

A NEW PROCESS TO PRODUCE 300 SERIES STAINLESS STEEL WITH ELECTRO-SILICOTHERMIC METHOD

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ABSTRACT

During the production of austenite stainless steel, the addition of scrap, electrolytic nickel plate and ferrochrome alloy (FeCr) consumes around 70% of the total production cost in China. The present authors developed a new method to produce stainless steel using low-cost lateritic nickel ore and chromium concentrate with the aim to reduce the cost, at the same time, enhance the energy efficiency.

The present new method is mainly producing un-refined stainless steel liquid with electro-silicothermic process, which is: Ferronickel alloy with high silicon content named nickel-silicon ferroalloy will be produced in the submerged arc furnace (SAF) for the first step, then the slag containing chromium oxide and calcium oxide which come from refining furnace is charged into shaking ladle together with liquid nickel-silicon ferroalloy for pre-desilication, at last, the liquid alloy with other chromium concentrate and lime is charged into a refining furnace for finally desilication to get the un-refined stainless steel liquid. If necessary, there is a reductive dephosphorization technology before the pre-desilication process. Argon Oxygen Decarburization (AOD) or Vacuum Oxygen Decarburization (VOD) process could then be followed to produce stainless steel. The method is different from the traditional way since it takes advantage of the characteristics of low grade lateritic ore with high SiO₂ content, besides, low cost chromium concentrate was used directly. The pre-experiments have been carried out in the present laboratory and the result showed that with the nickel-silicon ferroalloy, chromium concentrate and lime as the main raw materials, it is possible to produce un-refined stainless steel liquid with electro-silicothermic process. Theoretical calculations indicated that compared to the duplex process, the total energy consumption, carbon dioxide emission and material cost in the new process are decreased by 20%, 7% and 30% respectively.

KEYWORDS: *Stainless steel, electro-silicothermic process, nickel-silicon ferroalloy, lateritic nickel ore, chromium concentrate.*

1. INTRODUCTION

During the past ten years, more than 260 million tons stainless steel (figure 1) has been produced in the world, within that, 304 stainless steel took place more than 50%. The worldwide production increased from about 20 million tons to over 30 million tons in just ten years. The growth of stainless steel consumption is the highest one within all materials in the world (ISSF, 2009). Unfortunately, its growth has been restricted by price and the resource. The cost for nickel and chromium dominates the production cost largely, for example, nickel accounts for 62% of the total production cost while chromium takes 16% cost in the production of stainless slabs (overheads excluded) [1]. This indicates that it is possible to make profitable stainless steel production by reducing the cost of nickel and chromium. There are two methods to realize it currently. One is that ferronickel replaces nickel metal as the nickel source while the other one is that chromium ore fines

are directly reduced by carbon in an extended arc flash reactor without using ferrochromium alloy, which only applies to produce 400 series stainless steel.

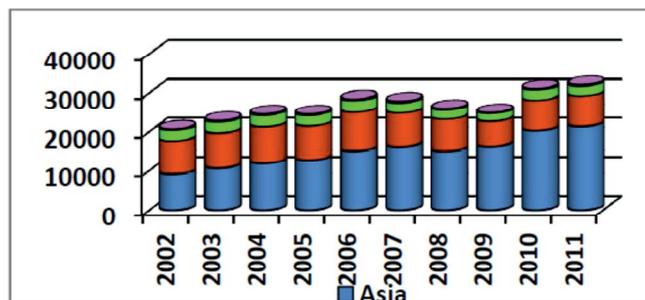


Figure 1: Crude stainless steel production during 2002-2011 (thousand metric tons, Source: ISSF 2004-2012)

Ferronickel is a ferroalloy typically containing about 70-90% iron and 10-30% nickel which could be produced by the rotary kiln - electric furnace smelting process (RKEF) from nickel laterite ores. The composition of a typical laterite ore used for ferronickel production is given in table 1 [2]. In RKEF process, raw saprolite ore is dried and fed into a rotary kiln together with a solid reducing agent (mainly coal) and the ore travels through the kiln in a co-current mode, during which, water is evaporated and the ore is partially reduced. The pre-reduced material is around 700-1000°C at the end of the process. The majority of reduction and smelting took place in a subsequent electric arc furnace (EAF). The charge is heated to 1400-1650°C in EAF to permit the separation of distinct metal and slag phases. Reduction condition and temperature are very important for the grade of ferronickel in this process. It needs to be pointed out that if the reduction condition in EAF is excessive, silica will also be reduced, then silicon content in final ferronickel will be over range. The problem stated here is common in China, hence, it is an important issue for ferronickel producers that how to reduce the silicon content in products.

