USE OF ALUMINIUM DROSS FOR SLAG TREATMENT IN SECONDARY STEELMAKING TO DECREASE AMOUNT OF REDUCIBLE OXIDES IN LADLE FURNACE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ONUR AYDEMİR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE MASTER DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

JANUARY 2007

Approval of the Graduate School of Natural and Applied Sciences

_____

Prof. Dr. Canan ÖZGEN

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

_____

Prof. Dr. Tayfur ÖZTÜRK

Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

_____

Prof. Dr. Ahmet GEVECİ

Supervisor

Examining Committee Members

Prof. Dr. Haluk ATALA   (METU,METE)   ———————————

Prof. Dr. Ümit ATALAY   (METU,MINE)   ———————————

Prof. Dr. Ahmet GEVECİ   (METU,METE)   ———————————

Prof. Dr. Naci SEVİNÇ   (METU,METE)   ———————————

Prof. Dr. Yavuz TOPKAYA   (METU,METE)   ———————————

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last Name: Onur Aydemir

Signature:

ABSTRACT

USE OF ALUMINIUM DROSS FOR SLAG TREATMENT IN SECONDARY STEELMAKING TO DECREASE AMOUNT OF REDUCIBLE OXIDES IN LADLE FURNACE

Aydemir, Onur

M.S., Department of Metallurgical and Materials Engineering

Supervisor: Prof.Dr. Ahmet Geveci

January 2007, 64 pages

In this study it was aimed to analyse refining processes such as decreasing reducible oxide content of ladle slag with affecting parameters in low carbon aluminum killed grades and for the research Erdemir low carbon steel grades 7112K and 7110K are selected. There was a negative correlation between reducible oxide amount in ladle slag and desulphurization capacity of ladle slag with metal-slag reaction and steel internal cleanliness. To refine these properties of slag, aluminium dross, which was aluminium production discard and has a metallic content around %30-35 was used and after ladle treatment operation, decrease in reducible oxides such as Fe_tO, MnO, SiO_2, P_2O_5 was analysed. After the study it was observed that 653 kg. of converter slag leaked during tapping of steel and SiO_2 ve P_2O_5 content of ladle slag had negligible change after ladle treatment. According to the results, it is observed that initial %10-12 (Fe_tO + MnO) content was reduced to % 4.5-5.0 (Fe_tO + MnO) after ladle treatment with use of aluminium dross. Beside of this, in order to

see the effect of this slag reduction on steel cleanliness, low carbon aluminium killed grades were compared with ultra-low carbon aluminium killed grades having (Fe_tO + MnO) content of %16-17 in slag. It was seen that reoxidation of aluminium (loss of dissolved aluminium) during continuous casting for ULC (ultra-low carbon) grades is 144 ppm but for LC grades it was 94 ppm and it was being expected that ULC steel group would have higher inclusion content after casting.

ÖZ

İKİNCİL ÇELİK YAPIMI POTA CÜRUFU MUAMELESİ İŞLEMİNDE İNDİRGENEBİLİR OKSİTLERİN MİKTARININ AZALTILMASI İÇİN POTA FIRININDA ALÜMİNYUM CÜRUFU KULLANIMI

Aydemir, Onur

Yüksek Lisans, Metalurji ve Malzeme Mühendisligi Bölümü
Tez Yöneticisi: Prof.Dr. Ahmet Geveci

Ocak 2007, 64 sayfa

Düşük karbonlu ve alüminyum ile deokside edilmiş çelik kalitelerinde pota cürufunun içerisindeki indirgenebilir oksitlerin azaltılmasına yönelik uygulamaları, etkileyen parametrelerle birlikte, inceleyen bu çalışmada Erdemir düşük karbonlu çelik kaliteleri olan 7112K ve 7110K seçilmiştir. Pota cürufundaki indirgenebilir oksitlerin miktarı ile, çelik içerisindeki kükürdü metal-cüruf reaksiyonuyla pota cürufuna alma ve çeliğin iç yapı temizliği arasında ters bir ilişki vardır. Cürufun bu özelliklerinin iyileştirilmesi amacıyla ikincil metalurji işlemleri sırasında, alüminyum üretimi prosesi atığı olan ve %30-35 metalik alüminyum içeren alüminyum cürufu kullanılmış ve cüruf içerisindeki (Fe_tO, MnO, SiO_2, P_2O_5) gibi birincil çelik yapımı kaynaklı olan indirgenebilir oksitlerin değişimi incelenmiştir. Çalışma sonucunda konvertörlerden potaya sıvı çelik alınırken ortalama 653 kg. konvertör cürufunun da potaya alındığı tespit edilmiştir. Yapılan incelemede pota cürufu içerisindeki SiO_2 ve P_2O_5 miktarlarının pota işlemleri sonrasında önemli miktarda değişmediği tespit edilmiştir. Yapılan analizler sonucunda, ikincil metalurji işlemleri öncesinde cüruf içerisinde % 10-12 olan ($Fe_tO + MnO$)%, alüminyum cürufu ile yapılan işlem sonucunda % 4.5-5.0 değerine kadar azaldığı görülmüştür. Bununla beraber cüruf indirgeme işleminin çelik temizliğine olan etkisini görmek amacıyla, düşük karbonlu

çelik grubu, üretim şekli gereği ikincil metalurji işlemi sonucunda cüruf içerisindeki Fe_tO ve MnO toplamı %16-17 olan ultra düşük karbonlu çelik grubu ile karşılaştırılmış ve sürekli döküm sırasında reoksidasyona uğrayan çözünmüş alüminyum miktarlarının (döküm sırasında azalan çözünmüş aluminyum miktarı) ultra düşük karbonlu çelik grubu için 144 ppm ve düşük karbonlu çelik grubu için ise 94 ppm olduğu görülmüş ve bunun ultra düşük karbonlu çelik grubunun daha fazla inklüzyon içermesine sebep olacağı beklenmiştir.

Anahtar Kelimeler: İkincil çelik yapımı, cüruf indirgeme, pota cürufu, indirgenebilir oksitler

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

CHAPTER 1

INTRODUCTION

The growth in scope and extent of secondary steelmaking has been one of the most significant features of steelmaking development in recent years and, particularly during the past 20 years high levels of investment in new secondary steelmaking (ladle treatment) facilities have been made by many steelmakers to accommodate changing product needs. The reasons for this are as follows :

Primary steelmaking is mainly concerned with decarburizing in the BOF (basic oxygen furnace) or melting in the EAF (electric arc furnace), with relatively crude control over temperature, sulphur, and phosphorus. The complex task of fine adjustment of composition, temperature, and steel cleanness is more effectively carried out by secondary steelmaking which has significantly improved the technical performance of BOF and the EAF process routes, so that the choice between them for stringent product specifications is now made more on economic grounds and less on technological factors.

Compared with ingot casting, continuous casting brings the benefits of higher yield, lower rolling and energy costs, and improved quality. However, the extensive and growing demands of continuous casting on control of analysis, temperature, and the level of non-metallic inclusions can only be met by secondary treatment in the ladle and it breaks the connection between the primary steelmaking operation and the casting operation and by providing a buffer stage in the process route for logistical control of process timing, allows them both to operate at maximum efficiency.

In general, in order to produce clean steel the melt is deoxidized and the deoxidation products should be removed. In addition, the reoxidation by the slag should be prevented effectively. The high oxygen potential in ladle slag may cause contamination by reoxidation of components such as Al, Si, Ti. The oxygen potential

of slag is critical factor which determines the likelihood of reoxidation by slag at ladle.

The purpose of this work was to reduce the main reducible oxides (Fe_tO+MnO) of ladle furnace slags by aluminium in a dross obtained from aluminium industry which is their discard product; ladle furnace slags were made of carry-over slag to pot during tapping of BOF furnace and additives for deoxidation and other purposes before secondary treatment of steel.

CHAPTER 2

LITERATURE REVIEW

2.1 Principles of Modern Steelmaking

Practically all steel products are made at the present time by the sequence of steps that are shown in Figure 2.1.

Iron-bearing materials containing principally iron oxides (iron ore, pellets, sinter, etc.) are reduced to molten iron (pig iron) in the blast furnace, using the carbon of coke as the reducing agent. In the process, the iron absorbs from 3.0 to 4.5 per cent of carbon. Iron containing 3.0 to 4.0 per cent of carbon can be used to make iron castings (cast iron). However, most modern steels contain considerably less than 1.0 per cent of carbon, and the excess carbon must be removed from the product of the blast furnace to convert it into steel [10].

The excess carbon is removed by controlled oxidation of mixtures of molten pig iron and melted iron steel scrap in steelmaking furnaces to produce carbon steels of the desired carbon content. The principal steelmaking furnaces include the basic-oxygen furnace and electric arc furnace. Various elements like chromium, manganese, nickel, molybdenum, etc. may be added singly or in combination to the molten steel during or after carbon-removal process to produce alloy steels. All of the modern steelmaking processes produce molten(liquid) metal.
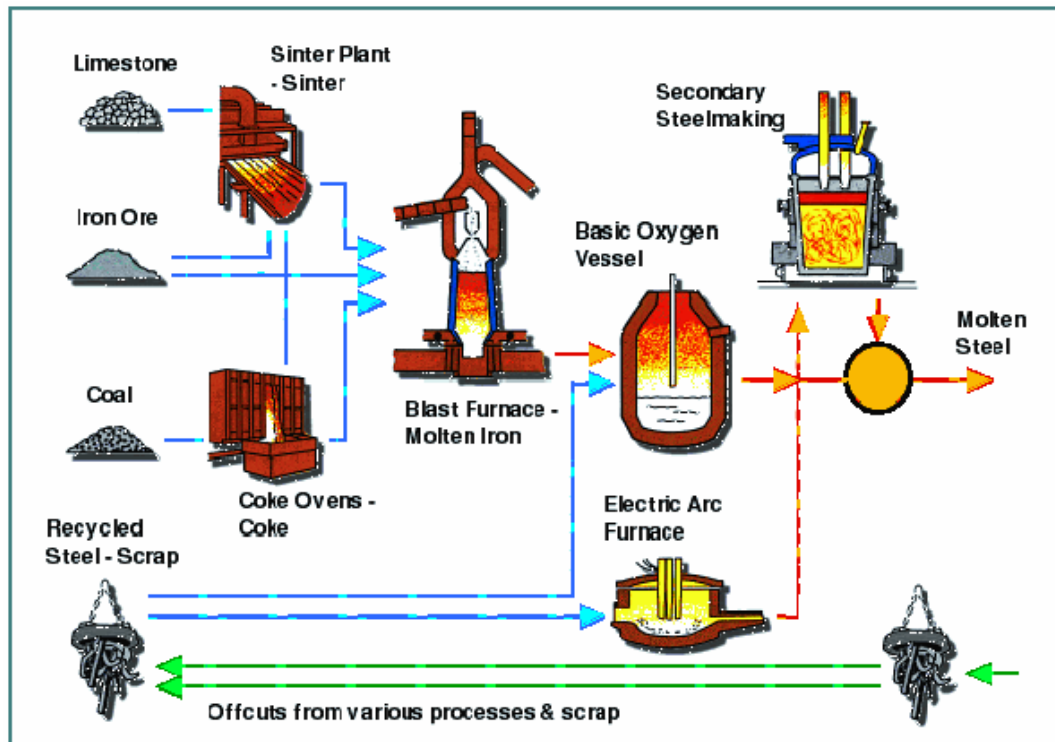
Figure 2.1 Flow Diagram Showing the Principal Process Steps from Raw Material to Liquid Steel before Casting [10].

After the molten steel has attained the desired chemical composition in the steelmaking process, it is tapped (poured) from the furnace into a ladle from whence most steel was teemed into tall usually rectangular molds where it solidifies to form ingots. Most ingots, after being removed from the molds, were reheated to a proper uniform temperature and rolled (in some cases, forged) into shapes known as blooms, billets and slabs which are referred to as semi finished steel: only a relatively small number are rolled or forged directly into finished forms. Increasing quantities of semi finished steel are being produced by pouring liquid steel into the top of open-bottomed molds in continuous-casting machines where it solidifies and is continuously withdrawn from the bottom of the molds in long lengths of the desired shapes.

Blooms, slabs, and billets are referred to as semi finished steel because they form the starting material for the production by mechanical treatment (hot rolling, cold rolling, forging, extruding, drawing, etc.) of finished steel products that include bars, plates, structural shapes, rails, wire, tubular products, and coated and uncoated sheet steel, all in many forms required by users of steel. Many of these products require some form of heat treatment at the steel mill to give them the best properties for their intended use.

 The above oversimplified sequence might make it appear that the steelmaking process is simple. Actually, the manufacture of steel in its many product forms involves a complicated series of interrelated operations [10].

2.2 Electric-arc Furnace Steelmaking Processes

The process of making steel in basic-lined electric-arc furnace can be divided into four periods as the melt down period, oxidizing period, the composition and temperature adjustment period and the tapping [10] .

When charging has been completed the bank in front of the charging door is built up with refractory material to form a dam to keep the molten metal from slopping out the door (or doors). The door is closed and the electrodes are lowered to about 25 mm. above the scrap. The main circuit breaker is closed, an intermediate voltage is selected with proper current setting on the rheostats, and the arcs are struck under automatic control. After 1 to 3 minutes (to allow the electrodes to bore into the scrap), maximum voltage and current should be applied for the fastest possible melting of scrap. The initial slow start is to shield the lining and roof from the heat of the arc.

The melting period in the basic electric furnace is the most expensive period in its operation because power and electrode consumption are at the highest rate during this interval.
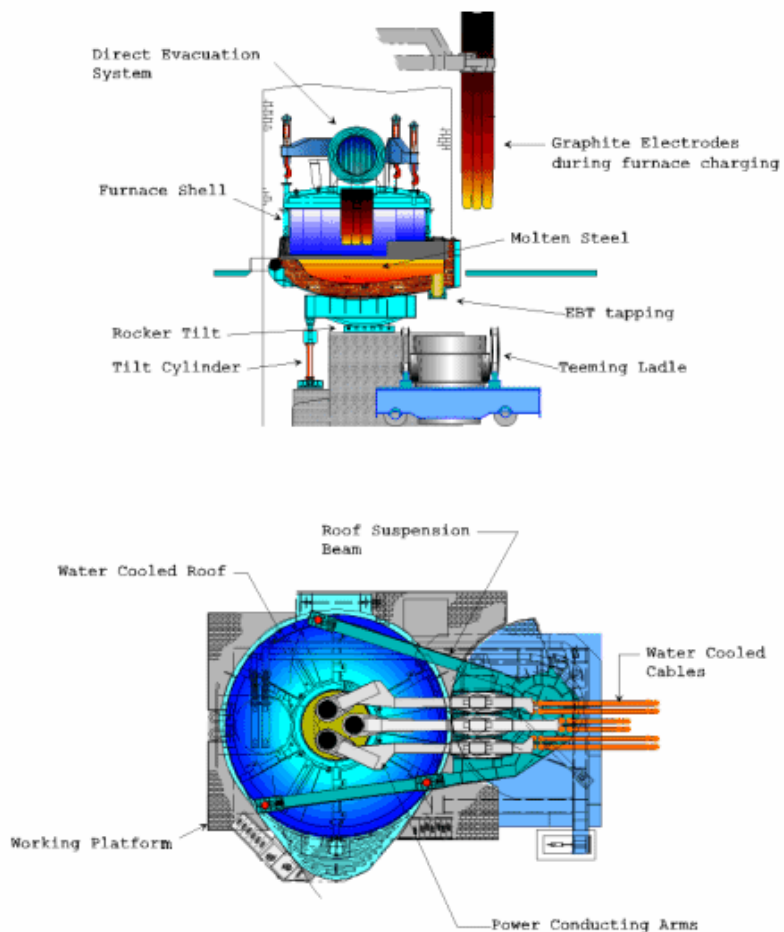
Figure 2.2 Sketch of Electric Arc Furnace

The electrode melts the portion of the charge directly underneath and around them, and continue to bore through the metallic charge, forming a pool of molten metal on the hearth. From the time the electrodes bore through the scrap and form a pool of molten metal on the hearth, the charge is melted from the bottom up by radiation from the pool, by heat from the arc, and by the resistance offered to the

current by the scrap. Burnt lime is usually blown on top of the bath near the end of the melting period of the first scrap charge. If blowing facilities are not available, burnt lime is added usually to the furnace before the second scrap charge is made. Heating of the charge material is continued until it is completely melted.

