

Fe-Ni-Cr Crude Alloy Production from Direct Smelting of Chromite and Laterite Ores

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Abstract—Ferrochromium and ferronickel which are obtained from the reduction of chromite and laterite ores, respectively, are the important alloying materials in the production of stainless steel. The present study is possibly the first of its kind related to production of crude stainless steel melt by direct smelting of chromium and nickel ore without use of ferrochromium and ferronickel alloys. The feasibility of producing Fe-Ni-Cr crude alloy by direct smelting of chromite and laterite ores from local sources with activated carbon as reducing agent at 1400° to 1550°C using graphite crucible under argon atmosphere were conducted in a vertical tube furnace. It was found that the grade and composition of chromite and laterite ores are the main factors to produce the alloy. The smelting of 10-13% SCO chromite ore and 87 – 90% LIM laterite ore produced alloys with average iron, nickel and chromium content about 82%, 6.22% and 2.17%, respectively, at an average iron, nickel and chromium recovery of 98%, 97% and 87%, respectively. The high recovery of iron and nickel in the alloy indicates a high reducing condition in the smelting experiment. It is also shown that the solubility of Ni in the slag increases with Ni concentration in the alloy and the FeO concentration in the slag.

Index Terms—smelting, chromite, laterite, slag, nickel

I. INTRODUCTION

Ferrochromium and ferronickel which are obtained from the reduction of chromite and laterite ores, respectively, are the important alloying materials in the production of stainless steel. The present study is possibly the first of its kind related to production of crude stainless steel melt by direct smelting of chromium and nickel ore without use of ferrochromium and ferronickel alloys, in order to save electricity and production costs. Several studies [1]-[4] have been conducted on the phase equilibria, thermodynamics, kinetics and slag-metal equilibrium distribution of chromium and nickel in the production of ferrochromium and ferronickel, respectively. It has been found [5] that the amount of Cr, Ni and Fe recovery in the metal phase is controlled by the slag composition, oxygen partial pressure and melting temperature.

The present study was undertaken to determine the iron, nickel and chromium recovery when nickeliferous laterite and chromite ores mixed together with solid carbon as reductant then brought into equilibrium at a certain smelting temperature to produce metal and slag. By con-

trolling the proportions of the laterite and chromite ores to achieve a composition of the mixture, the system may be operated at temperatures approaching that of the lowest melting point of liquid slag and alloy. The partitioning of Fe, Ni and Cr between the liquid metal and liquid slag phases was an important consideration when selecting the composition of the charges and temperature to be used in the separation process.

II. METHODOLOGY

A. Materials

The raw materials consisted of calcined laterite ores from Surigao and chromite ores from Misamis Oriental. Activated carbon was used as the reductant in all these tests. The compositions of the feed materials are shown in Table I. Raw materials were sized and calcined to remove combined water, volatiles and decompose compounds such as carbonates. The graphite crucible for equilibrium study was prepared by drilling 5 holes of 11.5 mm diameter and 40 mm depth each in a graphite rod of 40 mm diameter and 50mm length. This allowed to equilibrate 5 different samples simultaneously.

TABLE I. COMPOSITION OF FEED MATERIALS

Components	Chromite ores		Laterite ores	
	SCO (Sandy chromite from Opol)	SCM (Sandy chromite from Manticao)	SAP (Saprolite)	LIM (limonite)
Cr ₂ O ₃	35.33	30.77	1.55	2.60
Fe ₂ O ₃	33.16	23.98	38.51	73.83
MgO	13.44	21.05	18.50	0.74
Al ₂ O ₃	9.67	9.63	1.27	2.20
SiO ₂	5.82	9.55	23.40	2.49
MnO	0.29	0.17	0.46	1.60
NiO	0.02	0.31	2.64	1.71
LOI	0.43	2.77	13.10	13.50

B. Procedure

A vertical tube resistance furnace was used. The power input was controlled using a Eurotherm 3504 programmable controller and the temperature variation at the uniform hot zone was maintained within 2°C. A type B thermocouple was used to measure the system temperature. A total of three grams of different proportions of

chromite and laterite ores and mixed with carbon were placed in each graphite hole. A graphite lid was placed to cover all the holes of the crucible. High purity Ar gas was flown in the furnace at the flow rate of 700 ml/min. The crucible was raised to the position into the uniform hot zone of the vertical tube furnace. The samples were equilibrated for 2.0 h. The crucible was quickly pulled down to the lower temperature zone while the Ar gas still flowing and then taken out of the furnace. The Fe, Cr and Ni in the metal and in the slag were analyzed by wet analysis and atomic absorption spectrometry (AAS). The constituents of the ores were analyzed by X-ray fluorescence and XRD.