Table 1: Typical composition of laterite ore for ferronickel production (mass%) [2]

Ni	Fe	Cr	SiO ₂	MgO	Al ₂ O ₃	P	H ₂ O
2.4	13.4	0.7	38.8	25.1	1.07	0.0008	28.7

Besides Ni, Cr is another important element to make stainless steel. Stainless steel production takes 90% ferrochromium consumption of the world. Over 80% of the world's known exploitable chromite resources are located in South Africa, in which, 30% is lumpy ore while 70% is fine or friable ore. The composition of chromium ore varies with the origins. Table 2 shows the typical compositions of South African chromium ore as well as the average (on an un-weighted basis) of chromium ores from a number of countries [3]. Normally, chromium concentrate is pelletized in a pelletizing drum firstly and then charged into a sintering furnace to ensure it strong enough to bear the transport and impact. This process resulted in increasing the cost and energy consumption of ferrochromium production. Hence, it has big economical benefit to use the concentrate directly.

Table 2: Composition of chromite lumpy ores from different places (mass%) [3]

	Cr ₂ O ₃ (Cr)	FeO(Fe)	SiO ₂	MgO	Al ₂ O ₃	P	Cr/Fe
South Africa	39.5 (27.0)	22.4 (17.4)	8.0	11.2	14.4	0.004	1.55
Average of other countries	42.1 (28.8)	13.8 (10.7)	8.5	17.3	12.8	0.003	2.75

As stated above, cost, energy efficiency and gas emission are important factors to influence stainless steel production. Cr and Ni are important elements to stainless steel and their production related to those three factors strongly. T.E. Norgate [4] considered that when ferronickel is used as the nickel source in the duplex process of stainless steel production, the energy consumption and greenhouse gas emission are more than the process with the nickel metal as the nickel source.

In present paper, a new process routes for stainless steel production will be stated to decrease the energy consumption, greenhouse gas emission and production cost of stainless steel and utilize laterite ore and chromium concentrate more efficiently.

2. CONVENTIONAL PROCESSES ROUTES FOR STAINLESS STEEL PRODUCTION IN CHINA

There are basically two ways to produce 300 series stainless steel in industry, which are duplex process and triplex process, shown in figure 2 and figure 3 respectively. Both these two methods show that the whole stainless steel making process contains three operation units. At the first stage, the raw materials (including scrap and ferroalloy) are melted together in an EAF to obtain un-refined stainless steel liquid. It is necessary that the compositions of molten metal meet the requirements of desired steel product approximately, except carbon content. At the second stage, the molten metal is transferred to a refining vessel (AOD or VOD), in which the impurities (especially the carbon content) would be removed to meet the requirements of final product. At the third stage, the refined liquid metal will be continuously casted into slabs.