Oxidation occurs in varying degrees from the time the molten metal begins to form until the entire charge is in solution. During this period, phosphorus, silicon, manganese, carbon, and iron are oxidized. Oxygen for these, as well as for other oxidizing reactions is obtained from:

- Oxygen gas injected into the bath
- Oxygen in the furnace atmosphere
- Calcination of limestone (only small amounts of limestone are used on a flat low-carbon steel bath to minimize overheating of the furnace roof by heat radiation from a smooth bath)
- Oxides of alloying elements added in the furnace
- Ore, cinder and scale

The oxidizing materials added to the bath react with carbon in the bath to form carbon monoxide. If too much of the oxidizing material is added at one time, the carbon monoxide formation may be vigorous enough to eject slag and steel out of the furnace. The direct use of oxygen is extremely important in modern practice from the standpoint of rapidly removing carbon from the bath.

Enough carbon should be present in the charge so that the carbon content of the steel, when melted, is 0.15 to 0.25 % higher than the desired tap carbon content. This excess carbon is removed with oxygen and forms carbon monoxide gas, which bubbles out of the steel. This bubbling is called the carbon boil, which stirs the bath and makes it more uniform in composition and temperature. This facilitates meeting steel composition and temperature specifications. The carbon boil also removes some of the hydrogen and nitrogen from the steel which is generally desirable.

During the oxidation period, the reactions that occur in the bath of the basic electric arc furnace are similar to those in the basic open-hearth furnace and the basic oxygen furnace, except that the electric furnace bath can be made hotter. Hence, there is more chance of phosphorus reversion unless the slag is strongly basic.

Most carbon steel and low-alloy steel grades made in electric-arc furnaces are made by a single slag process. This means that the slag that forms during melting of the charge is not replaced by another slag as in the double slag process. In the single slag process, steelmaking is finished by adjusting the composition and temperature of steel bath to the desired values, after which the steel is tapped from furnace into a ladle. As soon as a charge is melted, a steel sample is taken and analyzed in the chemical laboratory. From this analysis, the required steel composition adjustments are determined. Several temperature measurements of the steel are made to determine the temperature adjustment required.

In tapping a heat, the electrodes are raised high enough to clear the bath in a tilted position, the tap hole is opened, and the furnace is tilted by a control mechanism so that the steel is drained from the furnace into a ladle. The ladle is usually held by a teeming crane during tapping to minimize exposure of the stream to air and minimize erosion of ladle refractory. The slag may be tapped before, with, or after the steel depending on the particular operation.

2.3 Primary Oxygen Steelmaking Process (BOF Process)

2.3.1 Principles

A schematic elevation showing the principal operating units of the basic oxygen process is shown in Figure 2.3 [9].

Most commonly, basic oxygen furnace operation starts with charging of furnace with the proper amount of scrap and molten iron typically containing 4.1

%C, 0.35 %Mn, 0.1 %P, 0.5 % Si. It is turned upright and the oxygen lance is lowered to a predetermined position above the surface of the bath. Pure oxygen gas issues from the jet nozzle at high velocity under a pressure that is normally held between 14 and 16 bars. The action of the oxygen jet is partly chemical and partly physical. The oxygen immediately starts reacting with the silicon, generating heat and producing molten silica. Slag-forming fluxes (chiefly burnt lime, dolomitic lime, and fluorspar) are added in controlled amounts from an overhead storage system immediately after oxygen ignition. These materials, which serve to produce a slag of the desired basicity and fluidity, are added through an inclined chute built into the side of a water-cooled hood that covers the furnace.
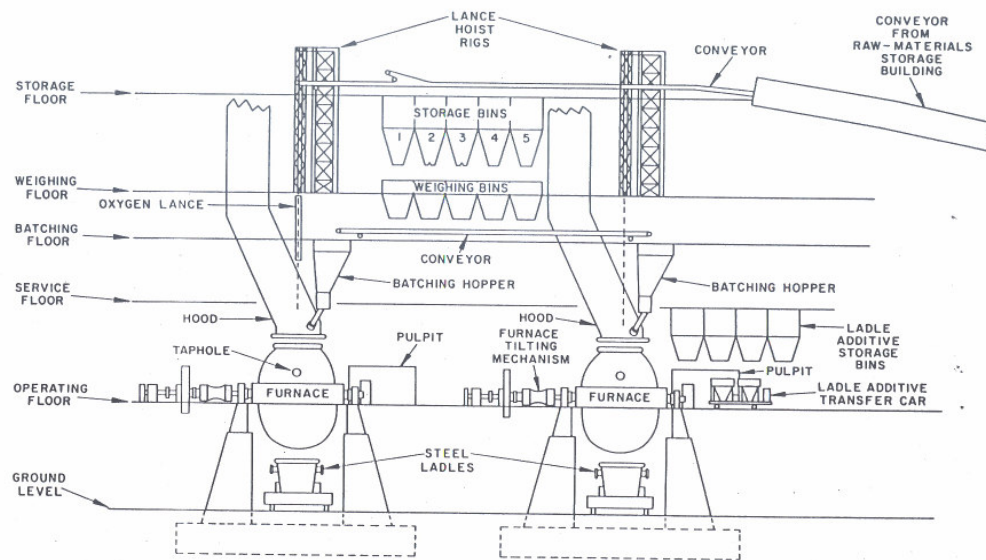
Figure 2.3. Schematic Elevation Showing the Principal Operating Units of the Basic Oxygen Process [9]

9

As the blow progresses, an emulsion is formed with the slag and metal, and the other metalloids are oxidized. Carbon monoxide is evolved, which gives rise to a vigorous boiling action and accelerates the refining metallurgical reactions.

When the blow is completed, as determined by the furnace operator utilizing the results of calculations by model computer, the lance is withdrawn and the furnace is tilted to a horizontal position toward the charging side. A temperature reading is secured with an immersion-type thermocouple, and a sample of the steel is obtained and sent to the nearby chemical laboratory for analysis. This analysis determines the individual chemical elements of the steel.

2.3.2 Oxidation Reactions

2.3.2.1 Oxidation of Iron

With hypothetical pure liquid FeO as the standard state, the activity of iron oxide is derived from the concentration of dissolved oxygen in liquid iron that is in equilibrium with the slag. For the reaction equilibrium [9]

$$FeO(l) = Fe + [O] \tag{1}$$

$$K_O = [a_O] / a_{FeO} \tag{2}$$

where $a_O = [\%O]\gamma_O$, using $\log \gamma_O = -0.1 * [\%O]$. The temperature dependence of the equilibrium constant K_O, as derived from the standard free energy equation for reaction (1), is given below:

$$\log K_O = -5730/T + 2.397 \tag{3}$$

A wide variety of formulations is carried out to represent the composition dependence of the iron oxide activity or activity coefficient in complex slags. Within the limits of uncertainty of the experimental data on slag-metal reaction equilibrium, there is a decisive correlation between the activity coefficient of FeO and the slag basicity B as shown in Figure 2.4. It is evident that γ_{Feo} reaches a peak at basicity of about B = 1.8 .
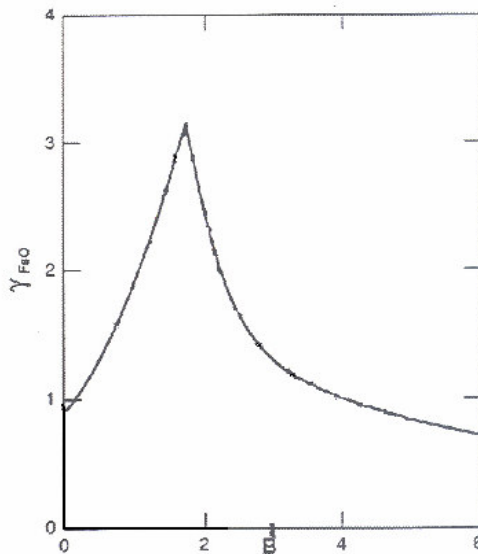
Figure 2.4. Effect of Slag Basicity on the Activity Coefficient of Iron Oxide in Simple and Complex Slags [9]

In steelmaking slags, the total number of g-mols of oxides per 100 g of slag is within the range 1.65 ± 0.05. Therefore, the analysis of the slag-metal equilibrium data, in terms of the activity and mol fraction of iron oxide, can be transposed to a simple relation between the mass ratio [ppm O] / (%FeO) and the sum of the acidic oxides $%SiO_2$ +0.84 x $%P_2O_5$ as shown in   Figure 2.5. For basicities of B>2, this mass ratio as function of slag basicity is given in Figure 2.6 [9].
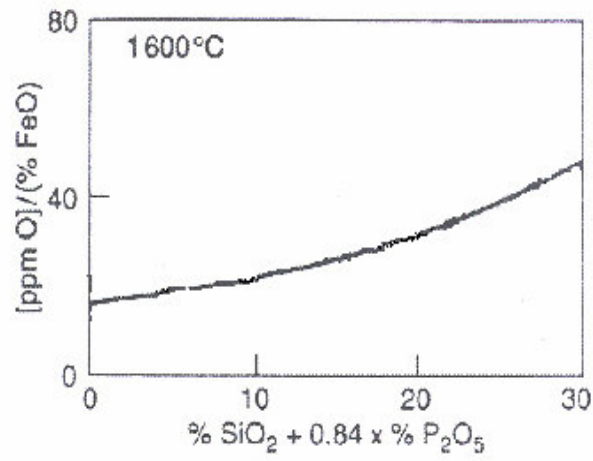
Figure 2.5. Equilibrium Ratio [ppm O] / (%FeO) Related to SiO_2 and P_2O_5 [9]
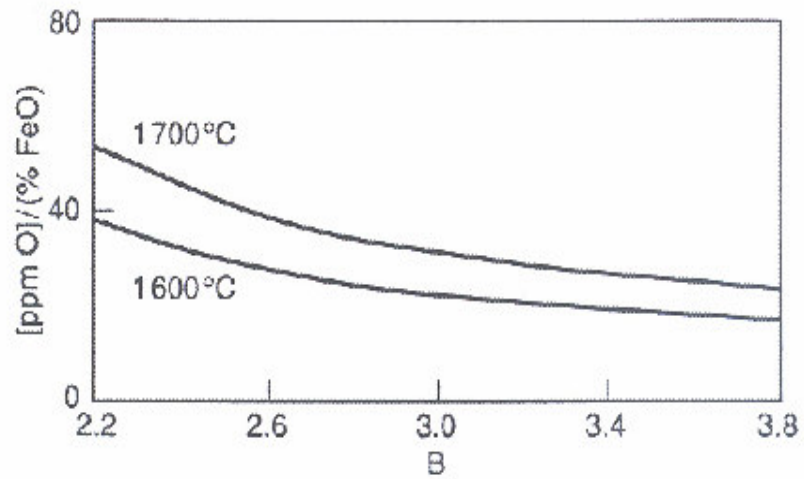
Figure 2.6. Equilibrium Ratio [ppm O] / (%FeO) Related to Slag Basicity [9]

2.3.2.2 Oxidation of Manganese

The slag metal distribution ratio is governed by two interrelated reaction equilibria. One reaction is oxidation of Mn with FeO in slag [9].

$$(FeO) + [Mn] = (MnO) + [Fe] \qquad (4)$$
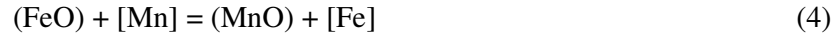
$$K_{FeMn} = a_{MnO} / a_{FeO} * [\%Mn] \qquad (5)$$

where the oxide activities are with respect to pure liquid oxides.

The second reaction to be considered is

$$[Mn] + [O] = (MnO) \qquad (6)$$

$$K_{Mn} = a_{MnO} / [\%Mn] [a_O] \qquad (7)$$

and temperature dependence of these equilibrium constants K_{FeMn} and K_{Mn} are,

$$\log K_{FeMn} = 7452/T - 3.478 \qquad (8)$$

$$\log K_{Mn} = 13182/T - 5.875 \qquad (9)$$

For the FeO and MnO exchange reaction involving the oxidation of manganese in steel, the equilibrium relation may be described in terms of the mass concentrations of oxides.

$$K'_{FeMn} = (\%MnO) / (\%FeO) [\%Mn] \qquad (10)$$

where, the equilibrium relation K'_{FeMn} depends on temperature and slag composition. The values of K'_{FeMn} against the slag basicity for tapping temperature from 1600°C to 1700°C is plotted in Figure 2.7. In most of the practices tapping temperature is around 1650°C for which the equilibrium K'_{FeMn} is about 1.8 ± 0.2.
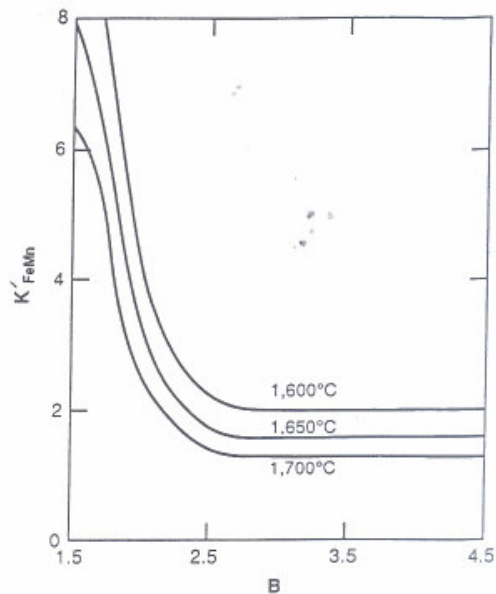
Figure 2.7 Equilibrium relation K'_{FeMn} related to slag basicity [9]

2.3.2.3 Oxidation of Carbon

For the reaction,

$$CO_{(g)} = [C] + [O] \tag{11}$$

the equilibrium constant for low alloy steels containing less than 1% C for steelmaking temperatures, is

$$K = [\%C][ppmO] / p_{CO}(atm) = 20 \tag{12}$$

With respect to slag-metal reaction, the equilibrium relation for carbon oxidation will be,

$$(FeO) + [C] = CO_{(g)} + [Fe] \tag{13}$$

$$K_{FC} = p_{CO} \text{ (atm)} / [\%C] \, a_{FeO} \tag{14}$$

$$\log K_{FC} = -5730/T + 5.096 \tag{15}$$

For the reaction,

$$(MnO) + [C] = CO_{(g)} + [Mn] \tag{16}$$

the following equilibrium relations apply

$$K_{MC} = p_{CO} \text{ (atm)} [\%Mn] / [\%C] \, a_{MnO} \tag{17}$$

$$\log K_{MC} = -13182/T + 8.574 \tag{18}$$

2.3.2.4 Oxidation of Silicon

For low silicon contents mass concentrations of Si and O in the equilibrium constant for the reaction are being used [9] .

$$[Si] + 2[O] = (SiO_2) \tag{19}$$

$$K_{Si} = a_{SiO2} / [\%Si][\%O]^2 \tag{20}$$

where the silica activity is with respect to solid SiO_2 as the standard state. The temperature dependence of K_{Si} is given by

$$\log K_{Si} = 30410/T - 11.59 \tag{21}$$

For the BOF tap temperatures $K_{Si} \approx 3 \times 10^4$ and for lime-saturated slags a_{SiO2} < 0.01, therefore for 800 ppm of O in steel at turndown the equilibrium content of silicon in the steel would be less than 1 ppm Si. In practice the steel contains 0.003 to 0.005% Si at turndown. Evidently, at these low concentrations of silicon the reaction kinetics are no longer favourable to reach slag-metal equilibrium with respect to silicon oxidation.