Scanning electron microscopy, X-ray diffraction analysis and metallographic examinations were conducted on metal and slag samples.

III. RESULTS AND DISCUSSION

In the absence of literature on the reduction of mixed chromite and laterite ores the present study explored several ore combinations and smelting temperature to be able to produce a metal alloy. Trial tests were conducted on several parameters until a promising result was obtained. Two hours of smelting time and SCO and SAP mixture was used for these trials.

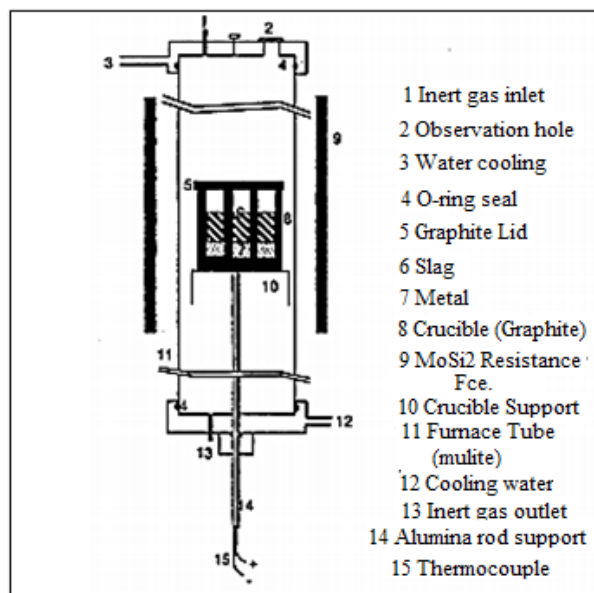


Figure 1. Schematic diagram of apparatus

A. Determination of Smelting Temperature and Charge Composition

Results show that at $T = 1400^{\circ}\text{C}$ and 1450°C , no distinct separation between the alloy and the slag was observed. At $T = 1500^{\circ}\text{C}$, there was already a distinct separation of the metal and the slag with 10% SCO and 90% LIM (10/90) and 20% SCO and 80% LIM (20/80) charge mixtures but not with the chromite and saprolite mixtures. At $T = 1550^{\circ}\text{C}$, a distinct separation of metal and slag was also observed at mixtures 10/90, 20/80 and 30/70 of SCO & LIM mixtures but not with chromite and saprolite ores combination. However, there were already droplets

of metals formed at the side and bottom of the mold for the later combination. The distinct separation of metal and slag in the mixture containing limonite ores may be due to the fact that limonite ores contain less MgO than that of the saprolite ores. MgO is a stable compound that this is hard to separate. Limonite ores also contains more Fe_2O_3 , which is readily reducible, than saprolite. This result indicates that the phase (metal – slag) separation is also influenced by the grade and composition of the ores.

B. Effect of Temperature and Smelting Time.

The appearance and composition of the reduction products varied with reduction time, the reduction temperature and other experimental conditions. The iron, nickel and chromium composition of the products at different temperatures and smelting time were determined by wet analysis and atomic absorption spectrometry (AAS). The concentration in wt% of Ni, Cr and Fe in the alloy are shown in Fig. 2, Fig. 3, and Fig. 4, respectively.

Generally, the iron, chromium, and nickel contents in the metal phase increases with increasing smelting time and increasing temperature. At higher temperature, 1550°C , the Fe, Cr and Ni contents in the metal are higher than that at $T = 1500^{\circ}\text{C}$. However, Fe content after 2 hrs of smelting is almost the same for both temperatures.

