Effects of the initial chromite concentration, CaO/SiO_2 ratio, CaF_2 addition and time were investigated.

2. EXPERIMENTAL STUDY

The chromite concentrate was provided from Eti Electrometallurgy Co. The chemical analysis and the sieve analysis of the chromite concentrate are given in Table 1 and Table 2, respectively. Nickel oxide which had a purity of 95.84 % was provided from INCO Co. The steel scrap which was used in the experiments, contained 0.04 % C, 0.01 % Si, 0.2 % Mn and 0.009 % P. High purity grade CaO and SiO_2 (>99.75 %) and technical grade CaF_2 (>97 %) were used as fluxing materials.

Table 1: Chemical analysis of the Turkish chromite concentrate (wt %)

Cr_2O_3	FeO	MgO	Al_2O_3	SiO_2	CaO	TiO_2	MnO
44.68	13.30	18.33	12.37	5.76	0.39	0.35	0.13

Table 2: Sieve analysis of the Turkish chromite concentrate

Sieve size(ìm)	*% Retained*	*Cum. % Retained*
850	0.00	0.00
710	1.12	1.12
630	0.43	1.55
500	1.77	3.32
315	7.61	10.93
250	5.77	16.70
100	32.07	48.77
75	10.20	58.97
45	17.03	76.00
38	5.14	81.14
-	18.86	100.00

Reduction smelting experiments were carried out in a High-Temperature Ruhstrat-Nernst Tammann tube furnace. Temperature was measured with a 6RhPt-30RhPt (EL-18) thermocouple. High purity argon gas was purged into the furnace in order to protect the carbon resistance tubes. The graphite crucibles used in the experiments, had a diameter of 50 mm, wall thickness of 5 mm and a height of 45 mm. The experiments were carried out in two steps. In the carbon saturation step, steel scrap (40 g each) was melted down in a graphite crucible for 30 min. at 1600 °C and then cooled down to room temperature. In the second step, a mixture of chromite concentrate, nickel oxide and fluxing materials was added to the carbon saturated iron alloy in the same crucible. The experimental program is summarized in Table 3. Argon gas was purged into the reaction zone at a rate of 500 cc/min in order to provide a protective atmosphere. The moment the temperature of the hot zone reached 1600 ^{o}C (50 ± 3 min.) was taken as the start of the reaction time. Reaction times from 0 to

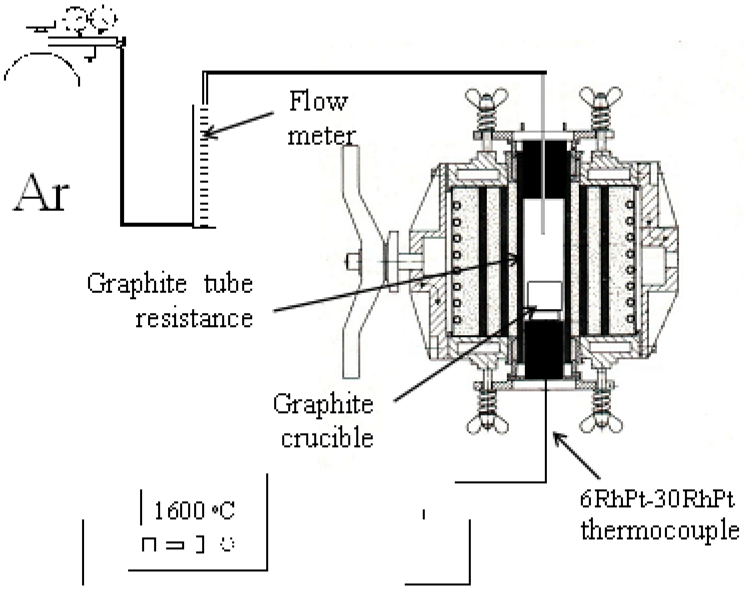

Figure 1: Experimental setup

180 min were examined. At the end of the experiments, the sample was quenched raising the crucible to the upper region of reaction tube using the alumina thermocouple shield. After the experiments, it was observed that besides alloy and slag phase, metal droplets on the wall of the crucible were also formed. These phases were separated, weighed and analyzed for Cr, Ni, Si, and C.