2.3.2.5 Oxidation of Phosphorus

Formulation of the phosphorus reaction is [9]

$$[P] + 5/2[O] + 3/2(O^{2-}) = (PO_4^{3-}) \tag{22}$$
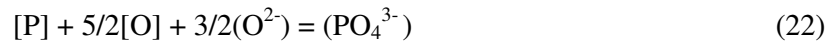
At low concentration of [P] and [O], as in most of the experimental melts, their activity coefficients are close to unity, therefore mass concentrations can be used in formulating the equilibrium relation K_{PO} for the above reaction.

$$K_{PO} = (\%P)[\%O]^{-2.5} / [\%P] \tag{23}$$

The equilibrium relation K_{PO} known as the phosphate capacity of the slag, depends on temperature and slag composition. After several studies [9] it is understood that sum of basic oxides is considered to be key parameter in describing the composition dependence of the phosphate capacity of slag.

$$BO = \%CaO + \%CaF_2 + 0.3 * \%MgO \tag{24}$$

The temperature and slag composition dependent formula of phosphate capacity of slag is

$$\log K_{PO} = 21740/T - 9.87 + 0.071 * BO \tag{25}$$

2.3.2.6 Oxidation of Sulphur

The sulphur transfer from metal to slag is reduction process as represented by the equation

$$[S] + (O^{2-}) = (S^{2-}) + [O] \tag{26}$$

for which the state of slag-metal equilibrium is,

$$K_{SO} = (\%S) [\%O]/ [\%S] \tag{27}$$

The concentration of acidic oxides, e.g. $\%SiO_2 + 0.84 * \%P_2O_5$ is to be a better representation of the dependence of K_{SO} on the slag composition. See Figure 2.8.
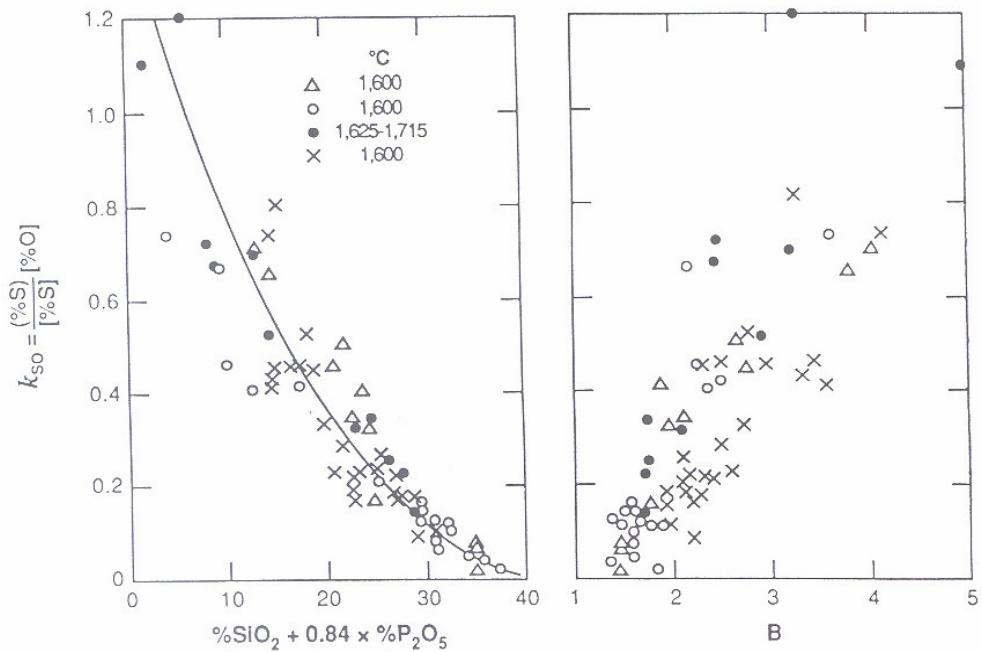
Figure 2.8 Sulphide Capacities of Slags [9]

In view of the relationship between the ratio [ppm O] / (%FeO) and the sum of the acidic oxides, the sulphide capacity of the slag may be represented also by formula given below.

$$K_S = (\%S)(\%FeO) / [\%S] \qquad (28)$$

2.3.3 Reactions During Tapping

2.3.3.1 Reactions with Furnace Carry-over Slag

Some of the additions to steel as Fe-Mn, Fe-Si, Al, etc are done during taping of BOF furnace, before ladle treatment (secondary metallurgy). The percentages of utilization of the ladle additions for low carbon heats are 85-95% for Mn, 60-70% for Si, 35-65% for Al. Some of manganese is lost during ladle additions because of the vaporization of metal. Part of slag from BOF furnace is carried over to the ladle for steel. Losses in the ladle additions of aluminium and silicon are due to reactions with this furnace slag that is carried into the tap ladle. There is also the iron oxide rich skull accumulating at the converter mouth, some of which falls into the ladle during furnace tapping and reacts with aluminium and silicon.

The reaction of aluminium and silicon with the furnace slag and fallen converter skull is represented in a general form by the following reaction

$$Fe(Mn)O_t + Al(Si) = Fe(Mn) + Al(Si)O_t \qquad (29)$$
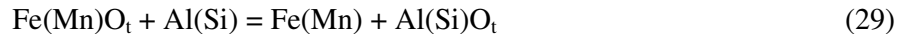
According to Turkdogan [9] using the average molecular masses and assuming 80% Fe_3O_4 for the converter skull, the following approximate relation is derived for the loss of aluminium and silicon to the ladle slag for 220 tons steel in the tap ladle.

$$[\%Al + \%Si]_s = \Delta(\%FeO + \%MnO)W_{fs} \times 10^{-6} + W_{sk} \times 10^{-4} \qquad (30)$$

18

where,

W_{fs} = mass of furnace slag carryover, kg

W_{sk} = mass of fallen converter skull, kg

Δ(%FeO + %MnO) = decrease in oxide contents of furnace slag during tapping.

[%Al + %Si]$_s$ = loss of Al and Si to the ladle slag, %

Another consequence of slag carryover is phosphorus reversion to the Al-killed steel in the tap ladle. For a 220 tons heat, the phosphorus reversion Δ[ppm P] is represented by:

$$\Delta[\text{ppm P}] = 0.045\ \Delta(\%P)\ W_{fs} \tag{31}$$

where Δ(%P) is the decrease in the phosphorus content of the furnace slag carried into the tap ladle.

For high phosphorus reversion of 45 ± 10 ppm., the mass of slag carry-over is estimated to be W_{fs} = 3214 ± 714 kg [9]. In most cases of furnace tapping, the phosphorus reversion is about 20 ± 10 ppm for which the estimated slag carry-over is about 1430 ± 714 kg.

2.3.3.2 Deoxidation Reactions

Deoxidation reactions can be described using the deoxidation equilibrium constant (K). The deoxidation reaction, when the alloying element (M) is added to the steel, can be represented by :

$$M_xO_y = x\underline{M} + y\underline{O} \tag{32}$$

The deoxidation constant assuming pure M_xO_y forms (i.e. unit activity for M_xO_y) is given by :

19

$$K = (h_M)^x \, (h_O)^y \qquad\qquad (33)$$

where h_M and h_O are the Henreian activities defined such that activity of the components is equal to its weight percent at infinite dilution in iron. [13]

$$h_i = f_i \, (\%i) \qquad\qquad (34)$$

where

f_i = activity coefficient of i

$\%i$ = weight percentage of i

For most low alloy steels encountered in ladle metallurgy the activity coefficient can be taken as unity and equation (33) reduces to :

$$K_M = (\%M)^x \, (\%O)^y \qquad\qquad (35)$$

There are primarily three elements used in steel deoxidation to remove dissolved oxygen while tapping from converter to ladle. Manganese (as low and high C ferro-alloy), silicon (or as silicomanganese alloy) and aluminium (about 95-98% purity).

For low carbon aluminium killed steel grades only aluminium bars are used to remove oxygen. The minimum amount of aluminium required to deoxidize the steel is computed based on the following reaction [6]:

$$2 \, [Al] + 3[O] = Al_2O_3 \, (s) \qquad\qquad (36)$$

For the reaction,

$$Al_2O_3(s) = 2[Al] + 3[O] \qquad\qquad (37)$$

$$K = [\%Al]^2[ppm\ O * f_o]^3\ /\ a_{Al2O3} \qquad (38)$$

$$\log K = -\ 62680/T + 31.85 \qquad (39)$$

In practice aluminium is used in conjunction with CaO and a complex aluminate will form; either CA, CA_2 or $C_{12}A_7$ (A represents Al_2O_3 and C represents CaO). It is desirable to form a liquid calcium aluminate nearly saturated with CaO so that the resulting inclusion is $C_{12}A_7$ in the solidified steel. For example, for 0.01% Al the activity of oxygen will be less than 2 ppm, whereas, for Al alone it would be about 10 ppm.

A second advantage of Al-CaO deoxidation is that, a liquid calcium aluminate inclusion forms which floats out more readily than Al_2O_3 and liquid inclusions will not clog casting nozzles.

$$(CaO) + 2[Al]\ + [3O] = (CaO.Al_2O_3) \qquad (40)$$
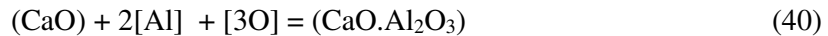
2.4 Secondary Steelmaking Process

2.4.1 Fundamentals of Secondary Steelmaking Process

The purpose of "Secondary Steelmaking" is to produce clean steel, steel which satisfies stringent requirements of surface, internal and micro cleanliness and requirements of mechanical properties. Ladle metallurgy (or secondary metallurgy) is a secondary step of the steelmaking process often performed in ladle after the initial refining process in a primary furnace is completed.

Although satisfactory for making steels for most of the steel applications, conventional steelmaking and refining practices such as BOP, Q-BOP and electric arc-furnaces could not consistently achieve the specifications the special steels had to meet. To remain competitive and maintain production, steelmakers reluctantly accepted the secondary steel refining processes. It is found that they were able to

exercise a control over the many processing conditions which contributed to an even higher quality steel including [9] :

- Teeming temperature, especially for continuous casting operations
- Deoxidation
- Decarburization (ease of production of steels with low carbon levels of less than 0.03%)
- Additional adjustment for chemical composition
- Increasing production rates by decreasing refining times in the BOF

Secondary steelmaking processes are adopted primarily to achieve various objectives. The fulfilment of these objectives result in a steel which meets the desired stringent requirements. These objectives (may be called as goals of secondary steelmaking) include:

- Control of gases (decreasing the concentration of oxygen and hydrogen in steel)
- Low sulphur contents (less than 0.01% and to as low as 0.002%)
- Micro cleanliness (removal of undesirable non-metallic, primarily oxides and sulphides)
- Inclusion morphology (Since steelmakers cannot remove undesirable oxides completely, this step allows steelmakers to change the composition and/or shape of the undesired matter left in the steel to make it compatible with the mechanical properties of the finished steel.)
- Mechanical Properties (Charpy V-notch toughness, transverse properties, and ductility in through-thickness of plates)

2.4.2 Ladle Furnace (LF)

The ever increasing users demand for higher quality steel particularly for critical applications and the advent of sequential continuous casting, made it necessary for steel plants to install ladle furnaces for steel reheating that is needed for extended time for steel refining and the adjustment of steel temperature for the caster on a correct timely basis.

There are several types of ladle furnaces for arc reheating of steel designed by different manufacturers but the basic features of the ladle furnace is given in Figure 2.9 [10].
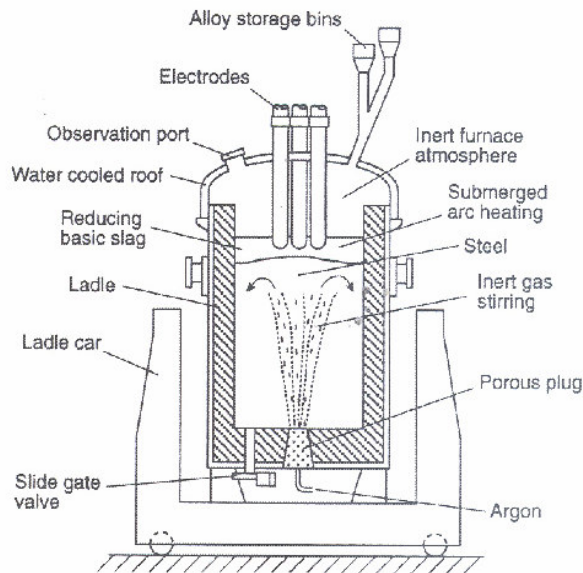
Figure 2.9. Sketch of Ladle Furnace [9]

The following statements summarise the basic requirements for efficient arc reheating in the ladle furnace.

1. To shorten reheating (submerged arcing) time, minimise refractory erosion and increase the efficiency of energy consumption a large capacity transformer and argon stirring with bottom porous plug at a flow rate of about 0.33 m^3/min, is used .

2. For high heating efficiency with a stable submerged arc and low refractory erosion, the thickness of the slag layer should be about 1.3 * arc length. The calculated arc length and electric power of arc are shown Figure 2.10 [9] .

3. With the tap voltage of 385 to 435 V and secondary current 40 to 50 kA the liquid steel temperature is raised at the rate of 3.5 to 4.5 °C /min.

After arc reheating and trim additions for composition adjustment, the rate of argon bubbling should be reduced to a low level of 0.10 m^3 / min. to float out the residual deoxidation and reoxidation products known as inclusions.
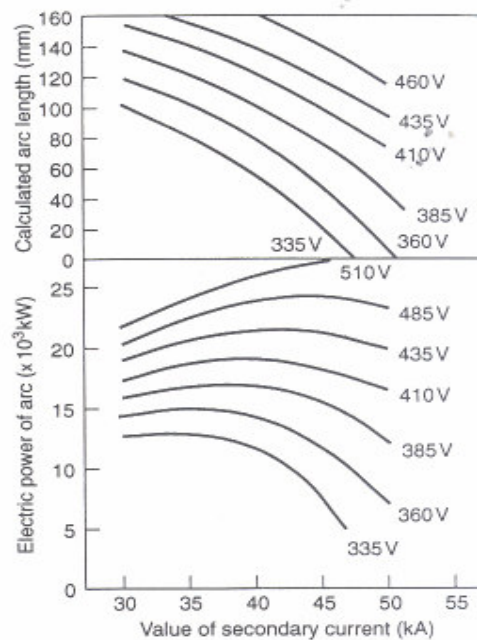
Figure 2.10 Calculated arc lengths and electric power of arc [9] .