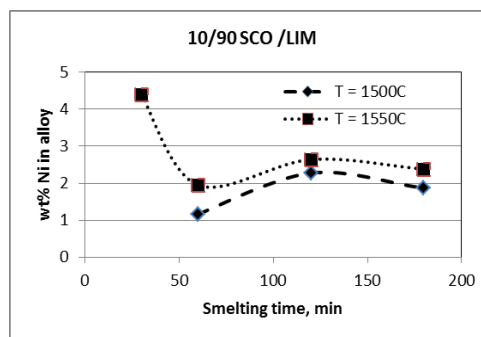


Figure 2. Weight% Ni in alloy vs smelting time at different temperatures

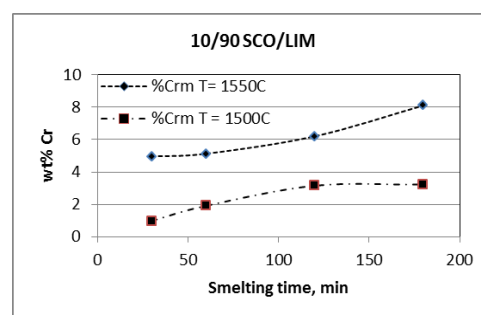


Figure 3. Weight% Cr in alloy vs smelting time at different temperatures

Ni content, on the other hand, basically increases with smelting time, and is higher at higher temperature. It was also observed that Ni is higher at the early stage of reduction. This may be due to the fact that Ni reduces more easily than iron. Iron dilutes the metal composition so that at longer reduction time the Ni content decreased. The reduction rate is expected to increase with increasing temperature due to increased rate of mass transfer or in-

creased rate of chemical reactions. The observed increase in reduction rate with the rise of temperature is an indication that the rate of chemical reaction is more important for the reduction rate than the oxygen potential of the system.

SEM image of the metal and slag produced after smelting 10/90 SCO/LIM charge mixture at $T = 1550^{\circ}\text{C}$ is shown in Fig. 5. Based on EDX, the metal phase of the smelted 10/90 SCO/LIM at $T = 1550^{\circ}\text{C}$ for thirty minutes contains in atom percent, 60.85% Fe, 3.66% Cr, 1.83% Ni, 25.43% C and trace amounts of Si while the slag phase contains 43.79% Fe, 6.1% Cr, 0.29% Ni, 4.63% Si, 3.06% Al, 2.29% Mg, 0.56% Mn and 22.1% C. The result reveals that Ni is almost 100% reduced while iron and Cr are only partially reduced at this reduction time. More of the Cr are dissolved in the slag than Fe although more of Fe is in the metal. The finding proves that Ni is more readily reduced than Fe and Fe is more readily reduced than Cr. This result is in agreement with the thermodynamic theory

C. Effect of Ore Composition

As stated above, the recovery of iron, chromium and nickel in the metal phase is also dependent on the type of ore. Higher concentration of iron, chromium and nickel in the metal is obtained for a charge mixture containing limonite ores than that charge mixture containing saprolite ores.

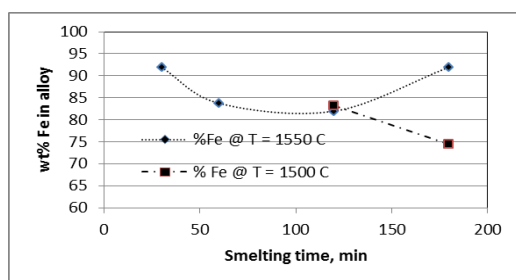


Figure 4. Wt% Fe in alloy vs. smelting time at different temperatures

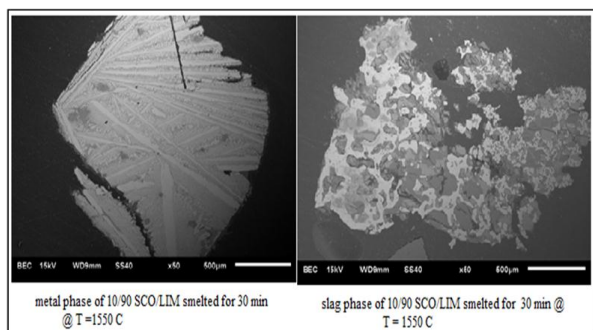


Figure 5. SEM image of metal and slag smelted at 30 min

Iron recovery in the alloy is higher for charge mixtures of limonite than that with saprolites (Fig. 6). It should be noted that based on XRF results limonite contains 73.83 wt% hematite (Fe_2O_3) while saprolite contains only 38.517 wt% hematite.