Table 3: The experimental program

Run	*Steel Scrap*, g*	*Initial Compositions, (wt % of steel scrap)*						*Reaction Time, min*
		Chromite Concentrate	*NiO,*	*CaO,*	*SiO_2,*	*$CaO:SiO_2$*	*CaF_2,*	
A	40	60	25	12.5	12.5	1:1	-	0-180
B	40	80	25	12.5	12.5	1:1	-	0-180
C	40	100	25	12.5	12.5	1:1	-	0-180
D	40	80	25	16.66	8.34	2:1	-	60
E	40	80	25	25	0	1:0	-	60
F	40	80	25	12.5	12.5	1:1	5	60
G	40	80	25	12.5	12.5	1:1	10	60

* weight before C saturation experiments

3. RESULTS AND DISCUSSIONS

Literature indicates that the reduction of chromite occurs in two steps. First, the dissolution of chromite into liquid slag and second, reduction of the dissolved chromium oxide in the slag [3-5]. This means undissolved chromite in slag has no significant importance on chromium reduction by graphite crucible or carbon saturated alloy. However NiO doesn't have to dissolve in the slag for its reduction and can be easily reduced by graphite at elevated temperatures [8]. At the end of experiments, metallic droplets with different diameters (=4 mm) were observed on the graphite crucible walls in contact with the slag. This result is in accordance with the previous studies which describe the reaction mechanism between chromite and graphite interface [4-5]. Even though, total amount of these droplets (0.2-5.3 g) were comparatively small to that of alloy (44.8-60.5 g), their chromium and nickel concentrations were considerably high (14.43 - 28.67 % Cr and 46.48-56.37 % Ni). Figure 2 and 3 represents the weight distributions of chromium and nickel between slag, droplet and alloy versus reaction time for Run A. As can be seen, highest chromium and nickel amounts in the drop-

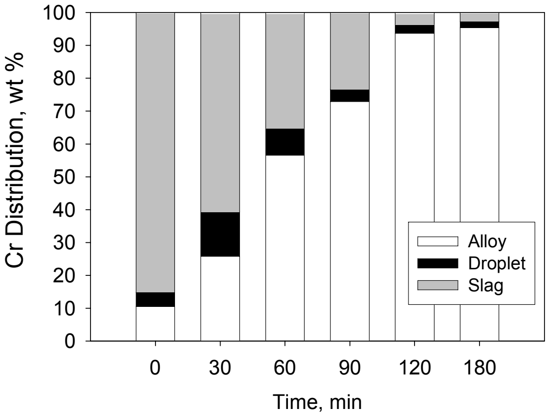

Figure 2: Weight distribution of chromium between slag, droplet and alloy phases versus reaction time for Run A

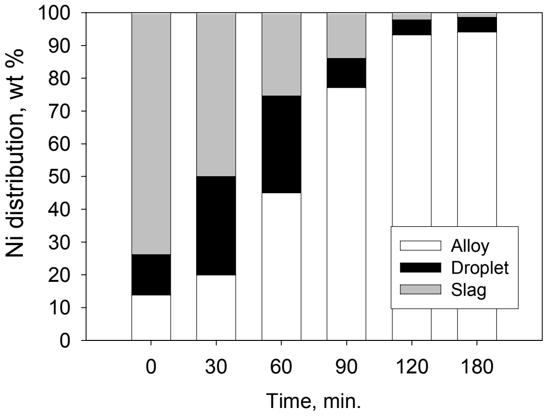

Figure 3: Weight distribution of nickel between slag, droplet and alloy phases versus reaction time for Run A.

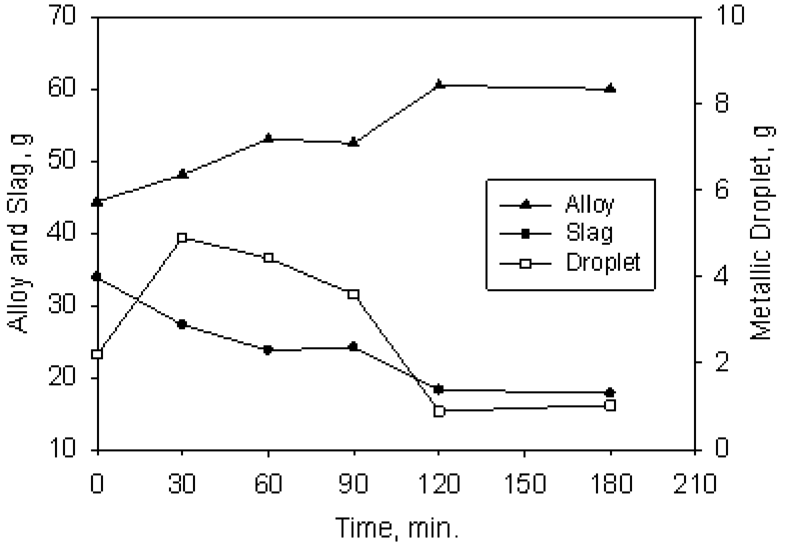

Figure 4: Weight amounts of slag, droplet and alloy versus reaction time for Run A

