EFFECTS OF CHARGE COMPONENTS ON REDUCTION OF CHROMITE CONCENTRATES BY ALUMINOTHERMIC PROCESS

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ABSTRACT

In the present study, the production of low carbon ferrochromium (LC-FeCr) from chromite concentrates containing 55.09% Cr_2O_3 *and 13.06% Fe via metallothermic process was investigated. For this aim, in the experiments, the aluminothermic reduction method was applied in an open crucible. 10%* CrO_3 *+ 10%* $NaClO_3$*, 15%* CrO_3 *+ 5%* $NaClO_3$ *and 20%* CrO_3 *by weight of concentrate were added to the charge, respectively and the charge was reduced with aluminium. The experiments were done with the additions of 90, 100, 110, 120 and 130% of stoichiometric requirement of aluminium. The highest Cr content in alloys was found as 71.7% at 120% of stoichiometric Al whereas the highest Cr recovery in alloys was found as 71.8% at 130% of stoichiometric Al when the both charge contained 15%* CrO_3 *+ 5%* $NaClO_3$ *by weight of chromite concentrate.*

1. INTRODUCTION

Ferrochromium is a ferroalloy which is used for alloying of steels [1]. Although Turkey has an important part of world's chromite reserves, only 100.000 tones per year high carbon ferrochromium and 10.000 tones per year low carbon ferrochromium can be produced by the use of 3930 and 9700 kWh/t energy, respectively [2]. In this study, parameters for ferrochromium production by lab-scale aluminothermic reduction from chromite concentrates without external energy supply were investigated. Effects of reductant amount and other additives on the ferroalloys and chromium recoveries were examined.

In a metallothermic reaction, "specific heat" of a reaction is the main guide in determining the heat evolved during the reaction and to estimate if the temperature achieved is sufficient to smelt the metal and the slag and to separate them due to the different density. Specific heat (J/g) of the product can be calculated by dividing the enthalpy of the reaction by the sum of the molecular weights of the reaction products. If the ratio is larger than 4500 J/g, the reaction will be violent and may even be explosive. When the ratio is less than 2250 J/g, the heat is insufficient to melt the charge and to separate due to their density difference. When the calculated value is between 2250 and 4500 J/g, a controlled and self-sustaining metallothermic reaction is indicated [3,4]. Enthalpies of reactions and heat generated per gram of the products related with the experiments were listed in Table 1. Since some oxides in the chromite concentrate such as Al_2O_3, SiO_2, MgO etc. may decrease the reaction heat during aluminothermic process, in the same cases, additives such as sodium chlorate ($NaClO_3$) and chromic acid (CrO_3) may be used to increase the reaction heat as shown in Eq 5 and 7 [5]. When CaO and CaF_2 are added to the charge to decrease the melting point of the slag, the heat of the reaction is still sufficient to advance the reaction.

Table 1. The heat generated by the metallothermic reductions [6]

Reaction	ΔH_{298}, kJ	Specific heat, J/g	Equation No
$Cr_2O_3 + 2\,Al \rightarrow 2Cr + Al_2O_3$	-535.573	-2600.45	(1)
$Cr_2O_3 + 2\,Al + CaO \rightarrow 2\,Cr + CaO.Al_2O_3$	-551.514	-2104.75	(2)
$Cr_2FeO_4 + 8/3Al \rightarrow Fe + 2Cr + 4/3Al_2O_3$	-775.016	-2620.17	(3)
$Cr_2FeO_4 + 8/3Al + 4/3CaO \rightarrow Fe + 2Cr + 4/3CaO.Al_2O_3$	-796.265	-2148.81	(4)
$CrO_3 + 2Al \rightarrow Cr + Al_2O_3$	-1085.748	-7052.24	(5)
$CrO_3 + 2Al + CaO \rightarrow Cr + CaO.Al_2O_3$	-1101.689	-5245.21	(6)
$NaClO_3 + 2Al \rightarrow NaCl + Al_2O_3$	-1728.661	-10776.9	(7)
$FeO + 2/3Al \rightarrow Fe + 1/3Al_2O_3$	-291.155	-3241.03	(8)

2. EXPERIMENTAL STUDY

Chromite concentrate used in the experiments was obtained from Göcek-Turkey. Aluminium powder used as the main reductant material for the metallothermic process was process residue of Seydişehir Integrated Aluminium Plant. Chemical analyses of the concentrate and aluminium powder were shown in Table 2. CaO and CaF_2 used as fluxing materials both had purity of 98.5%. CaO was obtained by calcination of $CaCO_3$ at 1000°C. $NaClO_3$ and CrO_3, used as other thermite materials, had purity of 99.5 and 98%, respectively. All of the raw materials had particle size less than 100 μm.