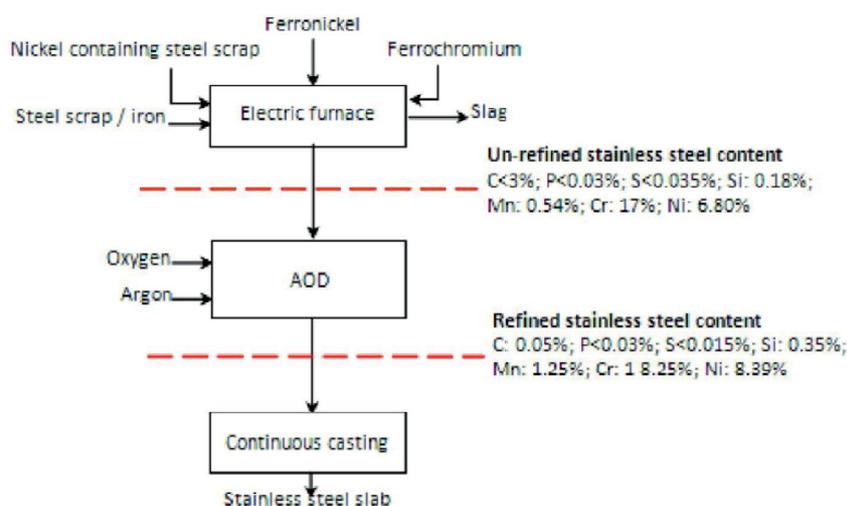


Figure 2: Duplex process for 300 series stainless steel production

At the end of the year 2002, the hot metal based process route was used at Taiyuan Iron & Steel Co. (TISCO). It includes a small EAF for producing high alloyed pre-melts which are charged together with dephosphorized hot metal in the K-OBM-S converter (figure 3). However, it must also be noted that the electric power consumption for melting raw materials such as ferronickel and ferrochromium has not been reduced, plus, the intensity of decarburization and the emission of CO₂ have not been decreased either. The developments of new process for stainless steel production must concentrate on the utilization of hot metal because large amounts of alloyed scrap are not available and electric energy is very expensive. Special materials containing Cr such as chromium ore or high carbon ferrochromium (HCFerCr) should be used and have been used to a certain extent.

The key for decreasing the cost of 300 series stainless steel production is obtaining hot metal containing high Ni, Cr and low C economically. Present authors consider to realize this aim with using laterite ore and chromium concentrate to produce mother liquid for 300 series stainless steel.

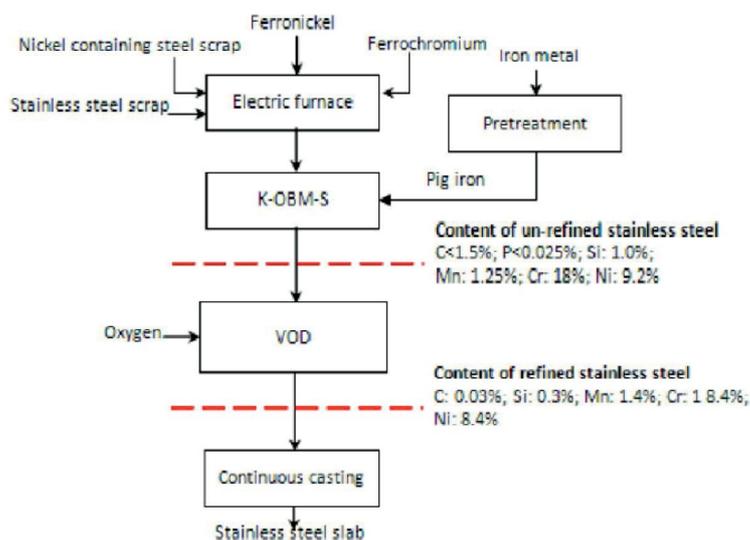


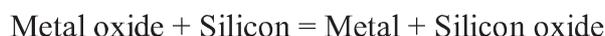
Figure 3: Triplex process for 300 series stainless steel production

3. NEW PROCESS TO PRODUCE 300 SERIES STAINLESS STEEL

3.1. Production routes

The hot metal containing nickel and chromium produced from electro-silicothermic process can be used as un-refined liquid stainless steel. Silicon from nickel-silicon ferroalloy (LCFeNiSi) that directly produced from nickel laterite ore in SAF is used as reducing agent in the process for producing low carbon nickel-chromium ferroalloy (LCFeNiCr) and its composition will be the same or similar to un-refined stainless steel liquid.

In ferroalloy industry, mid-carbon and low-carbon ferromanganese or mid-carbon and low carbon ferrochromium are normally produced by silicothermic reduction of oxide ores or concentrates. The following chemical reactions show the basic principle of silicothermic production routes:



Obtained from the practice experience that it is difficult to produce low silicon ferronickel using high silica containing nickel laterite ores, hence it will be a good idea to produce a ferronickel alloy with high silicon content (more than 10%) as the source of silicon in silicothermic process. This ferroalloy can be named as nickel-silicon ferroalloy. Then chromium concentrates can be reduced by this nickel-silicon ferroalloy so as to produce un-refined stainless steel metal. Figure 4 shows the process route for 300 series stainless steel production with electric-silicothermic method. The nickel-silicon ferroalloy is produced by sintering - SAF process. The molten metal will be then reacted with chromium concentrates in shaking ladle - electric furnace process to get un-refined stainless steel metal which is then provided to the stainless steel plants or followed by AOD/VOD process to produce stainless steel directly.