Chromium concentration is high for alloys of chromite and limonite combinations than that with chromite and saprolite combinations (Fig. 7). This is due to the fact that

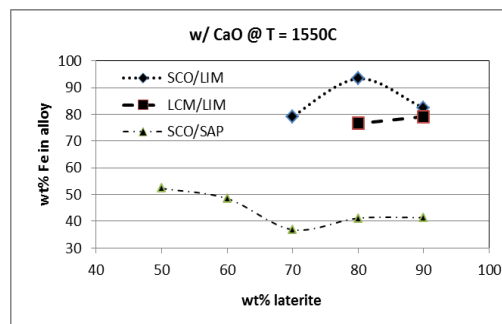


Figure 6. Fe concentration in the alloy vs wt% laterite

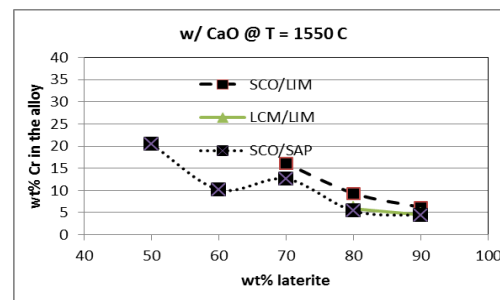


Figure 7. Cr concentration in the alloy vs wt% laterite

SCO contains higher chromium content than that of LCM and limonite having higher hematite content enhances reduction of chromite more than those with lower hematite. The higher the concentration of chromite in the mixture, the more chromium in the alloy.

Fig. 8 shows higher concentration of Ni in the alloy from the chromite and saprolite mixture than that from chromite and limonite mixtures. This is due to the high percentage of NiO in the saprolite than that in the limonite.

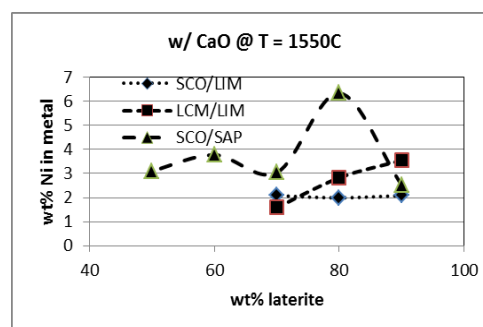


Figure 8. Ni concentration vs wt% laterite

D. The Slag System

Smelting operation at $T = 1500^{\circ}\text{C}$ to other mixture combinations especially with saprolite ores was not feasible because the slag produced is difficult to melt resulting in poor phases (metal–slag) separation. Fig. 9 shows the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ slag system indicating the slag compositions of the ore mixtures used in this investigation. It should be emphasized that high magnesia (MgO) concentration influences strongly the key physical characteristics of the slag. When its concentration in the slag increases beyond a few weight percent, the melting behaviour is modified significantly resulting in higher

smelting temperature and slag viscosity. And there was no distinct separation between the slag and the metal phase. Therefore, the composition of the slag largely determines the smelting temperature. Remarkable differences in smelting temperatures existed due to different slag compositions. It should also be noted that the composition of the slag varied in a wide range when the oxygen partial pressure will be changed. In this slag system, FeO will form at higher oxygen partial pressure that will result to a lower melting point due to fayalite or olivine formation.