2.4.3 Erdemir Steelmaking Plant Secondary Steelmaking Process

In Erdemir Steelmaking Plant there exists three Basic Oxygen Furnaces (BOF), two ladle furnaces and one recirculating type (RH-KTB) vacuum chamber. The process steps for low carbon steel are shown in Figure 2.11. The vacuum degasser is used to produce ultra low carbon steel grades and it is shown in Figure 2.12.

TAPPING FROM
CONVERTER TO
LADLE

ADDITIONS
- Aluminum (Deox. +
Alloying)
- Flux (CaO)
- Carry-Over Slag

LADLE FURNACE
- ARC HEATING OF
STEEL
- SLAG REFINING
- ALLOYING

-3 min. arc heating
for
homogenisation
-Initial Slag
Sampling

- FINAL SLAG
SAMPLING
- END OF
LADLE
TREATMENT

CASTING
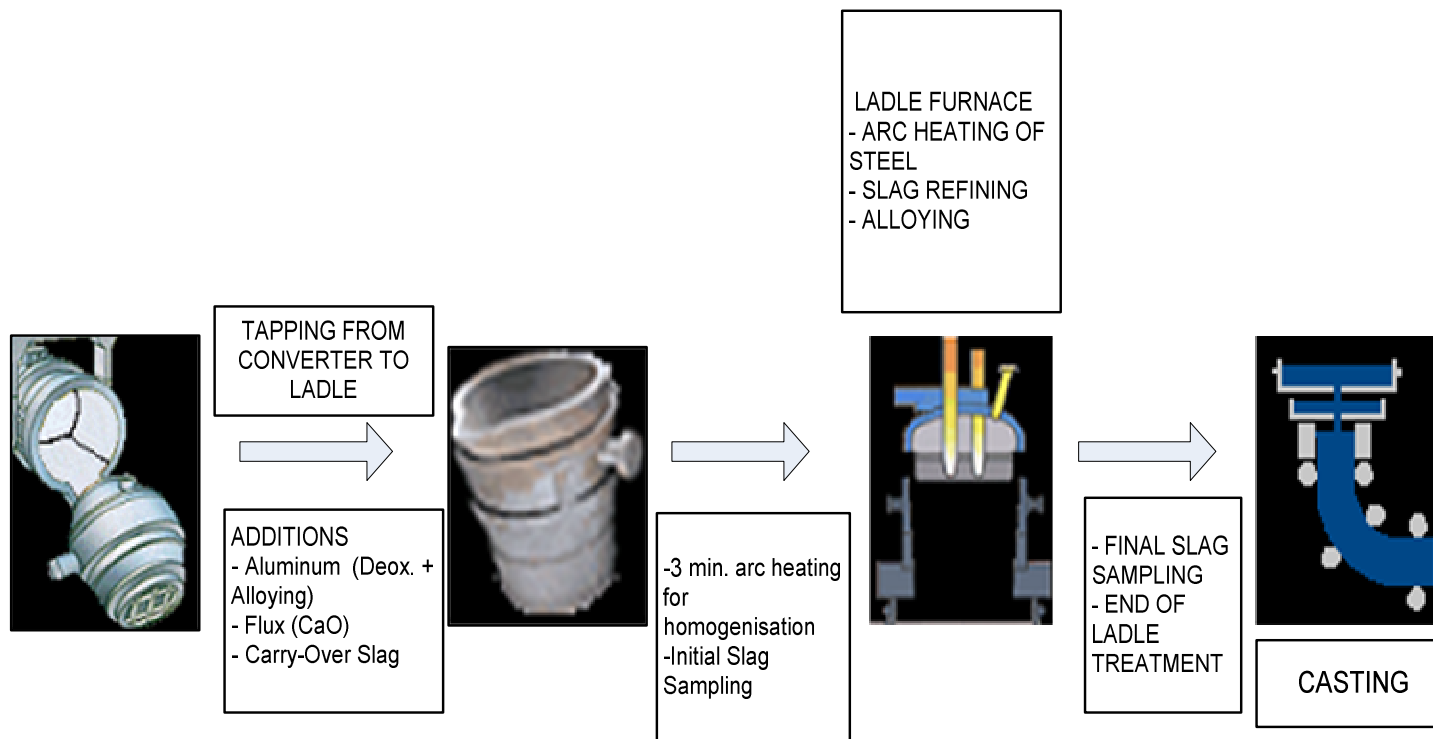
Figure 2.11 Erdemir Steelmaking Process Steps for Low Carbon Steel Production
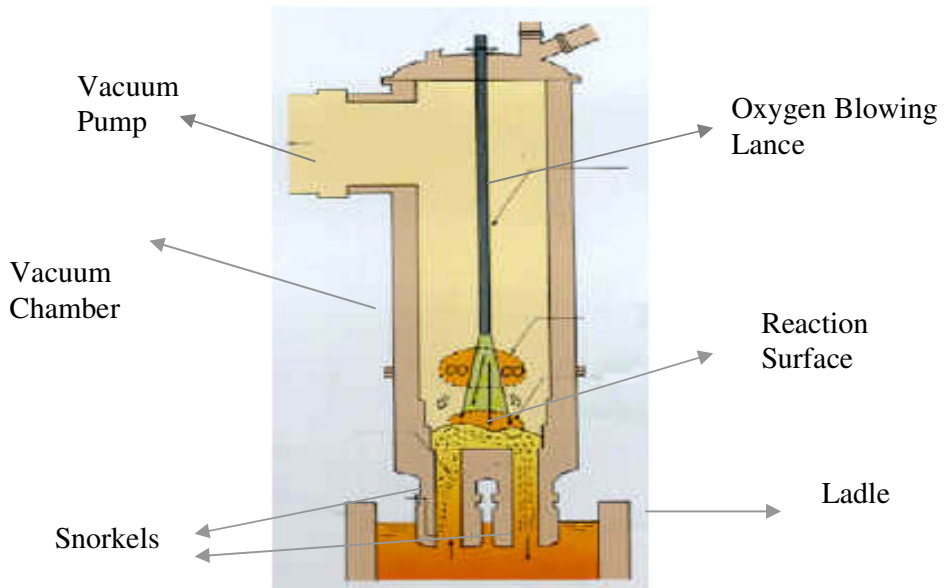
Figure 2.12 RH-KTB Type Vacuum Degasser

Typical properties of the ladle furnace are given in Table 2.1.

Table 2.1 Properties of Erdemir Ladle Furnace

Power	18 MVA
Primary Voltage	13.8 KV
Secondary Voltage	331 V
Secondary Current	38 KA
Electrode Diameter	500 mm.
Heating Rate	3-5 ° C / min

2.4.4   Slags for Ladle Treatment and Refining of Steel

Slags of certain type play an important role in the ladle treatment of steel, particularly in the production of killed steel low in residual concentration of oxygen and sulphur. The deoxidation of steel with aluminium to low levels of oxygen can be greatly enhanced by adding burnt lime together with aluminium so that the reaction product would be lime saturated liquid calcium aluminate. The fluxing of the reaction product alumina with lime is facilitated by also adding some fluorspar together with lime. Such a ladle treatment also brings about some removal of sulphur from the steel. In fact, lime and aluminium are considered to be the two essential ingredients of the ladle additions for effective deoxidation and desulphurization of the steel [8].

Also since steel refining and continuous casting operations control steel cleanliness, inclusion removal capacity of slag is important in terms of these parameters. Systematic studies show that ladle treatment lower inclusions by 65-75 %, the tundish removes inclusions by 20-25%, and, although some reoxidation occurs the mould removes 5-10 % of the inclusions. Thus ladle operations are particularly important and include control of tap oxygen, reducible oxide amount (Fe_tO and MnO) in the slag and ladle stirring [8].

2.4.4.1 Desulphurization in the Ladle Furnace

The basic chemical reaction describing the thermodynamics of desulphurization with synthetic slags can be written as:

$$3(CaO) + 2[Al] + 3[S] = 3(CaS) + (Al_2O_3) \tag{41}$$

The Al and S are dissolved in the metal and the CaO, Al_2O_3 and CaS are in the slag. From thermodynamics it is shown that [13] the quantity $(S) / [S] [Al]^{2/3}$ is

28

function of slag composition only and the slag that gives the highest value of this parameter is the optimum slag for the process. In ladle furnace tests it is found that [13] the best slag is one containing 10%SiO_2, 30%Al_2O_3, and 60%CaO. CaF_2 additions are beneficial for several reasons. It increases the sulphide capacity of the slag, the fluidity of slag, and the amount of CaO that can be dissolved in the liquid slag.

Also presence of unstable oxides (FeO+MnO) in ladle slag can reduce desulphurization capacity of slags significantly as it is shown in Figure 2.13.
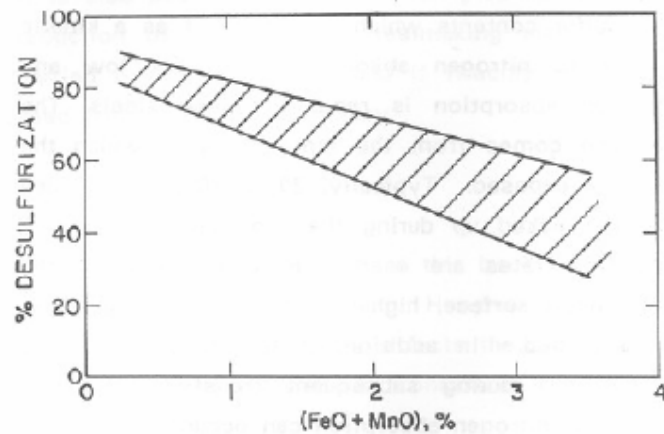
Figure 2.13 Effect of Unstable Oxides (FeO + MnO) in the Ladle Slag on Desulphurization

In order to evaluate the influence of the FeO content in the slag on desulphurization and aluminium loss, a parameter study is made by Andersson et al. [1] for three different slag compositions where the initial FeO contents in the slag were 0, 2 and 6%. The different initial slag compositions in the study are specified in Table 2.2.

29

Table 2.2 Initial Slag Compositions (wt%) Used in the Study by Andersson et al. [1]

FeO	Al$_2$O$_3$	CaO	MgO	MnO	SiO$_2$	S
0	29·0	50·0	9·2	0·0	11·2	0·5
2	28·4	48·9	9	0·2	11·0	0·5
6	27·2	46·9	8·6	0·2	10·5	0·5

Figure 2.14 shows the influence of different initial contents of FeO in the top slag on desulphurization at an isothermal temperature of 1600ºC. At 0% FeO, the average sulphur content decreased from 0.023 to 0.013% within 10 min. When the initial FeO content increased, the desulphurization rate decreased. At 2% initial FeO, the average sulphur content was 0.015% after 10 min treatment. When the initial FeO content was increased even further to 6%, the average sulphur content was 0.020 % after 10 min.
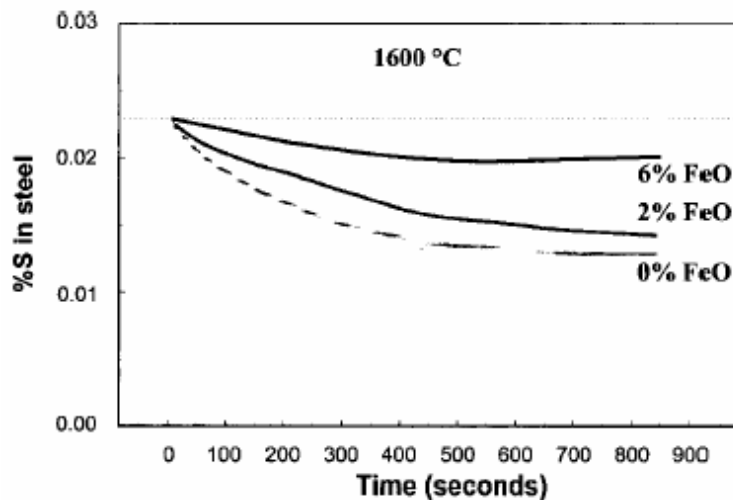
Figure 2.14. Influence of Different FeO Contents in Top Slag on Desulphurization (heat size 100 tons., isothermal temperature 1600ºC) [1]

30

2.4.4.2. Reoxidation

Once the steel has been properly deoxidized, care should be taken to avoid reoxidation. There are many problems concerning steel cleanliness and castability caused by reoxidation.

Reoxidation increases; the oxygen content of the steel bath, contributes towards new groups of oxide inclusions, reduces deoxidant efficiency and increases the opportunity for nozzle blockage at the caster. It can occur both during and after deoxidation and the main oxygen sources are; air entrainment, oxygen containing ladle slag, refractory lining and ladle glaze or bottom slag that results from earlier heats in the ladle. It can be particularly prevalent during intensive ladle stirring when a slag-free eye can open-up and expose the steel surface directly to the atmosphere. [7,12,13]

When the ladle top slag contains high level of reducible oxides (particularly FeO and MnO), then oxygen transfer from slag to steel can be a principal source of reoxidation, especially during ladle stirring. This situation often arises when a significant amount of tapping slag is carried over into the ladle. [4,5]

2.4.4.3. Effect of Tap Oxygen on Steel Cleanliness

Tap oxygen content is measured during tapping the molten steel in ladle from BOF or before deoxidant addition. The tap oxygen content is typically high, ranging from 450–1000 ppm for most of the basic oxygen furnaces. Aluminium additions to deoxidize the melt create large amounts of Al_2O_3 inclusions. This suggests that a limitation on tap oxygen content should be imposed for clean steel grades. However, as shown in Fig. 2.15 [8], there is no correlation between tap oxygen and steel cleanliness (given here as final total oxygen content of steel in tundish). This is consistent with claims that 85% of the alumina clusters formed after large aluminium additions readily float out to the ladle slag, and that the remaining clusters are smaller than 30μm. Naturally, the decision to ignore tap oxygen depends on the time

available to float inclusions and on the availability of ladle refining, which can remove most of the generated inclusions.
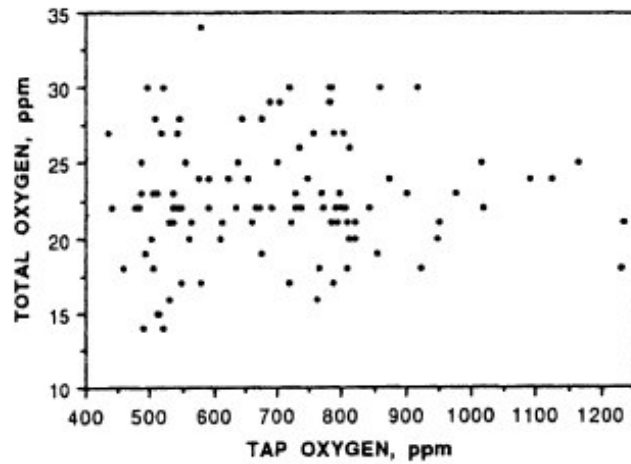
Figure 2.15. Tap Dissolved Oxygen and Final Total Oxygen in Tundish [8]

2.4.4.4.Effect of FeO and MnO in Slag on Steel Cleanliness

An important source of reoxidation is the carryover of slag from the steelmaking furnace to the ladle, which contains a high content of FeO and MnO [8].