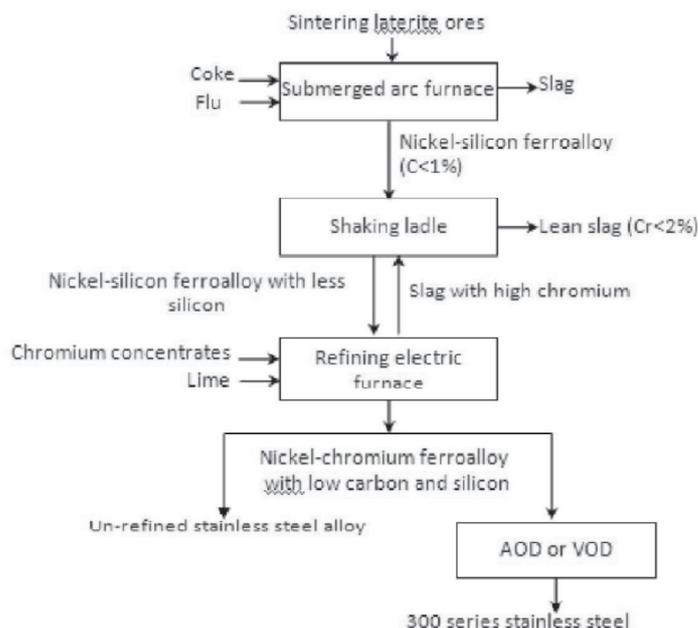


Figure 4: 300 series stainless steelmaking process with electric-silicothermic method

3.2. Ongoing research contents

The pre-experiments have been carried out in the present laboratory [5] in a refining electric furnace. The nickel-silicon ferroalloy with Si content of 10 mass% and Ni content of 10 mass% reacted with chromium concentrate with 54 mass% Cr_2O_3 and 22 mass% Fe_2O_3 . Three heats of this react were carried out and the main contents of the alloy from these experiments are 17 mass% Cr and 7 mass% Ni, which is similar to the content of un-refined stainless steel liquid. This means not only in theory but also in practices it is possible to produce stainless steel with electric-silicothermic. However, it needs much basic studies on following items to realize this new process, including:

- Thermodynamic properties of Fe-Ni-Si-j (j=C, P) alloy, especially for high Si containing alloy;
- Dephosphorization principle of nickel-silicon ferroalloy and the optimization of dephosphorization slag system;
- Reduction kinetics of the react between melting chromium ore and nickel-silicon ferroalloy;
- Behavior of “emulsion phase” and “phase separation” in shaking ladle;
- Equilibrium between nickel-silicon ferroalloy and slag;
- Heat and materials balance calculation of new process.

4. ESTIMATED ECONOMIC AND ENVIRONMENTAL BENEFITS OF NEW PROCESS

Economic and environmental benefits of electric-silicothermic process for stainless steel production have been studied by present authors. The comparisons of material cost, energy consumption and carbon dioxide emission of stainless steel production during duplex process (figure 2) and new process (figure 4) were estimated in present work.

The materials and their compositions used in this work for each process are given in table 3,

and some of data were sourced from literature [4] and [6]. The designed stainless steel here is grade 304 with composition of 68.6%Fe, 9.3%Ni, 19.0%Cr and 0.08%C. The main assumptions for ferrochromium and ferronickel production processes in the study have been presented in literature [4]. The current calculation is based on assumptions that the yield for Cr and Fe in chromium concentrate is 90% while the utilization ratio of Si in Ni-Si ferroalloy is 90% in new process.

Table 3: Processes and materials used for calculation

Metal products	Materials	Processes
Iron/steel	Iron ore (64% Fe)	Blast furnace & Basic oxygen furnace
Ferronickel	Laterite ore (table 1)	Rotary kiln / electric furnace
Ferrochromium	South African chromium ore (table 2)	Pellet/sintering/pre-reduction/submerged arc furnace
Cr concentrate	South African chromium ore (table 2)	Mining/concentrate
304 stainless steel	Pig iron (94%Fe, 4.4%C) Ferrochromium (55%Cr, 30%Fe, 1.5%Ni, 30%Fe,7%C) Ferronickel (23%Ni, 69%Fe, 1.9%C, 1.3%Cr)	Duplex process shown in figure 2
	Pig iron ((94%Fe, 4.4%C) Ni-Si ferroalloy (12%Ni, 67%Fe, 14%Si) Chromium concentrate (56% Cr ₂ O ₃ , 22%FeO)	Electro-silicothermic process shown in figure 4

4.1. Economic benefit

The calculated material costs of duplex process route and new process route for 304 stainless steel production are shown in the table 4. The result indicates that the material cost will be reduced 30% per ton steel when using the new process to produce 304 stainless steel. This is because chromite concentrate with the price of 338.5 USD per ton steel is lower than HCFeCr with the cost of 1292.3 USD per ton steel.