Table 2. Chemical analysis of chromite concentrate and aluminium powder, (wt%).

Raw Materials	Cr_2O_3	Fe	Al	Si	Mg	Ca	Ti	Zn
Chromite Conct.	55.09	13.06	5.31	1.96	7.93	0.33	-	-
Aluminum powder	-	0.7	>98.50	0.4	0.06	-	0.02	0.02

- : not analysed

Aluminothermic reductions were carried out in a laboratory scale and MgO-lined open crucibles. Experimental set-up were described in detail elsewhere [3,4,7,8,9]. 1000 g. chromite concentrate was mixed with aluminium and other additives in a turbula mixer and dried at 105 °C in an oven. In the experiments, sum of aluminium requirement for Eq. (1),(5),(7) and (8) was determined as 100% of stoichiometric Al. In each group experiments, 10% CrO_3 + 10% $NaClO_3$, 15% CrO_3+ 5% $NaClO_3$ or 20% CrO_3 by weight of chromite concentrate and different amount of stoichiometric Al were used as thermite materials. In some experiments CaO and CaF_2 were also added as fluxing materials. Small amount (10 g) of aluminium powder and sodium chlorate mixture was placed on the top of the packed charge for igniting the reactions. A heater coil was embedded in the mixture so that the reaction can be initiated remotely by passing current through the coil. Upon cooling, crucible was discharged, metal and slag phases are crushed, separated, ground and analysed by wet chemical techniques.

3. RESULTS AND DISCUSSION

Figure 1 shows the influence of the aluminium amount used as a reductant on Cr concentration in alloys for different thermite mixtures. As can be seen, chromium content in alloy increases with the increase of stoichiometric Al, but when Al content increases beyond 120%, Cr content fell due to the increase of other metallic contents in the alloy phase. It can be also seen that CrO_3 is more effective than $NaClO_3$ addition up to 100% of stoichiometric Al. For example Cr contents were determined to be 50.2, 53.0, 59.8% with 90% Al addition and 66.3, 71.7, 71.1% with 120% Al addition for 10% CrO_3+ 10% $NaClO_3$, 15% CrO_3+ 5% $NaClO_3$ and 20% CrO_3 additions, respectively.

Figure 2 represents changes in chromium recovery in alloy versus aluminium addition. As it is seen in the figure, increase in stoichiometric Al from 90% to 130% increased recoveries from 19.7, 20.9, 8.7% to 64.2, 71.3, 54.7% for 10% CrO_3+10% $NaClO_3$, 15% CrO_3+ 5% $NaClO_3$ and 20% CrO_3 additions, respectively.

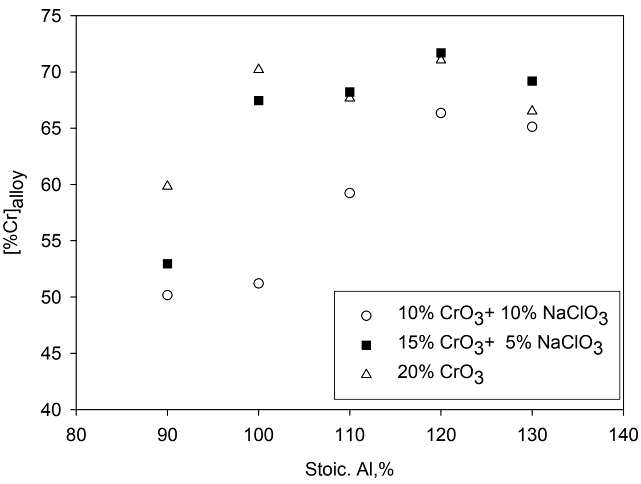

Figure 1. Cr content in alloy as a function of stoichiometric Al amount for different additions.

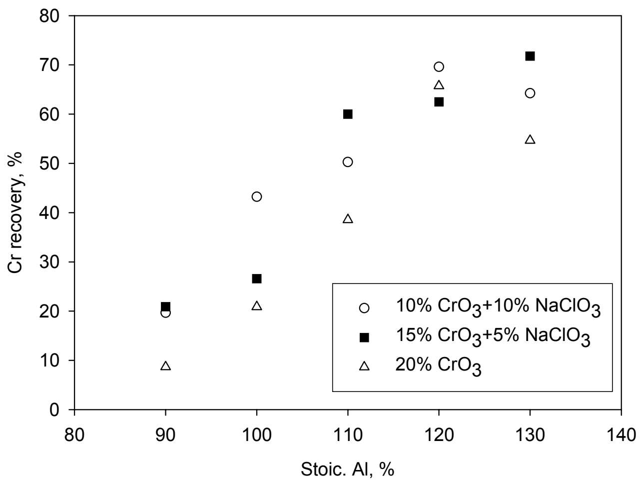

Figure 2. Cr recovery to alloy phase as function of stoichiometric Al amount for different additions.