These molten oxides react with the dissolved aluminium to generate solid alumina in the liquid steel, owing to the strong favourable thermodynamics of the following reactions:

$$3(FeO) + 2[Al] = (Al_2O_3) + 3[Fe] \tag{42}$$

$$\Delta G^\circ = -853\ 700 + 239.9T\ (J\ mol^{-1}) \tag{43}$$

$$3(MnO) + 2[Al] = (Al_2O_3) + 3[Mn] \tag{44}$$

$$\Delta G° = -337\ 700 + 1.4T \text{ (J mol}^{-1}) \tag{45}$$

The higher is the FeO and MnO content in the ladle slag, the greater is the potential for reoxidation and the corresponding generation of alumina inclusions. Many slivers in the final product have been traced to reoxidation that originated from FeO in the ladle slag [8,11]. Figure 2.16 [8]   shows how total oxide in the ladle, tundish and mould correlates roughly with the %FeO + %MnO in the ladle slag.
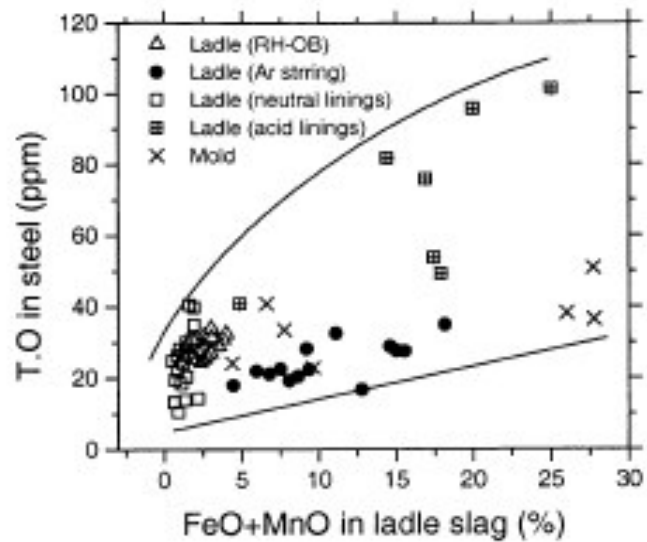
Figure 2.16. Relationship between FeO + MnO in Ladle Slag and Total Oxygen in Steel after Different Ladle Practices and in Steel in Continuous Casting Mould [8].

These slag impurities are particularly damaging when the ladle lining material is high in silica. Figure 2.17 [8] shows a similar influence on the loss of dissolved Al and the increase of tundish inclusions.

33
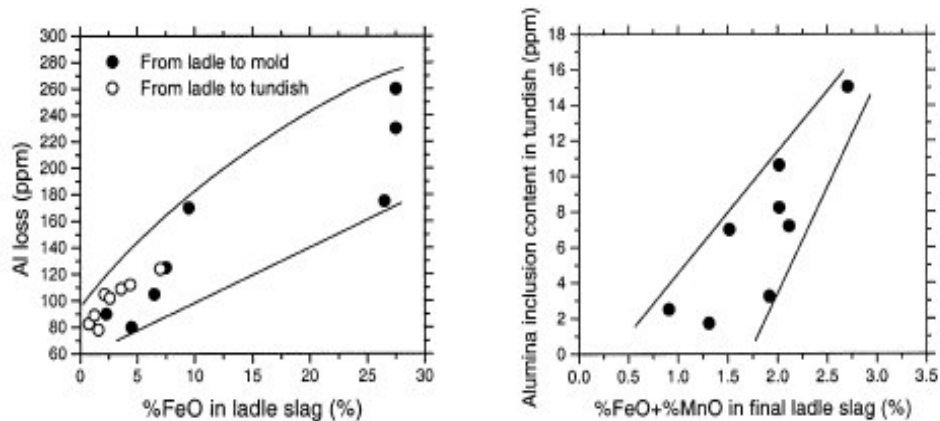
Figure 2.17 Effect of FeO + MnO Content in Ladle Slag on Increasing Dissolved Al
and so on Increasing Alumina Content of Steel [8]

Countermeasures to lower FeO and MnO contamination are summarized as
follows:

1) Minimize slag carryover from steelmaking furnace to ladle during tapping:

- Increasing aimed carbon at the end of oxygen blowing, avoiding reblows,
  thus minimizing the dissolved oxygen content in the steel, can lower the
  amount of FeO in the furnace slag.
- Use of a sublance in the BOF substantially lowers the frequency of reblows.
- An efficient slag stopper, such as a slag ball (that floats in steel and sinks in
  slag), can lower the amount of furnace slag carried over to the ladle during
  tapping to 3 kg/t steel. To improve yield, other sensors are available, which
  detect the slag after a little has been carried over. These include infra-red and
  electromagnetic systems.
- The furnace geometry and tap hole location can be designed to minimize
  vortexing and slag carryover.
- A thick ladle slag layer after tapping suggests high slag carryover problems,
  as shown in the rough relationship in Fig. 2.18. Ladle slag depth after
  skimming should be controlled to 25–40 mm.

34
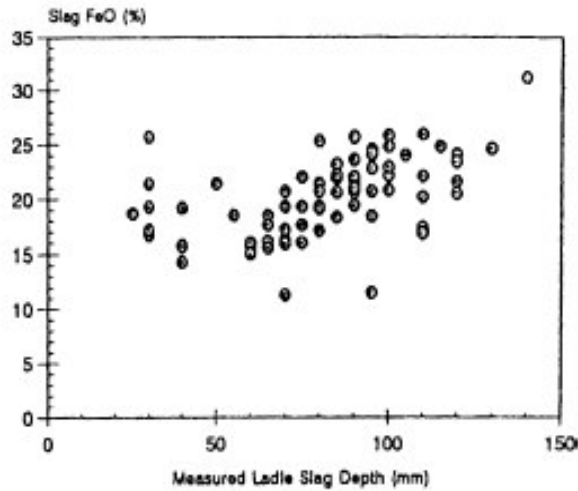
Figure 2.18 Correlation of FeO content in Ladle Slag with Ladle Slag Depth [8]

2) Use a ladle slag reduction treatment.

Another way to lower the FeO + MnO content of the ladle slag is to add a slag conditioner (*i.e.* slag reduction or deoxidation treatment), which is a mixture of aluminium and burnt lime or limestone. Table 2.3 [8] summarizes the decrease in FeO + MnO content after ladle slag reduction treatment at several steel plants. On the average, this treatment lowers FeO + MnO to below 5 %, as shown in Fig. 2.19. Minimizing slag carryover, together with adding a basic ladle slag and using a basic lining, was found to lower the ladle slag FeO + MnO content to less than 1–2%, which lowered the total oxygen in steel to 10 ppm for Low Carbon Aluminium Killed (LCAK) Steel.

Table 2.3 Effect of Ladle Slag Reduction Treatment Reported for LCAK Steel [8]

Steel Works	FeO+MnO composition in ladle slag		Year
	Before reduction treatment	After reduction treatment	
LTV Steel, Cleveland Works	FeO 3.9%, MnO 1.6 FeO 25.9%, MnO 2.9%	FeO 1.6%, MnO 0.9 FeO 4.2%, MnO 2.0%	1993 1993
Inland Steel, No.4 BOF Shop	FeO 8.1%, MnO 5.2%	FeO 2.4%, MnO 1.4%	1990
National Steel, Great Lake Div.	FeO 25%	FeO 8%, Best 2.0 %	1994
USS/Kobe Steel Company	FeO 30%	FeO 1.23%, Best 0.64%	1991
Algoma Steel, Canada		FeO 1.5%, MnO 0.8%	1999
Sollac Dunkirk, France	FeO 12-25%	FeO 2-5%	1997
Krupp Stahl AG, Bochum Steelwork		FeO + MnO %<1	1991
POSCO, Kwangyang Works, Korea	FeO + MnO 9-18%	FeO + MnO 3-5%	1998
Kawasaki Steel, Mizushima Works		FeO 2%	1996
Chian Steel, Taiwan	FeO 26.8%, MnO 4.7%	FeO 6.8%, MnO 5.5%	1996
WISCO No.3 Works, China		FeO <1%	2000
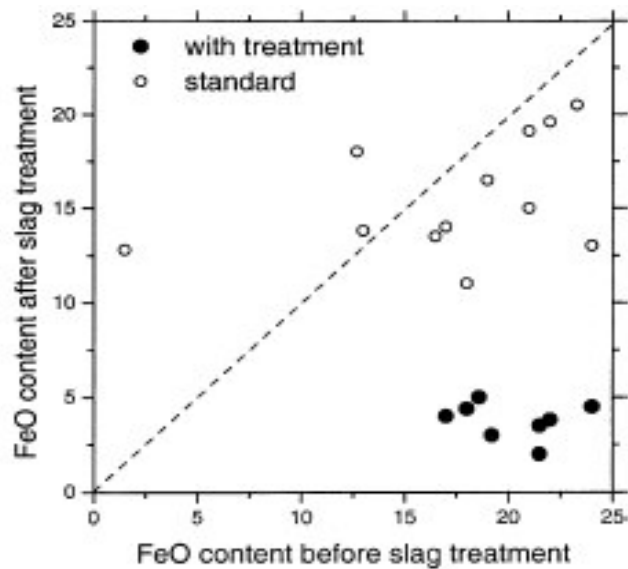
Figure 2.19. Reduction of FeO Content in Ladle Slag by Ladle Slag Reduction Treatment [8].

2.5 Aluminium Dross

Two methods are applied in the industry to manufacture aluminium products. The first one depends on the bauxite and cryolite as the main raw materials, where pure alumina (Al_2O_3) is extracted by Bayer process. The second method consists of refining, remelting, and alloying the scrap of the manufactured aluminium [14]. This process is applied in "Akdağ Aluminium" and "Şahinler Metal" company. The factory sells the coarse fraction of the dross to local enterprises which manufacture low grade aluminium wares.

Aluminium dross is formed at the surface of the molten metal due to its uncontrolled reaction with the furnace atmosphere. It may contain up to 70% free aluminium in an oxide layer. Many trials have been done all over the world to minimize the formation of dross and to recycle it in most economic ways. The chemical and phase composition of the Al-dross vary within a wide range according to the technology used for Al-metal production and recycling. The major phases detected are aluminium oxides with different crystalline forms and metallic aluminium [14,15].

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Starting Materials

As stated before the purpose of this thesis work was to decrease the amount of reducible oxides (Fe_tO+MnO) in the carry-over slag (it can not be prevented to leak during tapping of steel in the ladles) from BOF furnace by adding some aluminium dross (slag conditioner) in the ladle furnace. These reducible oxides in the slag increased the oxidation potential and so oxide content of steel. Some analytical plant data from production of Ereğli Iron and Steel Works Co. (Erdemir), were specially followed and taken for this purpose. The analytical data taken are for slags in connection with Erdemir's special low carbon aluminium killed steel grades, 7112K and 7110K; the chemical analysis of these steels are given in Table 3.1.

Table 3.1. Low-Carbon Aluminium Killed Steel Analysis*

Grade	%C	% Mn	%P	%S	%Al
7110K	0.02-0.05	0.15-0.25	0.020 max.	0.020 max.	0.020-0.060
7112K	0.02-0.04	0.10-0.20	0.015 max.	0.015 max.	0.020-0.060

*Rest of analysis can be taken as Fe, excluding Oxygen in ppm levels.

The aluminium dross is procured from Turkish Akdağ Aluminium and Şahinler Metal companies. The average composition ranges and particle size distribution of aluminium dross used are shown in Tables 3.2 and 3.3, respectively.

Table 3.2. Analysis of Al Dross

%Al$_2$O$_3$	%Al	%SiO$_2$	%Fe	%C	%K	%Mg	%Cu
55-60	30-35	5-10	0.5-1.0	0.10-0.20	0.5-1.0	0.5-1.0	0.10-0.20

Table 3.3 Particle Size Distribution of Al-Dross

Size	<0.5 mm.	0.5-30 mm	>30 mm
Weight %	4.8	91.1	4.1

3.2 Outline of Experimental Procedure

In Erdemir Steelmaking Shop, primary steelmaking starts with oxygen blowing in basic oxygen furnaces (converters). For characterizing of converter slag, while taking steel samples for usual process practice, slag samples are also taken with a 2.5 m steel rod from the contact surface of liquid steel with slag just after the oxygen blowing.

For the production of low-carbon aluminium killed steel usual practice followed the sequence given below, after steel composition was determined:

- Steel was tapped from converter to a ladle and during tapping period (4-6 minutes) aluminium bar addition (changes with dissolved oxygen amount) to kill the steel and 600 kg of burnt lime addition was done to the escaped (carry-over) converter slag.

- Ladle with 120 tons of liquid steel was brought to ladle furnace station with crane. Before taking initial steel and slag samples, steel was heated for 3 min. by arc-heating and bottom-stirred with argon (0.33 m^3/min).

- After this pre-treatment process, steel samples with a spoon, and slag samples with a steel rod from contact surface, were taken.

- After obtaining initial steel composition, determined by spectometer instantly , according to aimed time for sending treated steel to continuous casting, heating and alloying was done at the ladle furnace to set the chemical composition of steel in a narrow specification range. Just before sending the ladle from ladle treatment station to continuous casting plant, final steel and slag samples were taken in the same way initial samples were taken.

3.3 Slag Sample Preparation

As it was explained in part 3.2 slag samples were collected with a steel rod and prepared for analysing in XRF Spectrometer. Slag sample preparing procedure was made up of the following steps:

- Representative slag pieces (3-4 cm.) were collected from the surface of the steel rod.
- These slag samples were crushed and ground with a grinding mill to 100 microns.
- Metallic iron which remained suspended in slag was seperated with a magnet.
- Ground slag particles were pressed into cylindrical pellets in a hydraulic press under 100 kN.