4.2. Environmental benefits

In this work, the environmental impacts of stainless steel production were considered as carbon dioxide emissions and total energy consumption. Table 5 showed the comparisons of environmental effects between duplex process and new process. Some data for calculation were quoted from literature [4]. It could be seen from Table 5 that the total energy consumption in new process is approximately 20% lower than that in duplex process in China, plus, CO₂ emission in new process has been decreased 7%. The reasons for the difference are: Firstly, the raw materials in duplex process are cold and must be heated in the EAF first, that consumes energy of 1.4 MJ/kg steel, while, the raw materials are hot metal directly tapping to the reactor in the new process. Energy for getting the hot metal comes from electricity and CO₂ emission is 0.4 kg/kg steel in this step. Secondly, the energy consumption of Ni-Si ferroalloy is lower than that of ferronickel (viz. $110 \times 0.41 - 71 \times 0.78 = 10.8$ MJ/kg steel from table 4 and table 5). The specific calculation process will be described in other papers.

5. SUMMARY

It is an important task for ferroalloy researchers developing a new process to use low grade laterite nickel ore and chromite fines efficiently, with the aim to realize energy saving and emission

reduction for stainless steel production. The new process for stainless steel production with electro-silicothermic method presented in this paper maybe one of the new developments.

Table 4: Material cost comparison between duplex process and new process

Materials	Duplex process route			New process route		
	Consumption (ton/ton steel)	Cost (USD/t)	Ratio (%)	Consumption (ton/ton steel)	Cost (USD/t)	Ratio (%)
Iron	0.32	147.7	5.1	0.09	39.8	2.0
Ferronickel	0.41	1450.8	50.0	/	/	/
Ni-Si ferroalloy	/	/	/	0.78	1500	80.3
Lime	0.08	2.3	0.1	0.21	6.1	0.3
Fluorite	/	/	/	0.02	1.4	0.1
Oxygen	0.05	9.2	0.3	/	/	/
SiCaBa	/	/	/	0.01	11.5	0.6
HCFeCr	0.35	1292.3	44.5	/	/	/
Cr concentrates	/	/	/	0.55	338.5	16.8
Total	1.21	2902.4	100.0	1.66	1897.4	100.0

Table 5: Environmental impacts for stainless steel production with different routes

Environmental impact	Materials for stainless steel production					304 stainless steel	
	Iron	Ferro nickel	Ferro chrome	Ni-Si ferroalloy	Chromium concentrate	with duplex process	with new process
Total energy, MJ/kg	22	110	56	71	0.18	78	62
CO ₂ , kg/kg	2.0	8.9	5.1	8.1	0.04	6.8	6.3

6. ACKNOWLEDGEMENT

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**MATHEMATICAL MODEL FOR FAST COMPUTATION OF EROSION PROFILE
IN SUBMERGED ARC FURNACE WITH FREEZE LINING**

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ABSTRACT

Lining of submerged arc furnace is subject to chemical and physical erosion during smelting process. In this paper, a new 2D mathematical model is developed for monitoring the erosion profile of freeze lining in submerged arc furnace which is used for smelting ferronickel. Temperatures monitored by thermocouples at different positions of refractory are utilized for solving an inverse heat conduction problem, namely estimating the shape and location of the wear-line in melting furnace. In order to solve this inverse problem, the optimization procedure which is used to minimize the sum of the squared residual between calculated and measured temperature at different thermocouple locations should be executed with the aim to enhance computational efficiency. Temperatures at thermocouples' locations are calculated by Boundary Element Method. Modified simplex optimization method is employed. The result obtained from numerical experiments indicates that this algorithm could reduce the computational memory and time, at the same time improve the computational accuracy.

Furthermore, thermal conductivity of the refractory in freeze lining may decrease after smelting for a period of time. This is mainly due to refractories has experienced the thermal cycling for many times. The accuracy in computation of erosion profile will be affected either. The influence degree is also discussed in this paper.

KEYWORD: *Submerged arc furnace, freeze lining, erosion profile, boundary element method.*

1. INTRODUCTION

Submerged arc furnace (SAF) is still the main equipment for smelting Ferroalloys. The refractory of SAF is gradually destroyed by hot molten iron and slag due to physical and chemical erosion during the smelting process. Before the appearance of SAF with large capacity, not enough attention has been paid to the lifetime of SAF lining because the cost to relining is low. The investment to building linings of SAF with large capacity has been increased significantly and this project should be carefully prepared for several months. It is critical that continuous monitoring the residuary thickness of lining and estimating the precise time to blow down and relining.