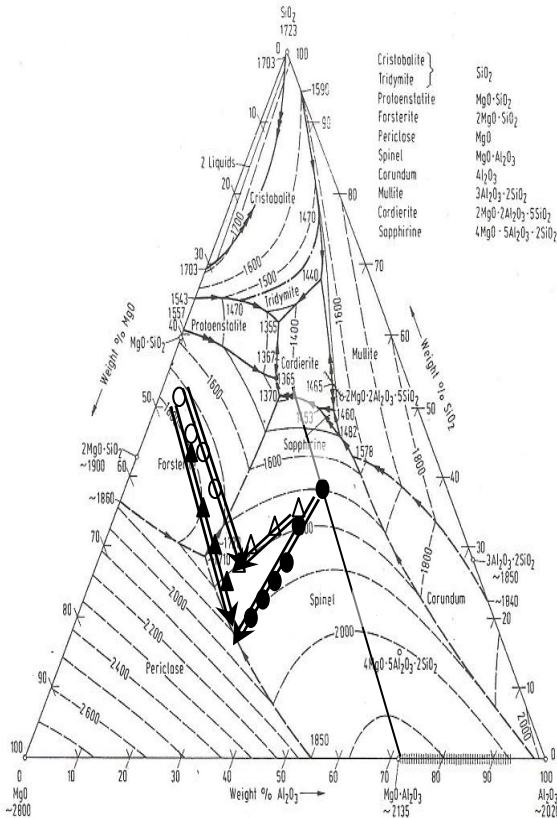


Figure 9. The MgO-Al₂O₃-SiO₂ system. Slag compositions used in this investigation. The higher chromite proportions in the mixture are marked with arrowheads.

●-SCO-LIM; ▲-SCO-SAP; ▼-SCM-LIM; ○-SCM-SAP

Source: Slag Atlas

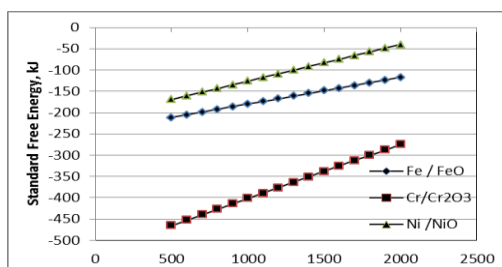


Figure 10. Free energy of formation of FeO, NiO, and Cr₂O₃

The distribution of chromium and nickel between Fe-Ni-Cr alloys and MgO-Al₂O₃-SiO₂ slag is of particular importance because most gangue minerals from laterite and chromite ores are aluminosilicates and magnesias. Thus by controlling the proportions of dissolve quantities of magnesia, alumina and silica in the gangue, the liqui-

duous temperature of the material can be lowered quite considerably. The lowest melting point liquid in this particular three-component system is 1355°C as shown in Fig. 8. Slags in the SCO-SAP and LCM-SAP mixtures consist of liquid and solid forsterite. Slags in the SCO-LIM and LCM-LIM consist of liquid mixed with solid spinel and forsterite.

Fig. 10 shows the free energy of formation of NiO, FeO and Cr₂O₃. It is apparent that iron is more readily oxidized than nickel and thus with proper control of the reduction potential of the system, ores with a low Ni/Fe ratio can be smelted to yield an acceptable ferronickel grade and thus a low nickel slag for discard. However, chromium is more readily oxidized than iron thus adjustment of the oxygen potential has to be balanced to permit the complete reduction of nickel oxide while limit the degree of oxidation on chromium to slag.

E. Distribution of Fe, Cr and Ni between Metal and Slag

The distribution ratios of Fe, Cr and Ni between the slag and the metal at a lower oxygen partial pressure suggest that most of nickel and chromium can remain in the metal phase. However, most of the iron also goes to the metal thus diluting the alloy and producing a low concentration of nickel and chromium. Iron can be eliminated adequately from alloys using higher oxygen partial pressure but chromium will not be reduced at high oxygen potential. To overcome these compositional problems, a blending of different ores is recommended. The goal is to establish a suitable slag composition using an ore with lower Fe content. The basicity ratio of the slag (MgO/SiO₂) in the blended ore is set in such a way as to have it between 0.45 and 0.65. It is also suggested that addition of flux to the blended ore be made to assist smelting. Therefore, the grade and composition of the ore are the main factors determining the feasibility of smelting a mixture of laterite and chromite ores to produce a Fe-Ni-Cr crude alloy.

A reaction between the iron oxide and the chromium oxide components of the slag and iron and chromium in the metal on the assumption that all the iron in the slag is present as FeO shown in Equation 1:



Since the activity coefficients of FeO, CrO_x, Cr and Fe are not known, an 'apparent equilibrium constant' could be used by employing the concentrations as shown in "(2)"

$$K' = \frac{(\% \text{CrO}_x)(\% \text{Fe})^x}{[\% \text{Cr}](\text{FeO})^x} \quad (2)$$

if the partition ratios are defined as $L_{\text{Fe}} = (\% \text{ Fe in slag})/(\% \text{ Fe in metal})$ and $L_{\text{Cr}} = (\% \text{ Cr in slag})/(\% \text{ Cr in metal})$, "(1)" can be rearranged into

$$\log L_{\text{Cr}} = x \log L_{\text{Fe}} + \log K' \quad (3)$$

Equation (3) is linear, with slope 'x' and intercept log K'. A typical plot is shown in Fig. 11 for the data in all

the series of experiments at 1550 °C under an argon atmosphere.