3.4. Reducible Oxides

As it was explained in literature review section, Fe_tO and MnO were the main reducible oxides in ladle slag which affected adversely the desulphurization capacity of slag and internal cleanliness of steel. Besides these oxides, SiO_2 and P_2O_5 which formed during primary oxygen steelmaking process, also leaked with carry-over slag from converters during tapping; these can be also reduced by dissolved aluminium during ladle treatment. In Erdemir Steelmaking Plant, there were two alternative converter slag stoppage systems (magnetic wave system and thermal camera) and amount of carry-over slag which escaped to ladle was kept between 264 kg. and 1143 kg. . For the carry-over slag with such an amount, reduction of SiO_2 and P_2O_5 were also determined according to initial and final ladle slag analysis. For 7112K and 7110K steel grades, average initial SiO_2 and P_2O_5 contents of ladle slag were 4.96% and 0.37%, respectively. For 80 trial heats, differences in P_2O_5 and SiO_2 percentages during ladle treatment are shown in Figure 3.1.
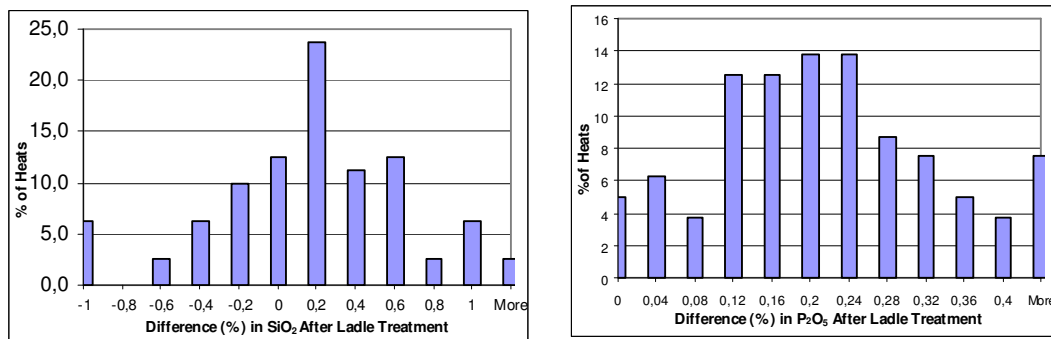
Figure 3.1 Difference in SiO_2 and P_2O_5 content of ladle slag after ladle treatment

According to these results, during secondary steelmaking process, in low carbon aluminium killed steel grades, on the average 0.10% of SiO_2 and 0.17% of P_2O_5 were reduced by aluminium. Therefore, under Erdemir Steelmaking Plant

process conditions, reduction of SiO_2 and P_2O_5 could be neglected and for this study Fe_tO and MnO were taken into account as reducible oxides.

3.4 Experimental Parameters

Parameters affecting the final reducible oxide amount of the ladle slag were determined before trial heats were carried out. These were as follows:

- Initial (Fe_tO+ MnO) % of ladle slag, that increases with increasing amount of carry-over slag.
- Slag reducing agent amount (Al-dross).
- Reaction duration (ladle treatment duration which was until ladle were sent to caster).
- Similar slag analysis data collected without using Al-dross; this was necessary to see the difference when Al-dross was not used.

After the effect of these parameters were determined in this way, the relation of this slag reducing practice to the reoxidation during continuous casting process, was clarified. Using the data obtained for reoxidation of aluminium in steel (soluble aluminium fade) as function of reducible oxide (Fe_tO + MnO) amount in ladle slag, a correlation was obtained.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Basic Oxygen Furnace Slag Chemistry

In Table 4.1, basic oxygen furnace slag analyses of low carbon aluminium killed (LCAK) steel grades are given. The CaO and SiO_2 analyses data of Erdemir converter slags given in this table are represented as block diagrams in Figure 4.1. From this figure, within limits, the average values of %CaO and %SiO_2 in the converter slag were determined as 49.6 and 10.7, respectively. When the basicity (B= %CaO/%SiO_2) of slag in equilibrium with liquid steel is between 2 and 4, it is known that the ratio of %Fe_2O_3/%FeO is less than 0.05 [2,3]. However, calculated average basicity of Erdemir converter slag was 4.6 and so it was out of the range 2-4; therefore, the ratio of %Fe_2O_3/%FeO was not known exactly for this basicity. In any case, the ratio of 4.6 was not much out of the given range, so, iron oxide was taken entirely as FeO and Fe_tO + MnO was used to represent the total reducible oxides. Of course, metallic iron is excluded from the total iron analysed by X-Ray Fluorescence.

Using the data given in Table 4.1, Fe_tO and MnO contents of Erdemir converter slags are drawn as block diagrams in Figure 4.2. It was seen that average percentages of Fe_tO and MnO in converter slags were 26.66 and 3.76, respectively.

Table 4.1. Analyses of Basic Oxygen Furnace Slag for LCAK Steels (%)

No of Heat	Fe$_t$O	SiO$_2$	MnO	Al$_2$O$_3$	CaO	MgO	P$_2$O$_5$	S	Na$_2$O	K$_2$O	TiO$_2$	Cr$_2$O$_3$
1	29.34	9.72	4.73	1.29	45.44	7.32	1.407	0.048	0.001	0.008	0.271	0.273
2	25.34	10.52	3.66	0.57	54.08	2.38	1.448	0.016	0.001	0.003	0.253	0.132
3	23.60	10.63	3.68	0.72	53.48	6.94	1.214	0.024	0.001	0.018	0.249	0.129
4	27.20	10.23	3.34	0.92	50.87	6.11	1.174	0.386	0.001	0.015	0.129	0.148
5	39.92	6.99	2.52	0.99	44.65	4.43	0.835	0.076	0.001	0.012	0.154	0.156
6	25.33	11.37	3.90	1.42	49.06	8.18	1.306	0.036	0.001	0.020	0.350	0.127
7	26.49	8.36	3.81	0.83	54.73	2.65	1.305	0.013	0.001	0.008	0.242	0.125
8	27.76	11.06	3.02	1.28	49.58	6.87	1.308	0.095	0.001	0.011	0.145	0.141
9	28.88	10.49	4.01	0.90	48.34	6.37	1.100	0.082	0.001	0.014	0.336	0.135
10	25.54	12.06	3.68	0.94	49.92	7.61	1.324	0.112	0.001	0.010	0.245	0.146
11	31.58	11.31	5.35	2.09	42.08	6.43	1.311	0.301	0.002	0.020	0.365	0.244
12	27.62	12.18	3.86	1.30	48.77	3.79	1.217	0.055	0.001	0.007	0.312	0.206
13	29.32	9.61	4.07	0.96	47.13	8.00	1.266	0.029	0.001	0.013	0.290	0.152
14	24.81	11.52	3.21	1.05	51.05	7.50	1.411	0.070	0.001	0.010	0.239	0.181
15	23.26	9.48	3.73	0.67	57.13	2.66	1.642	0.014	0.001	0.004	0.219	0.144
16	21.70	10.71	3.59	1.09	54.70	6.99	1.290	0.040	0.001	0.009	0.314	0.093
17	30.17	9.89	4.76	1.05	44.73	8.01	1.676	0.025	0.001	0.012	0.194	0.193
18	26.88	7.55	3.47	0.67	53.80	5.82	1.329	0.044	0.001	0.007	0.196	0.137
19	27.32	9.61	3.33	2.35	46.68	7.98	0.825	0.353	0.001	0.033	0.216	0.071
20	31.08	10.95	3.39	0.48	47.91	4.36	1.188	0.041	0.001	0.008	0.325	0.220
21	25.81	11.89	3.46	0.90	52.30	2.16	1.367	0.025	0.001	0.006	0.294	0.142
22	24.12	9.89	3.61	0.56	56.30	1.40	1.596	0.001	0.001	0.005	0.234	0.122
23	22.41	13.88	3.18	0.66	50.87	7.72	1.432	0.095	0.001	0.012	0.272	0.107
24	25.29	12.17	3.59	1.12	48.25	7.93	1.347	0.016	0.001	0.016	0.239	0.124
25	22.70	10.67	3.05	1.56	56.37	6.26	1.220	0.048	0.001	0.034	0.165	0.081
26	26.05	8.73	4.50	0.91	51.06	6.03	1.432	0.051	0.001	0.013	0.211	0.152
27	27.69	12.17	4.22	1.04	46.06	8.06	1.386	0.039	0.001	0.012	0.254	0.172
28	26.34	10.80	2.89	1.24	50.91	6.41	1.278	0.075	0.001	0.007	0.180	0.141
29	36.56	7.75	4.28	0.97	42.40	6.40	1.362	0.060	0.001	0.008	0.259	0.180
30	26.49	7.95	4.00	1.08	51.70	0.89	1.116	0.062	0.001	0.009	0.180	0.137
31	25.60	9.68	4.03	3.30	45.52	9.98	0.921	0.282	0.001	0.048	0.179	0.102
32	23.29	11.78	3.10	0.58	42.75	4.22	1.022	0.018	0.001	0.008	0.235	0.161
33	31.03	10.50	4.06	1.03	45.28	6.96	1.465	0.032	0.001	0.019	0.236	0.174
34	22.84	13.02	3.80	1.83	49.89	7.40	1.407	0.073	0.001	0.012	0.348	0.200
35	24.95	11.42	5.67	1.03	46.20	8.66	1.761	0.004	0.001	0.010	0.386	0.159
36	20.83	10.83	2.93	0.77	57.94	5.83	1.247	0.023	0.001	0.014	0.191	0.112
37	27.07	12.09	3.32	0.90	48.50	6.18	1.351	0.033	0.001	0.010	0.195	0.123
38	25.96	12.56	4.50	0.99	46.32	8.53	1.368	0.024	0.001	0.016	0.417	0.170
39	32.47	8.76	3.73	0.94	44.97	7.02	1.399	0.058	0.001	0.013	0.203	0.230
40	20.74	13.01	3.55	1.12	55.45	2.48	1.565	0.012	0.001	0.006	0.298	0.107
41	23.00	13.33	3.85	1.75	51.05	3.55	1.416	0.032	0.001	0.008	0.299	0.145
42	27.82	13.04	3.12	1.82	48.08	4.67	1.132	0.062	0.001	0.023	0.263	0.333

Table 4.1(Continued) Analyses of Basic Oxygen Furnace Slag for LCAK Steels (%)

No of Heat	Fe$_t$O	SiO$_2$	MnO	Al$_2$O$_3$	CaO	MgO	P$_2$O$_5$	S	Na$_2$O	K$_2$O	TiO$_2$	Cr$_2$O$_3$
43	27.33	9.46	4.67	1.26	48.13	8.99	1.169	0.012	0.001	0.013	0.230	0.185
44	28.22	10.41	3.67	1.11	47.89	7.44	1.314	0.044	0.001	0.012	0.213	0.174
45	29.72	8.09	3.25	1.27	49.91	5.83	0.986	0.073	0.001	0.010	0.240	0.167
46	20.48	14.73	4.45	1.50	52.17	3.49	1.670	0.004	0.001	0.008	0.415	0.128
47	23.06	12.08	3.94	1.41	53.09	3.08	1.327	0.102	0.001	0.010	0.363	0.198
48	27.62	10.09	3.79	1.52	47.52	8.17	1.342	0.041	0.001	0.009	0.232	0.208
49	24.83	11.20	3.49	1.22	50.82	7.78	1.155	0.042	0.001	0.013	0.272	0.156
50	30.05	8.61	3.37	1.02	48.09	6.82	1.055	0.095	0.001	0.009	0.255	0.142
Avg.	**26.67**	**10.70**	**3.76**	**1.16**	**49.60**	**6.01**	**1.30**	**0.07**	**0.00**	**0.01**	**0.26**	**0.16**
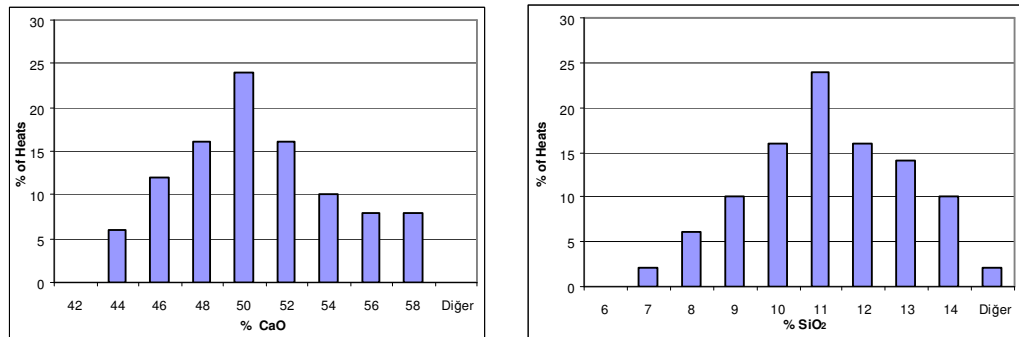
Figure 4.1 CaO and SiO$_2$ contents of Erdemir BOF Slag
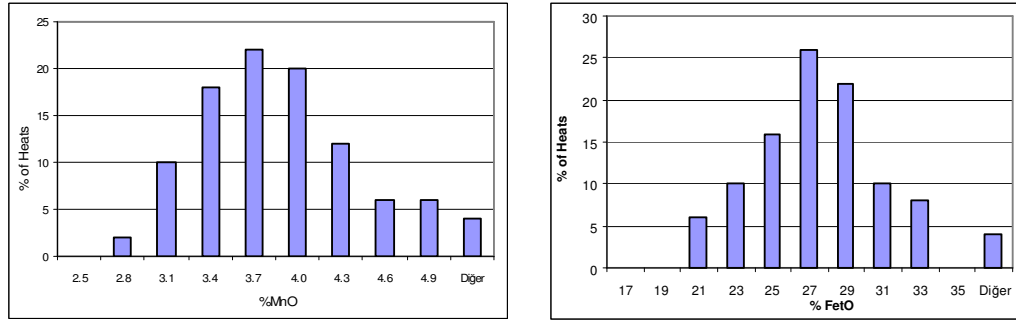
Figure 4.2 Fe$_t$O and MnO contents of Erdemir BOF Slag

.

4.2 Carry-over Slag Weight

After the primary oxygen steelmaking process, when ladle was ready for secondary treatment process, slag contained 5 main ingredients. These were:

- Burnt Lime as flux (98 % CaO): 600 kg. for every heat.
- Al$_2$O$_3$ formed during tapping by aluminium bar addition.
- Ladle slag remained from previous heat.
- Carry-over slag from converter.
- Eroded refractory from ladle walls.

To find the quantity of carry-over slag following equation was written:

$$W_s^t = W_f + W_s^{Al_2O_3} + W_s^l + W_s^c + W_s^r \tag{46}$$

where,

W_s^t :   total weight of slag, kg

W_f :   weight of flux (burnt lime) added during tapping, kg .

$W_s^{Al_2O_3}$: weight of alumina formed after deoxidation, kg .

W_s^l :   weight of slag remained from previous heat, kg .

W_s^c :   weight of carry-over slag tapped from converter, kg .

W_s^r :   weight of refractory eroded from ladle lining, kg .

Then,

$$W_s^c = W_s^t - W_f - W_s^{Al_2O_3} - W_s^l - W_s^r \qquad (47)$$

In order to find the total weight of slag (W_s^t), below formula for initial alumina content of slag after tapping steel from converter, was used:

$$\%(Al_2O_3)_i = [\,[W_s^{Al_2O_3}] + (W_s^l * (\%Al_2O_3)_a /100)] / W_s^t \qquad (48)$$

where,

$$W_s^{Al_2O_3} = [(W_{Al}^t - W_{Al}^a) * M_{Al_2O_3} / 2M_{Al}]$$

and,

     W_{Al}^t : weight of aluminium bar added during tapping from converter, kg .

     W_{Al}^a : weight of aluminium that dissolved in liquid steel (from initial steel analysis at the ladle furnace)

     $M_{Al_2O_3}$: molecular weight of Al_2O_3

     M_{Al} : atomic weight of Al

     $(\%Al_2O_3)_a$: average final (Al_2O_3) content in ladle slag after ladle treatment.

     $(\%Al_2O_3)_a$ was taken as 26%, which was the average of experimental results given in Table 4.2, and since W_s^l can not be calculated, this value was taken as 100 kg . Also, since the weight difference between new-lined ladle and a ladle that made 75 heats was 7500 kg (average value), W_s^r was taken as 100 kg for every heat. The results of calculations done using the formula given above are given in Table 4.2.