The influence of the amount of aluminium used for reduction on Al amount in alloy phase was given in Figure 3. Increasing Al amount from 90% of stoichiometric requirement to 130% increased the Al content in alloy from 0.09, 0.13 and 0.08% to 4.18, 3.97 and 2.92% for 10% CrO_3+10% $NaClO_3$, 15% CrO_3+ 5% $NaClO_3$ and 20% CrO_3 additions respectively.

Figure 4 shows the variation of silicon content in alloy phase as a function of Al amount in charge for different additions, it is clearly visible that, for each group experiment, Si content in alloy increased with increasing aluminium amount in charge up to 5.23%.

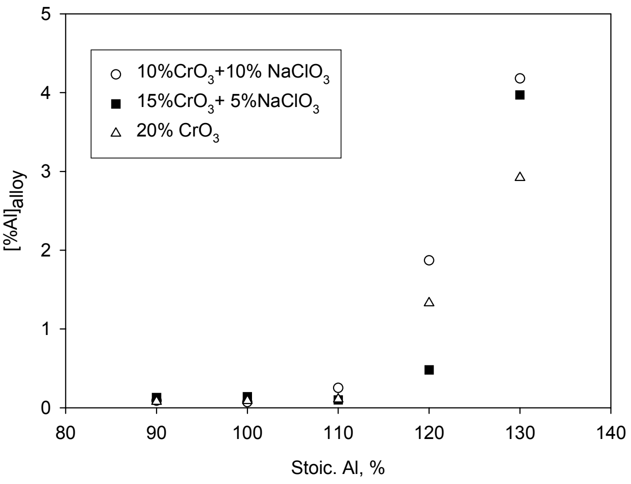

Figure 3. Aluminium content in alloy phase as function of stoichiometric Al amount for different additions.

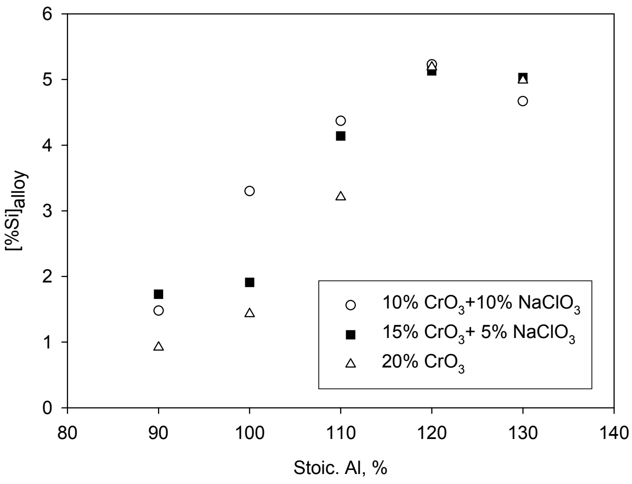

Figure 4. Silicon content in alloy phase as function of stoichiometric Al amount for different additions.

Figure 5 shows the influence of the amount of reductant Al on Fe amount in alloy phase. As it is seen, for 15% CrO_3+ 5% $NaClO_3$ and 20% CrO_3 additions, 90% of stoichiometric Al amount was insufficient for iron reduction. However beyond 100% of stoichiometric Al addition, iron content began to decrease due to increasing Cr, Al and Si contents in alloy phase.

Some experiments were done for determining the effect of CaO and CaF_2 addition at 100% of stoichiometric aluminium and 20% CrO_3 addition. Flux addition which didn't provide expected advantage for alloy composition, had also negative effect on chromium recovery (Figure 6). For example, flux additions decreased the Cr recovery from 20.87 to 17.7 and 14.2%, when the charge had 20% CaO and CaF_2 by weight of chromite concentrate, respectively.

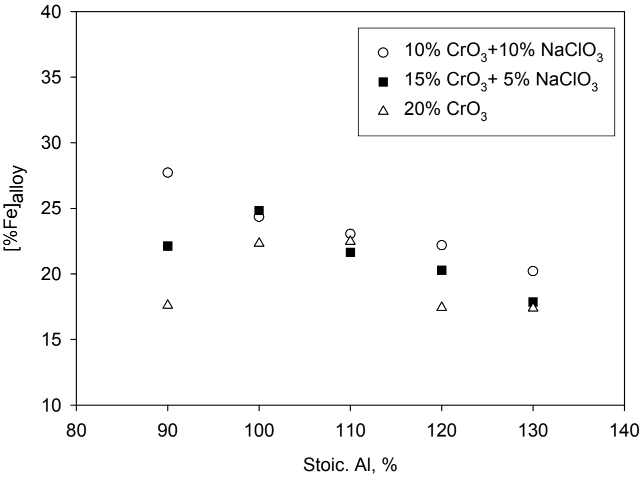

Figure 5. Iron content in alloy phase as function of stoichiometric Al amount for different additions.