In order to monitor the thickness of refractory accurately, some online monitoring methods have been developed to acquire the erosion profile of SAF since 2004. The method adopted in SAF is similar to the one that is used in Blast Furnace (BF). A large number of thermocouples are arranged in refractory to measure temperature and mathematical models that monitoring how wear-line is formulated. These models make use of measured temperature to seek the shape of erosion boundary. A.De Kievit [1] utilized the 1-d steady heat transfer method to monitor a SAF smelting ferromanganese. The date that blast furnace using 1-d method to monitor inner contour can trace back to 1966. Some corporations still employ this technique due to its simplicity and lower requirement for thermocouple displacement [2]. L.Rodd [3] developed a 2-d mathematical model to monitor a SAF smelting ferronickel. 1550°C isotherm is the wear-line in the temperature field,

which is obtained by Finite Element Method (FEM). Karstein.S [4] exploited two types of numerical algorithms solving inverse heat conduction problem for an ilmenite melting furnace. One algorithm is based on utilizing a fixed boundary with control nodes. The other algorithmic approach is to approximate the wear-line as close as possible with as few curve representing parameters as possible.

Monitoring the wear-line of SAF is still at early stage compared with BF. Many effective monitoring methods have been developed, which mainly includes direct method [5-6] and numerical simulation [7-14]. In direct method, some sensors with the same thickness as refractory will be imbedded in the linings. The destructive progress of sensor is synchronized with lining erosion, so the residual thickness of sensors can reflect the erosion condition. This technique has the advantage of supplying extremely precise information but only at sensor location. And the implementation is difficult and costly. With respect to numerical simulation, the heat conduction equation describing mathematical model of lining is solved by some types of numerical method mainly including FEM, and the 1150°C isotherm in the temperature field is defined as erosion boundary. There are two aspects of heat transfer problem in numerical simulation: direct and inverse heat conduction problem. Boundary conditions and thermo-physical properties are known in direct heat conduction problem (DHCP) [7-9]. A remarkable limitation to the DHCP model need to be take noticed is that the domain area of model is not immutable. Hence it is necessary change the model along with the lining erosion. Either the thermo-physical properties or the boundary conditions can be known in inverse heat conduction problem (IHDP); instead, the temperature of the interior has to be known for some points in the domain [8]. Generally speaking, the shape of inner boundary in model is unknown. Some authors [10-12] parameterize the inner border and combine the optimization method with FEM to conquer the IHDP. However, because of the ill-posed property in inverse problem, regularization method is introduced to make the optimization process stable. Apart from FEM, Wu [13] attempted to employ the Boundary Element Method (BEM) to calculate the temperature field. Constructing 6 points to constitute the inner profile and adopting the orthogonal test to compute the positions of these points. Except for heat conduction model, computational fluid dynamics model was introduced to perform a numerical analysis of the BF hearth inner profile [14]. In brief, many excellent scholars have made a contribution to figuring out the complex erosion process of BF hearth. In addition to borrow ideas from monitoring method in BF, the particularity of SAF should also be considered carefully. Hearth of BF is always inhabited by molten iron. That region of SAF is occupied by molten metal-slag and charging alternately. Together with some other factors like that scheduling stoppages and intermediate repairs, the lining has inevitably experienced thermal cycling, which means the refractory temperature will rise and fall repeatedly for many times. Furthermore, there are some differences about configurations between “Freeze lining” [15-16] (figure 1) of SAF and BF lining. The ceramic protection layer will be gone shortly after the furnace reaches full productivity [16]. With the carbon brick holding a high percentage in this system, the “Skull” will forms at the surface of that. Hence, the erosion degree of carbon brick can be known, it is possible to monitor the lining erosion of SAF.

In this paper, a new methodology that uses a 2d inverse heat conduction model and measured temperature obtained from thermocouples in the smelting process has been developed to estimate the erosion profile. The present model has a number of special characters by which differs from earlier ones. First, Kirchoff transform is introduced to transfer the nonlinear differential equation to Laplace equation. In order to solve the differential equation faster, BEM and modified simplex optimization method is applied simultaneously. Second, the thermal conductivity of model is analyzed through the thermal cycling, whose influence on calculation accuracy of erosion boundary is also discussed. This methodology has been used to monitor an actual-scale submerged arc furnace smelting ferronickel with 16500 Kva at Shandong liangda factory.