Table 4.2. Calculated Weight of Carry-over Slag Using Experimental Data

W_{Al}^{t} (kg)	% $(Al_2O_3)_i$	%Al	W_{Al}^{a} (kg)	$W_s^{Al_2O_3}$ (kg)	W_s^{t} (kg)	W_s^{c} (kg)
175	16.49	0.062	74	319	2091	946
220	21.15	0.017	20	412	2073	834
200	21.53	0.032	38	372	1847	650
220	23.04	0.033	40	409	1889	654
215	19.5	0.045	54	398	2172	949
210	18.86	0.053	64	387	2188	975
210	20.65	0.068	82	384	1985	775
200	18.91	0.056	67	367	2079	886
200	23.41	0.022	26	374	1707	507
230	27.26	0.002	2	434	1688	428
220	26.75	0.011	13	413	1643	403
180	18.77	0.036	43	333	1914	754
200	24.51	0.045	54	369	1613	417
225	21.01	0.032	38	419	2118	873
220	28.52	0.016	19	413	1538	299
200	22.34	0.024	29	373	1787	588
220	22.81	0.026	31	411	1914	678
245	25.28	0.011	13	461	1925	639
175	24.16	0.029	35	325	1453	302
210	27.97	0.05	60	387	1477	264
240	28.59	0.004	5	453	1674	395
230	18.86	0.066	79	422	2375	1127
200	25.55	0.041	49	370	1550	354
210	25.58	0.058	70	386	1610	398
190	19.82	0.028	34	354	1915	736
200	22.47	0.026	31	373	1775	576
200	20.28	0.029	35	372	1964	766
235	27.93	0.02	24	440	1669	403
240	23.99	0.053	64	443	1956	687
230	25.11	0.017	20	431	1821	564
235	30.23	0.016	19	441	1544	278
220	22.06	0.043	52	407	1965	731
180	20.02	0.005	6	339	1823	658
200	24.79	0.027	32	373	1608	410
220	23.57	0.036	43	409	1845	610
200	25.74	0.009	11	376	1562	360
210	20.85	0.033	40	390	1997	781
210	21.31	0.045	54	388	1944	729
170	15.52	0.025	30	316	2206	1064
220	19.72	0.04	48	408	2201	967

Table 4.2.(Continued) Calculated Weight of Carry-over Slag Using Experimental Data

W_{Al}^t (kg)	% $(Al_2O_3)_i$	%Al	W_{Al}^a (kg)	$W_s^{Al_2O_3}$ (kg)	W_s^t (kg)	W_s^c (kg)
220	18.17	0.048	58	406	2380	1148
225	29.14	0.032	38	419	1527	282
210	23.22	0.06	72	385	1771	560
230	28.3	0.015	18	432	1617	359
230	20.99	0.02	24	431	2176	919
220	24.78	0.045	54	407	1748	515
220	20.24	0.037	44	409	2147	913
230	21.16	0.022	26	430	2156	900
240	28.05	0.003	4	453	1707	428
230	21.69	0.068	82	422	2064	816
200	24.23	0.022	26	374	1649	450
220	22.04	0.033	40	409	1975	740
240	27.48	0.038	46	446	1718	446
200	23.21	0.024	29	373	1720	521
200	22.45	0.028	34	372	1775	577
220	21.67	0.041	49	408	2002	768
200	18.97	0.038	46	371	2091	894
200	20.94	0.078	94	363	1858	669
190	20.52	0.018	22	355	1859	678
200	23.04	0.033	40	372	1725	528
200	27.19	0.008	10	376	1479	277
210	25.13	0.023	28	392	1665	446
210	20.11	0.042	50	389	2062	848
210	19.33	0.047	56	388	2141	927
220	18.67	0.049	59	406	2315	1083
220	23.74	0.051	61	406	1819	587
225	21.77	0.032	38	419	2044	799
225	25.08	0.035	42	418	1772	527
200	22.69	0.038	46	371	1748	551
200	17.02	0.057	68	367	2309	1116
220	21.8	0.023	28	411	2006	768
220	20.52	0.032	38	410	2122	887
180	24.08	0.024	29	335	1501	340
212	*23*	*0.034*	*40*	*394*	*1873*	*653*

As it can be seen from Table 4.2 carry-over slag amount changed between 264 kg and 1148 kg. The possible reasons for this can be listed as:

- Erosion in tapping hole of the converter
- Variation in converter slag viscosity
- Difference between operator experiences.

4.3 Effect of Initial Slag Composition on Final Reducible Oxide Percentage

In this part of the thesis work, it was aimed to assess the data according to relationship of initial and final reducible oxide amount of ladle slag. Since the weight and composition of the carry-over slag would change, initial total reducible oxide amount of ladle slag was between 7-19 % and on the average it was taken as 13.49 %. From a standard ladle treatment process that consisted 100 kg. of aluminium dross addition and 45 minutes of average reaction time, final reducible oxide (R.O.)% in slag was analysed.

Table 4.3 Ladle Furnace Treatment Data Including Initial and Final Slag Compositions

Data No	Steel Grade	$(Fe_tO+MnO)i$ (%)	$(Fe_tO+MnO)f$ (%)	Reaction Time (min)	Al Dross Amount (kg)	W_s^c (kg.)	W_s^t (kg.)
1	7110K	8.65	6.23	42	100	547	1554
2	7112K	9.93	6.41	61	100	491	1503
3	7110K	10.31	4.12	33	100	692	1643
4	7112K	10.25	4.29	50	100	488	1470
5	7110K	10.65	6.89	66	100	433	1427
6	7112K	11.36	6.03	49	100	505	1516
7	7112K	12.10	6.96	40	100	410	1378
8	7112K	12.19	5.64	31	100	400	1366
9	7112K	12.33	4.27	44	100	410	1369
10	7112K	12.66	5.14	58	100	633	1604
11	7112K	12.65	5.55	44	100	684	1673
12	7112K	12.31	4.56	47	100	534	1508
13	7112K	13.25	4.52	43	100	679	1660
14	7112K	13.70	5.96	48	100	704	1672
15	7112K	13.91	10.02	50	100	588	1559
16	7112K	14.08	7.89	43	100	645	1681
17	7112K	14.17	8.10	37	100	664	1623
18	7112K	14.57	9.72	51	100	715	1669
19	7112K	15.07	8.09	35	100	459	1408
20	7112K	15.22	9.90	41	100	483	1457
21	7112K	15.44	7.60	68	100	810	1797
22	7112K	15.43	8.94	33	100	641	1669
23	7112K	15.42	8.76	34	100	787	1762
24	7112K	16.36	10.01	35	100	530	1501
25	7112K	16.57	12.69	46	100	262	1213
26	7112K	16.50	8.74	33	100	804	1765
27	7112K	19.19	11.07	65	100	677	1630
Avg.		**13.49**	**7.34**	**45**	**100**	**580**	**1558**

It was seen from data given in Table 4.3 that the initial reducible oxide (Fe_tO + $MnO)_1$ % in slag varied between 8-19 %, and, as initial reducible oxide percentage in slag decreased, final reducible oxide (Fe_tO + $MnO)_f$ % decreased also, which varied between 4-12 %. This relation is given graphically in Figure 4.3.

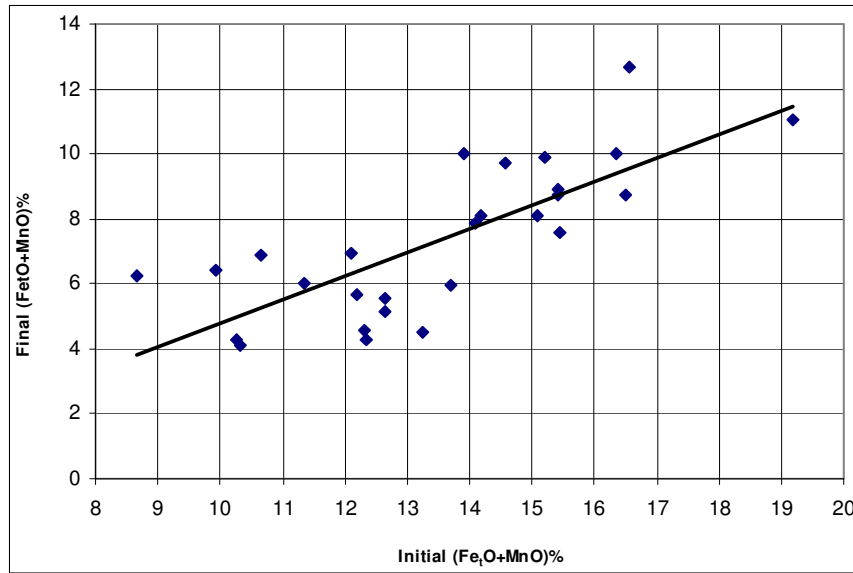**Figure 4.3.** Effect of Initial Reducible Oxide Content on Final Reducible Oxide %

For initial (Fe_tO + MnO) % =14, it decreases to 8% with 100 kg of Al dross addition. If average total ladle slag weight is taken as 1558 kg, total weight of reduced FeO and MnO is calculated as:

$$W^R_{FeO+MnO} = \Delta(FeO + MnO) * W_s^t / 100 = 93.4 \text{ kg}$$
$$W_{Al} = W^R_{FeO+MnO} *2\, M_{Al} / (3 * M_{R.O.}) = 23.5 \text{ kg}$$

$W^R_{FeO+MnO}$ = weight of (FeO + MnO) reduced after ladle treatment, kg

$\Delta(FeO + MnO)$ = difference in (FeO + MnO) after ladle treatment, %

W_{Al} = weight of aluminium used for reduction, kg

$M_{R.O.}$ = average molecular weight of R.O., kg

4.4. Effect of Reaction Duration on Final Reducible Oxide Percentage

In order to analyse the process kinetically, the treatment time at the ladle furnace was taken as a variable parameter and called 'reaction duration'. Other parameters such as initial R.O. %in slag (data taken in a narrow range of 11-14 %) and Al dross addition (100 kg) were taken constant.

The data given in Table 4.4 were used to determine the effect of reaction duration on the final reducible oxide percentage of ladle treatment slag. It was clear from these data that the longer the reaction duration, lower would be the final reducible oxide content of slag.

Table. 4.4. Data to Show the Effect of Reaction Duration

Data No	Steel Grade	$(Fe_tO+MnO)i$ %	$(Fe_tO+MnO)f$ %	Reaction Time (min)	Al Dross (kg)	W_s^c (kg.)	W_s^t (kg.)
1	7112K	13.87	9.63	27	100	463	1424
2	7112K	11.59	9.70	27	100	517	1493
3	7112K	14.38	10.22	28	100	606	1641
4	7112K	12.19	9.47	30	100	544	1500
5	7112K	12.19	5.64	31	100	400	1366
6	7112K	14.17	8.10	37	100	664	1623
7	7112K	12.11	7.12	40	100	410	1378
8	7112K	13.25	7.93	43	100	679	1660
9	7112K	14.08	7.89	43	100	645	1681
10	7112K	12.32	5.01	44	100	410	1369
11	7112K	12.65	5.55	44	100	684	1673
12	7112K	12.31	4.56	47	100	534	1508
13	7112K	13.70	5.96	48	100	704	1672
14	7112K	11.28	6.03	49	100	505	1516
15	7112K	12.66	5.14	58	100	633	1604
Avg.		*12.85*	*7.20*	*40*	*100*	*560*	*1540*

The data in Table 4.4 was used to plot Figure 4.4. It was seen from this figure that for an average ladle treatment duration of 30 minutes, the final Fe_tO + MnO % in slag was between 8 and 9, and as the duration increased to 45-50 min. the reducible oxide content of final slag decreased to 4 to 5 %.
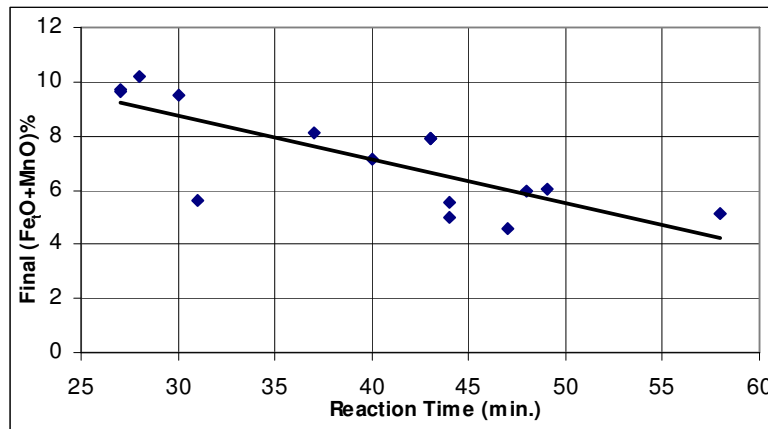

Figure 4.4 Effect Reaction Time on Final Reducible Oxide %

4.5. Effect of Aluminium Dross Amount on the Final Reducible Oxide Percentage

To understand the relation between amount of aluminium dross used and final reducible oxide content of slag after ladle treatment, similar trial heats were made with 60, 80, 100, 120 and 150 kg aluminium dross addition during ladle treatment. During these trials data taken constant were initial Fe_tO + MnO content of slag as around 12.5%, average dissolved aluminium in steel as 0.035% and average reaction duration as 35 minutes. Then, decrease in the final reducible oxide in slag was

calculated from the analysis of slag for R.O. %. The data are shown in Table 4.5 and are given graphically in Figure 4.5.

Table 4.5 Data to Show The Effect of Al Dross Amount (kg)

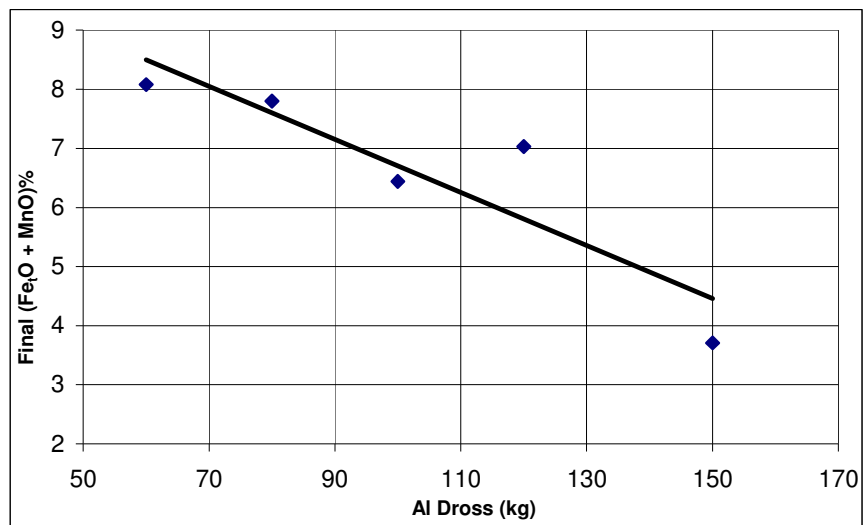| Heat No	Al Dross (kg)	Steel Grade	$(Fe_tO+MnO)i(\%)$	$(Fe_tO+MnO)f$ (%)	$\Delta(Fe_tO+MnO)$ (%)
1	60	7112K	11.99	8.08	3.91
2	80	7112K	13.09	7.80	5.29
3	100	7112K	12.74	6.44	6.30
4	120	7112K	13.52	7.03	6.49
5	150	7112K	11.57	3.71	7.86

Figure 4.5. Effect of Aluminium Dross Addition to Ladle Treatment Slag.