lets were found at 30 min. After 30 min, these values decreased with increasing reaction time. The sum of the weight distributions of alloys and droplets show that the chromium reduction rate was much slower than that of nickel until 120 min. Besides, the nickel reduction rate in the droplet was faster than in the alloy until 30 min. The weight change of slag, droplet and alloy versus reaction time for Run A is also shown in Figure 4.

As seen in Figure 5, chromium concentration in the alloy increased with increasing reaction time and also with increasing the chromite amount in the mixture after 90 min. For example, at 90 min, the chromium concentrations were obtained as 9.49, 10.0 and 11.12 % for Runs A, B and C, respectively. After 120 min, no significant difference in chromium concentration was observed in the alloy for Run A (14.3 % Cr). Figure 6 represents the chromium concentration in the slag versus reaction time. For example, at 90 min, the chromium concentrations were obtained as 8.45, 12.90 and 18.98 % for Runs A, B and C, respectively. The lowest chromium concentration in the slag obtained was 0.76 % at 180 min for Run A. Figure 7 shows that chromium recovery in the alloy increased with increasing reaction time. However, increasing the chromite amount in the initial mixture decreased the recovery values, because of the high amount of undissolved chromite in the slag.

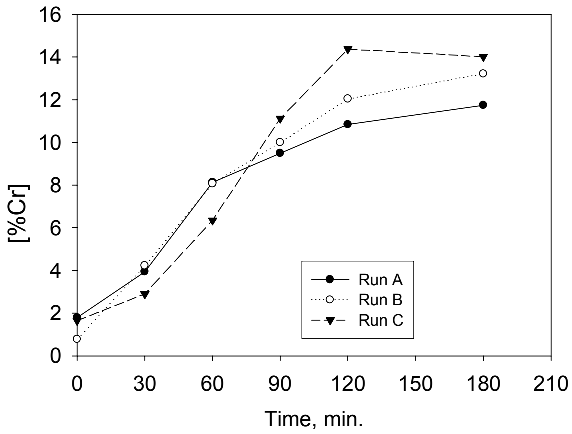

Figure 5: The change of chromium concentration in alloy versus reaction time

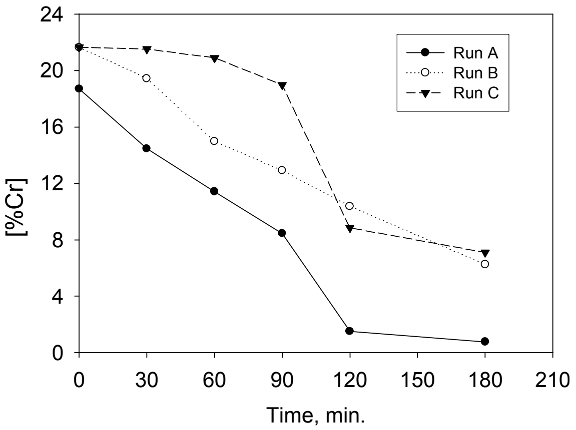

Figure 6: The change of chromium concentration in slag versus reaction time

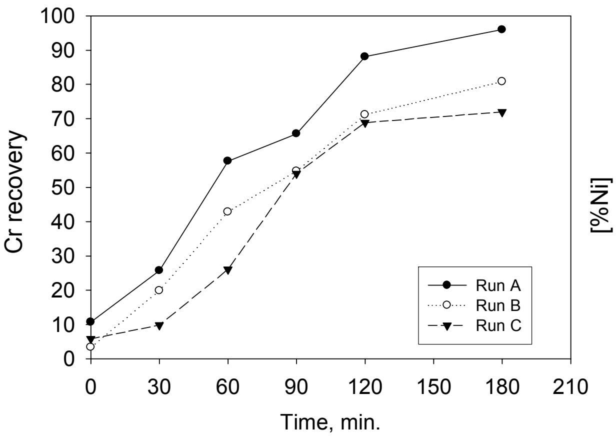

Figure 7: The change of chromium recovery in alloy versus reaction time

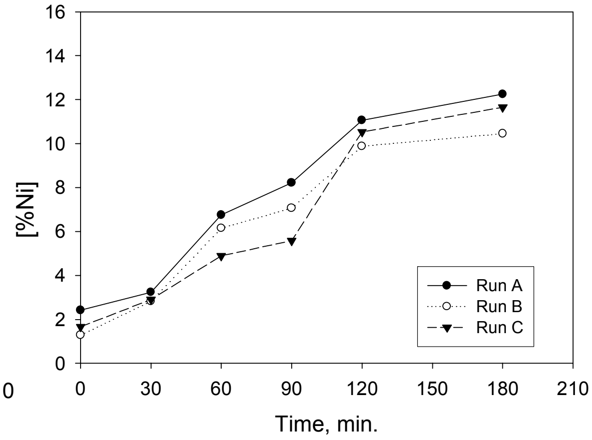

Figure 8: The change of nickel concentration in alloy versus reaction time

For example at 180 min, the chromium recoveries were obtained as 95.95, 80.82, and 71.99 % for Runs A, B and C, respectively.

The change of the nickel concentrations in alloy and slag versus reduction time are given in Figure 8 and 9, respectively. As expected, nickel concentration in the alloy increased with an increasing reaction time and its reduction was not affected much by the chromite concentration in the mixture. For example, at 180 min, the nickel concentrations in the slag phase decreased to 0.54, 1.89 and 1.21 % for Runs A, B and C, respectively. The change of nickel recovery values in the alloy phase obtained in the experiments are given in Figure 10. The highest nickel recovery value obtained was found as 94.1 % at 180 minute for Run A.

In the experiments, different CaO:SiO_2 ratio and CaF_2 additions were also performed for 60 min. Figure 11 shows that increasing CaO:SiO_2 ratio decreased the chromium, nickel, silicon concentrations in alloy whereas that of the carbon increased. The highest chromium and nickel concentrations in the alloy were found as 8.07 and 6.15 %, respectively for Run B. Figure 12 shows that CaF_2 addition up to 10 wt % of steel scrap also increased the Cr and Ni concentrations in the alloy to 8.50 and 8.63 %, respectively.