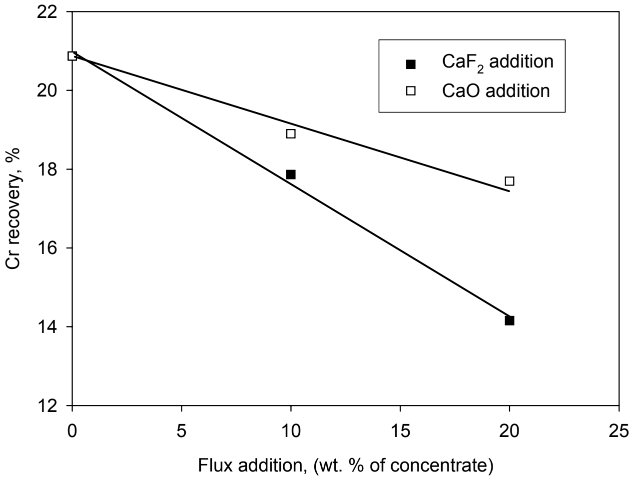

Figure 6. Effect of CaF2 and CaO addition on chromium recovery (%100 stoic. Al, 20% CrO3 of concentrate).

The experimental data obtained for chromium distribution ratio between slag and metal, (%Cr)/[%Cr], were plotted as function of Al addition. As can be seen in Figure 7, chromium partition decreases with increasing stoichiometric Al for each group experiments. As expected 20% CrO_3 addition showed highest ratio, since slag had much higher Cr content.

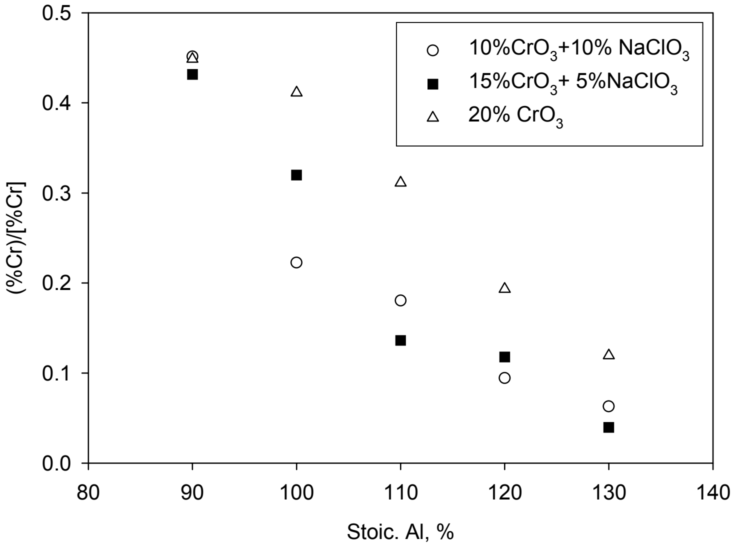

Figure 7. Distribution Ratio of Chromium as function of Al amount for different additions.

4. CONCLUSIONS

It can be concluded that the laboratory scale LC-FeCr production from chromite concentrates via aluminothermic method is possible without external electrical energy. However, in some experiments without any other thermite additions, reduction of chromite concentrates couldn't be achieved using only aluminium. In this case, unreacted charge or only slag form was obtained.

Thus, in the experiments, additives such as sodium chlorate ($NaClO_3$) and chromic acid (CrO_3) were used with Al to increase the reaction heat and to obtain high chromium concentration and recovery into alloy phase. For this aim, chromite concentrate containing 55.09% Cr_2O_3, 13.06% Fe, 7.93% Mg, 5.31% Al and 1.96% Si was reducted with different amount of stoichiometric Al and 10% CrO_3 + 10% $NaClO_3$, 15% CrO_3 + 5% $NaClO_3$ or 20% CrO_3 additions by weight of concentrate, respectively. The highest Cr content in alloys was found as 71.7% at 120% of stoichiometric requirement of Al and the highest Cr recovery in alloys was found as 71.8% at 130% of stoichiometric requirement of Al when the both charge contained 15% CrO_3 + 5% $NaClO_3$.

5. REFERENCES

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