4.6 Slag Reduction by Dissolved Aluminium in Steel

As it was indicated before, lowering the oxidation potential of ladle slag was a reduction reaction between aluminium, and, iron and manganese oxides as given by reactions (49) and (50) below.

$$3(Fe_tO) + 2[Al] = (Al_2O_3) + 3[Fe] \tag{49}$$

$$3(MnO) + 2[Al] = (Al_2O_3) + 3[Mn] \tag{50}$$
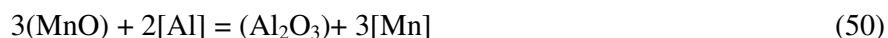
Therefore, dissolved aluminium in liquid steel would also reduce the reducible oxides in slag and in order to clarify the effect of aluminium dross usage, ten extra heats were produced without aluminium dross addition. The results are given in Table 4.6.

Table 4.6. Data for Heats With and Without Aluminium Dross Addition

Data No	Steel Grade	$(Fe_tO+MnO)i$ (%)	$(Fe_tO+MnO)f$ (%)	Reaction Time (min)	Al Dross (kg)	W_s^c (kg.)	W_s^t (kg.)
1	7112K	10.31	4.12	33	100	692	1643
2	7112K	10.76	5.40	39	100	799	1831
3	7112K	12.19	5.64	31	100	400	1366
4	7112K	12.59	4.52	26	100	309	1295
5	7112K	13.87	9.63	27	100	463	1424
6	7112K	14.17	7.96	37	100	664	1623
7	7112K	14.38	6.61	28	100	606	1641
8	7112K	15.07	8.09	35	100	459	1408
9	7112K	15.43	8.94	33	100	641	1669
10	7112K	16.36	10.01	35	100	530	1501
11	7112K	9.74	7.87	24	-	305	1384
12	7112K	13.59	9.23	36	-	385	1443
13	7112K	11.02	7.55	21	-	827	1864
14	7112K	17.81	12.12	30	-	761	1848
15	7112K	12.46	7.81	25	-	620	1762
16	7112K	9.41	6.03	32	-	595	1654
17	7112K	14.03	10.04	29	-	534	1596
18	7112K	15.98	9.94	35	-	642	1632
19	7112K	8.70	5.90	36	-	429	1495
20	7112K	16.44	12.60	27	-	565	1674

For a fixed reaction time (average 31 min.) initial and final slag compositions are obtained and differences between two cases, with and without Al-dross addition, can be seen from Figure 4.6.
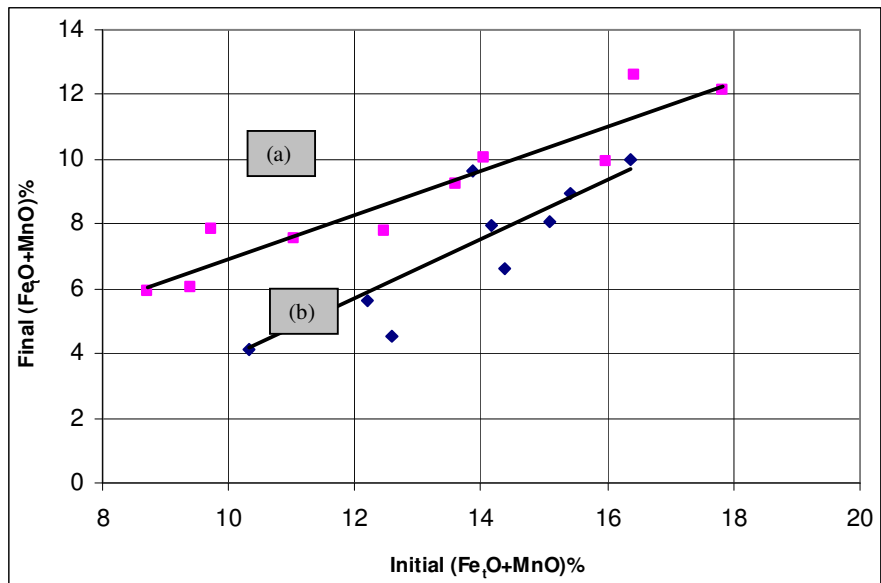

Figure 4.6 Reduction (a) without and (b) with Al Dross Addition

For an initial reducible oxide content of about 10-12 %, using 100 kg aluminium dross, after about 30 minutes of ladle treatment, it decreased to 4.5-5.0 % R.O. On the other hand, without using the aluminium dross, the reducible oxide content of slag decreased from 12% R.O. to about 7.5 %. This meant that dissolved aluminium in steel did some reduction but it was more effective by aluminium dross usage.

4.7. Effect of Final Reducible Oxide Content on Reoxidation of Steel

As explained in section 2.4.4.4, $Fe_tO + MnO$ represented the oxygen potential of slag and acted as reoxidation source for steel. To be able to see the effect of reducible oxide content of slag on reoxidation of steel, another steel grade (ultra low carbon) produced with a different process route was selected and compared with typical low carbon aluminium killed grade, according to aluminium dissolved(loss) during continuous casting. Table 4.7 gives comparison of these two grades.

Table 4.7. Comparison of Low Carbon and Ultra Low Carbon Grades of Steel

	ULC GRADES	LC GRADES
PLANT	RH-KTB	Ladle Furnace
%C	0.003-0.004	0.02-0.04
% Final R.O.	16-17	6-7
%Al	0.02-0.06	0.02-0.06
Tundish Cover	Ca-aluminate + rice hulls	Ca-aluminate + rice hulls
Other Casting Parameter	Same	Same

For ultra low carbon (ULC) aluminium killed steel production, RH-KTB type vacuum degasser is used to reach lower carbon than basic oxygen furnace and deoxidation of steel was done after vacuum treatment. It meant that reduction of slag could not be carried out because of process type and deoxidation method.

In RH-KTB plant steel was just circulating (60 ton/min), so slag-metal reaction was not so effective in this process. Also, deoxidation was carried out at the end of the vacuum degassing process rather than in BOF and naturally final average reducible oxide percentage was 16-17% while it was 6-7 % for low carbon aluminium killed steel grade which was treated with aluminium dross and which is the main topic of this thesis.

In order to see the effect of difference in between reducible oxide contents of these two different steel groups, reoxidation (or dissolved aluminium percentage in steel) during casting because of air entry from nozzles, and, oxygen sources as tundish flux and ladle slag was analysed for 1000 heats from each group. Figures 4.7 and 4.8 show the distribution of dissolved aluminium loss in Ultra-Low Carbon (ULC)and Low Carbon (LC) steels, respectively
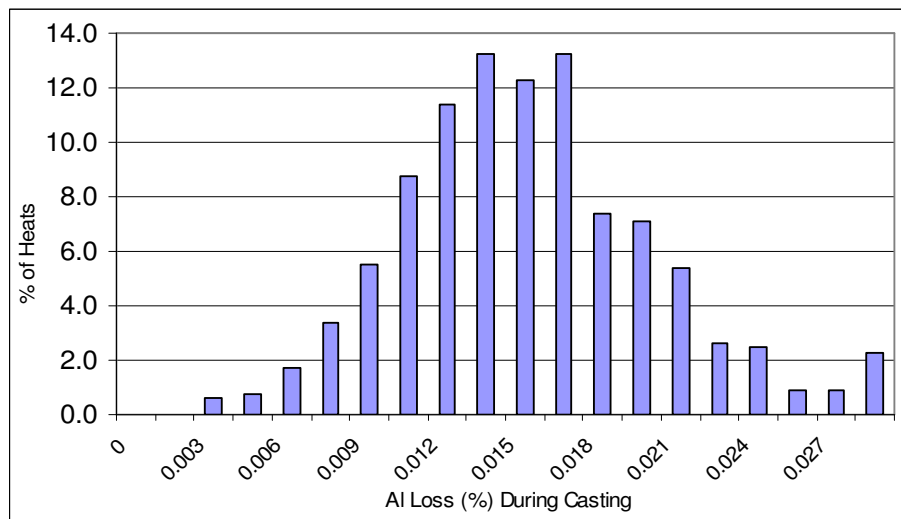

Figure 4.7. Aluminium Loss Distribution during Casting Ultra-Low Carbon Steel Grades.
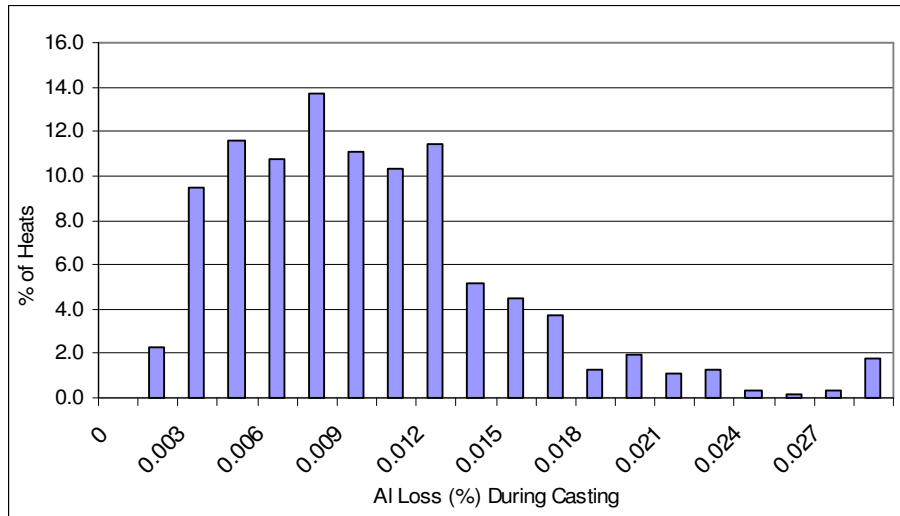
Figure 4.8. Aluminium Loss Distribution during Casting Low Carbon Steel Grades.

As it can be seen from Figures 4.7 and 4.8 average aluminium losses for ULC and LC aluminium killed steel grades were, on the average, 144 ppm. and 94 ppm., respectively. As a result, alumina content of ULC steel was being expected to be more than LC grade steel and this would affect the steel internal cleanliness, mechanical properties, and would increase the nozzle blockage frequency.

CHAPTER 5

CONCLUSIONS

The aim of this study was to investigate how the reducibility of Erdemir ladle slag changed according to certain properties by using aluminium dross as slag refiner. For this study Erdemir Steelmaking Plant Basic Oxygen Furnace and Ladle Furnace slag analysis were used. This slag was produced during production of low carbon steel containing 0.02-0.04 %C, 0.10-0.20 %Mn, 0.020 %P (max.), 0.020 %S (max.) and 0.020-0.060 %Al.

Slag samples, collected with a steel rod from slag-steel contact surface, were analysed by XRF to determine slag composition. Converter (BOF) slags were mainly composed of CaO, Fe_tO, SiO_2, MgO, MnO and P_2O_5, and, ladle slags were composed of CaO, Al_2O_3, SiO_2, MgO, Fe_tO and MnO.

For aluminium killed steel grades Fe_tO and MnO in slag represented the oxidizing capacity of ladle slag and were carried with carry-over slag of converter which leaked to ladle during tapping. The higher the Fe_tO and MnO contents (called R.O.- reducible oxides) in the ladle slag, the greater was the potential for reoxidation and the corresponding generation of alumina inclusions. Many slivers in the final product were traced to reoxidation that originated from Fe_tO and MnO in the ladle slag.

There were several factors which affected the reducing ability of aluminium dross that was tried to be used in the ladle furnace in Erdemir and these were, amount of aluminium dross, initial reducible oxide content of steelmaking slag, reaction (treatment) duration and reduction with dissolved aluminium in steel.

The amount of reducible oxides in the mentioned steelmaking slags decreased with increase in the amount of aluminium dross added. For an average of 12-13 % initial reducible oxide in slag, addition of 100 kg. aluminium dross decreased final reducible oxide in slag to 7-8 %. As the amount of initial reducible oxide content of slags increased, the final reducible oxide content of slags also increased, but the degree of reducible oxide content decrease was relatively high when the treatment was started with high reducible oxide in slag. In any case a low initial reducible content obtained during converting of steel would be preferred.

As the treatment duration in the ladle furnace increased, reaction of aluminium dross with the slag increased and so reducible oxide content of slag decreased. Comparing the heats with and without the use of aluminium dross (dissolved aluminium in steel acted as deoxidizer) showed that aluminium dross usage resulted in comperatively more decrease in reducible oxide content of ladle furnace slags.

Reoxidation of steel shown by the soluble aluminium loss (fade) during casting was higher in the ultra-low carbon steels which were not treated with aluminium dross, as compared to low-carbon aluminium killed steels which were the types considered in this work. This oxidation would promote ladle and tundish nozzle clogging, and casting problems while decreasing steel cleanliness.

REFERENCES

[1] Andersson M., Hallberg M., Jonsson L., and Jonsson P., "Slag–Metal Reactions during Ladle Treatment with Focus on Desulphurisation", Ironmaking and Steelmaking, 29(3), p. 224-232, 2002.

[2] Huh W. W., Jung W-G., "Effect of Slag Composition on Reoxidation of Aluminium Killed Steel", ISIJ International, 36(9),p136-139, 1996.

[3] Turkdogan E.T., "Rationale on Composition of Slags in Oxygen Steelmaking Processes", Iron and Steelmaking, 26(5), p.358-362, 1999.

[4] Beskow K., Sichen Du., "Ladle Glaze: Major Source of Oxide Inclusions during Ladle Treatment of Steel", Ironmaking and Steelmaking 31(5), p.393-399, 2004.

[5] Peter J., Peaslee K.D., Robertson D.G.C., Thomas B.G.,"Experimental Study of Kinetic Processes during the Steel Treatment at Two LMF's", AISTech 2005 Proceedings, Vol.1, p.959-973, 2005.

[6] Conejo A.N., Hernandez D.E., "Analysis of Aluminium Deoxidation Practice in the Ladle Furnace", AISTech 2005 Proceedings, Vol.l, p.947-957, 2005

[7] Millman M.S., "Clean Steel Fundamentals", International Iron and Steel Institute, p 1-6, 2005.

[8] Zhang L., Thomas B.G., "State of the Art in Evaluation and Control of Steel Cleanliness" . ISIJ 43 (3), p.271-291, 2003.

[9] Turkdogan E.T., "Fundamentals of Steelmaking", The Institute of Materials,p.180-259, 1996.

[10] Lankford W.T., Samways N.L., Craven R.F., McGannon H.E.,"The Making, Shaping and Treating of Steel", United States Steel, 1982.

[11] Sumida M., Nadif M., Burty M., Tusset V., "ULC and LC Steel Qualities", IISI p.365-406, 2005.

[12] Nadif M., Burty M., Soulard H., Boher M., Pusse C., Lehmann J., Ruby-Meyer F., Guiban M.A., "Reoxidation in Steel and CC Nozzle Blockage", IISI, p.87-152, 2005.

[13] Fruehan R.J., "Ladle Metallurgy Principles and Practices", Iron and Steel Society, p.21-42, 1985.

[14] Lucheva B., Tosenov Ts., Petkov R., "Non-waste Aluminium Dross Recycling" , Journal of the University of Chemical Technology and Metallurgy, p 335-338, 2005

[15] Ghorab H.Y., Rizk M., Matter A., Salama A.A., "Characterization and Recycling of Aluminium Slag", Polymer-Plastics Technology and Engineering, p.1663-1673, 2004