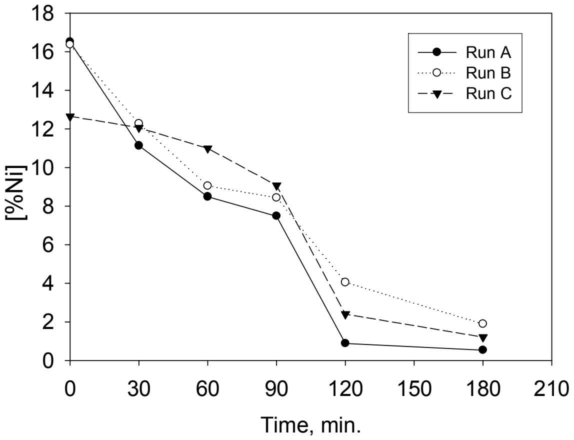

Figure 9: The change of nickel concentration in alloy versus reaction time

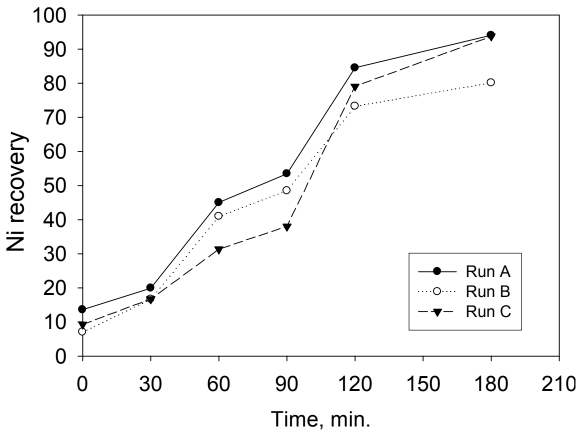

Figure 10: The change of nickel concentration in alloy versus reaction time

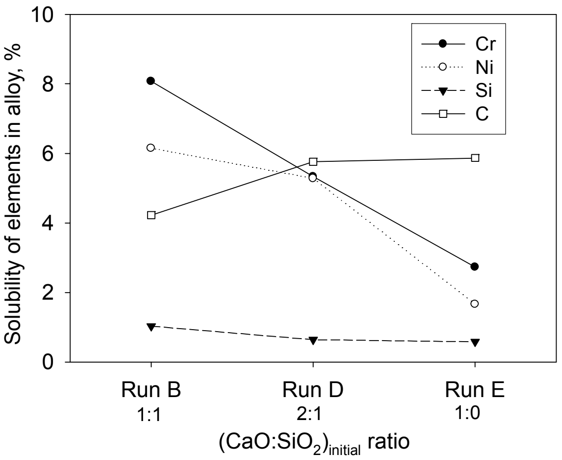

Figure 11: The effect of initial $CaO:SiO_2$ ratio on concentration of elements in alloy

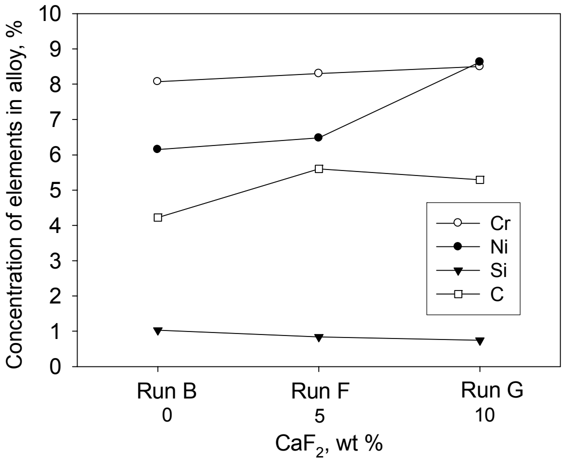

Figure 12: The effect of CaF_2 addition on concentration of elements in alloy

4. CONCLUSIONS

On the basis of the results of the present study of carbothermal reduction of chromite and NiO by carbon saturated iron and a graphite crucible at 1600 °C and different reaction times, following conclusions can be made. Metallic droplets containing high amount of Cr and Ni occurred on the crucible wall shows reduction reaction between graphite and mixture or subsequent formation slag. The increasing chromite amount in the mixture increased the chromium concentration in the alloy but decreased the chromium recovery. NiO reduction was not affected much by the chromite amount in the initial mixture. The initial CaO/SiO_2 ratio as 1:1 and CaF_2 addition up to 10 % of steel scrap to the mixtures had positive effects on Cr and Ni reduction rate.

REFERENCES