The slope is around 0.63 which is less than unity. The slopes being close to unity indicate the presence of divalent chromium ions in the slag in significant amounts. It was stated [6] that Cr_2O_3 is the stable oxide of chromium below 1400°C but did not discuss which oxide was stable at higher temperatures.

However, in this investigation, it is suggested that chromium occurs in the slag phase mainly in divalent form at high temperatures. But another possible reason for the value of x being less than unity is the presence of metallic chromium entrapped in the slag.

The yield of nickel is governed mainly by the reduction of nickel oxide and can be described by the following slag and metal equilibria:

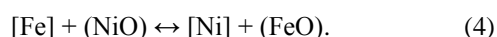


Fig. 12 illustrate the relation between the nickel and iron contents of the slag and the metal. It shows that the solubility of Ni in the slag increases with Ni concentration in the metal and the FeO concentration in the slag. Moreover, the solubility of the Ni changes significantly with change in temperature and that low temperatures favor dissolution of Ni in the slag. This indicates that the equilibrium constant (K) for the reaction decreases with increase in temperature and this is due to the fact that the reaction is exothermic, thus increase in temperature lowers the solubility of Ni in the slag. Since the activity coefficient in this slag-metal system are not known, we cannot compare the calculated concentration and determine if the system is in equilibrium.

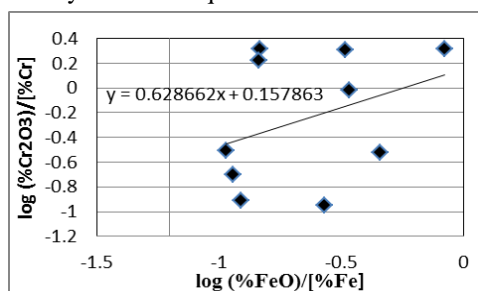


Figure 11. The variation in the log partition ratio of chromium with the log partition ratio of iron at 1550°C under argon

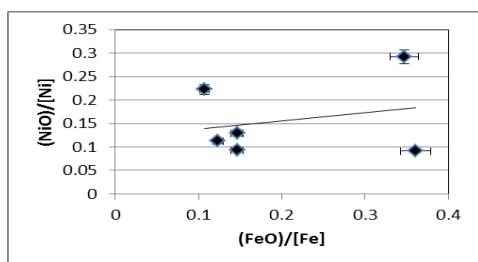


Figure 12. The relation between the nickel and iron contents in the metal and slag @ T = 1550°C

IV. CONCLUSIONS

Smelting of chromite and laterite ores mixtures in a vertical tube furnace using graphite crucible at various temperatures under argon atmosphere revealed that the composition of the slag largely determines the smelting temperature. It was shown that the grade and composition of the ore are the main factors determining the feasibility of smelting a mixture of laterite and chromite ores to produce a Fe-Ni-Cr crude alloy.

The smelting of 10-13% SCO chromite ore and 87-90% LIM laterite ore produced alloys with average iron, chromium and nickel content about 82%, 6.22% and 2.17%, respectively, at an average iron, chromium and nickel recovery of 98, 87% and 97%, respectively. The alloy also contains carbon, silicon and manganese.

The high recovery of iron and nickel in the alloy indicates the highly reducing condition prevailing in the smelting reduction experiments. However, a low chromium and nickel content in the alloy was due to the diluting effect of iron.

The distribution ratios of Fe, Cr and Ni between the slag and the alloy at a lower oxygen partial pressure suggest that most of nickel and chromium can remain in the alloy phase. It was shown that the solubility of Ni in the slag increases with Ni concentration in the alloy and the FeO concentration in the slag. The chromium content of the slag increases with increasing iron content of the slag.

It was also shown that chromium occurs in the slag phase mainly in divalent form (CrO) at 1550°C.

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