[1] Demir, O., and Eric, R.H., "The reduction of Chromite in Fe-Cr-C-Si Alloys" 6th International Ferroalloys Congress (INFACON) ,Cape Town, South Africa, 1992, 1, 99-105.

[2] Dresler, W., Jena, B.C. and Mclean, A., "Carbothermic reduction and desulphurization of Chromite with Nickel Oxide and Sulphide" 6th International Ferroalloys Congress (INFACON), Cape Town, South Africa, 1992, 2, 111-116.

[3] Pei, W. and Wijk, O., "Chromite ore smelting reduction by a carbon saturated iron melt", Scandinavian Journal of Metallurgy, 1994, 23, 216-223.

[4] Pei, W. and Wijk, O., "Mechanism of reduction of chromium oxide dissolved in the $CaO-SiO_2-MgO-Al_2O_3$ slag by solid carbon", Scandinavian Journal of Metallurgy, 1993, 22, 30-37.

[5] Pei, W. and Wijk, O., "A kinetic study on chromite ore smelting reduction" Scandinavian Journal of Metallurgy, 1993, 22, 38-44.

[6] Ding, Y.L., Warner, N.A. and Merchant, A. J., "Reduction of Chromite by Graphite with CaO-SiO2 fluxes" Scandinavian Journal of Metallurgy, 1997, 26, 55-63.

[7] Ding, Y.L. and Warner, N.A., "Smelting reduction of carbon-chromite composite pellets-Part 1" Transaction Institution of Mining and Metallurgy 106, C55-63.Scandinavian Journal of Metallurgy, 1993, 22, 38-44

[8] Sharma, S.K., Vastola, F. J. Ad Walker, P. L., "Reduction of nickel oxide by carbon, III: Kinetic studies of the interaction between nickel oxide and natural graphite" Carbon, 1997, 35, 535-541.