The Complete Book on Ferroalloys

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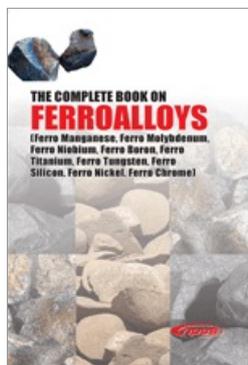
The Complete Book on Ferroalloys

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The Complete Book on Ferroalloys

(Ferro Manganese, Ferro Molybdenum, Ferro Niobium, Ferro Boron, Ferro Titanium, Ferro Tungsten, Ferro Silicon, Ferro Nickel, Ferro Chrome)

An alloy is a mixture or solid solution composed of metals. Similarly, Ferroalloys are the mixture of Iron with high proportion of other elements like manganese, aluminium or silicon. Alloying improves the physical properties like density, reactivity, Young's modulus, electrical and thermal conductivity etc. Ferroalloys thus show different properties as mixture of different metals in different proportion exhibit a wide range of properties. Also, Alloying is done to alter the mechanical properties of the base metal, to induce hardness, toughness, ductility etc.

The main demand of ferroalloys, nowadays is continuously increasing as the major use of such products are in the field of civil construction; decorative items; automobile; steel industry; electronic appliances. The book provides a wide idea to readers about the usage of appropriate raw material and the treatment involved in the processing of raw material to final produce, safety, uses and properties of raw material involved in the processes.

This book concisely presents the core principles and varied details involved in processing of ferroalloys. The work includes detailed coverage of the major products like ferroaluminium, ferrosilicon, ferronickel, ferromolybdenum, ferrotungsten, ferrovanadium, ferromanganese and lesser known minor ferroalloys.

Progress in thermodynamics and physico-chemical factors in ferroalloy production has developed rapidly during the past twenty-five years or so. The book presents the principles and current knowledge of processes in the production of various ferroalloys.

The production of a particular ferroalloy involves a number of processes to be followed in order to give the alloy desired physical and mechanical properties. The slight difference in the temperature or heating or composition can lead to entirely different alloy with different properties. This book is not only confined to the different processes followed in the production of ferroalloys but also describes the processes used and other information related to product, which are necessary for the manufacturer's knowledge. Also, the book gives the reader appropriate knowledge regarding the selection the best of available raw materials.

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Sample Chapters

(Following is an extract of the content from the book)

INTRODUCTION

Alloy is a mixture with metallic properties and is composed of two or more elements, of which at least one is metal. Some Alloys are definite compounds, some are solid solutions of one metal in another. Some are more mechanical mixture and others are combinations of these conditions.

An alloy is a mixture or metallic solid solution composed of two or more elements. Complete solid solution alloys give single solid phase microstructure, while partial solutions give two or more phases that may or may not be homogeneous in distribution, depending on thermal (heat treatment) history. Alloys usually have different properties from those of the component elements.

Theory

Alloying a metal is done by combining it with one or more other metals or non-metals that often enhance its properties. For example, steel is stronger than iron, its primary element. The physical properties, such as density, reactivity, Young's modulus, and electrical and thermal conductivity, of an alloy may not differ greatly from those of its elements, but engineering properties such as tensile strength and shear strength may be substantially different from those of the constituent materials. This is sometimes a result of the sizes of the atoms in the alloy, because larger atoms exert a compressive force on neighboring atoms, and smaller atoms exert a tensile force on their neighbors, helping the alloy resist deformation.

Interstitial Alloy

When a molten metal is mixed with another substance, there are two mechanisms that can cause an alloy to form, called atom exchange and the interstitial mechanism. The relative size of each atom in the mix plays a primary role in determining which mechanism will occur. When the atoms are relatively similar in size, the atom exchange method usually happens, where some of the atoms composing the metallic crystals are substituted with atoms of the other constituent. This is called a substitutional alloy. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms. fit into the interstices, but some of the iron atoms are replaced with nickel and chromium atoms.

Alloys are often made to alter the mechanical properties of the base metal, to induce hardness, toughness, ductility, or other desired properties. While most metals and alloys can be work hardened by inducing defects in their crystal structure, caused by plastic deformation, some alloys can also have their properties altered by heat treatment. Nearly all metals can be softened by annealing, which repairs the crystal defects, but not as many can be hardened by controlled heating and cooling. Many alloys of aluminum, copper, magnesium, titanium, and nickel can be strengthened to some degree by some method of heat treatment, but few respond to this to the same degree that steel does.

FERROALLOYS

Ferroalloys are one of the important inputs in the manufacture of alloys and special steel. Ferroalloys impart special properties to steel. The function of the alloy is to increase resistance to corrosion, oxidation to improve hardness, tensile strength at high temperatures, wear and abrasion resistance with addition of carbon to increase creep strength, etc. The growth of Ferroalloys industry is, thus, linked with the development of the iron and steel industry, foundry industry and to some extent, electrode industry. The principal ferroalloys are of chromium, manganese and silicon. The product series consists mainly of ferro-manganese, silico-manganese, ferro-silicon and ferro-chrome.

FERRO BORON

Melting Range	1450-I550°C
SPECIFIC GRAVITY	6.6

Used by steel makers and malleable iron founders to improve hard enability and to control the micro structure of flat rolled HSLA steels. William Rowland Ltd offers a full range of sizes including those specified by cored wire producers together with any number of packing options. The boron content is determined by individual customer requirements and can range from B 15% to in excess of 20%.

FERRO CHROMIUM

Melting Range	1575-1675°C (Low Carbon)		1350-I450°C (High Carbon)
SPECIFIC GRAVITY	7.35 (Low Carbon)		7.20 (High Carbon)

We supply Ferro Chromium to various specifications. Chromium is a vital alloying element in iron and steel. It promotes corrosion and oxidation resistance and aids high temperature strength. Ferro Chromium not only finds application in stainless steel production but also as an additive in a range of constructional and tool steels. High Carbon Ferro Chromium is added to a range of cast irons to import strength and wear resistance.

Available as a high carbon grade and complemented by a range of low and medium carbon alloys together with a special nitrided ferro manganese providing the steel maker with the ability to add nitrogen in controlled amounts. Specification for the high carbon grade is typically Mn 75-80%, C 6-8%, Si 1.0% max, P 0.2% max (Lower Phos' levels of 0.1% max are available). For the medium and low carbon grades the manganese ranges between 78-98%, with carbon options of 1.5% max. 1.0% max and 0.1% max with variety of sizes and packing to suit customer requirements.

Ferro Molybdenum

More commonly referred to in the trade as "ferro moly" it is an extremely versatile alloy used mainly in HSLA (high strength low alloy) and stainless steels, however, its numerous properties mean that is equally at home in cast irons, certain high speed tool steels, nickel based and superalloy applications.

The properties which ferro molybdenum imparts vary depending on the grade of steel or iron being produced. Additions of ferro moly can lead to improvements in weldability, corrosion and wear resistance while also serving to increase ferrite strength. Ferro moly is produced by Thermit reduction of technical oxide in the presence of iron.

William Rowland Ltd is the UK distributor for The Kennecott Molybdenum Company supplying western grade ferro molybdenum produced by European conversion plants.

We are able to offer a range of sizes suitable for a wide range of addition practices.

The typical specification of 5 × 30mm ferro molybdenum offered by The Kennecott Molybdenum Company is as follows:

Mo 67% min, Cu 0.50% max, Si 1.5% max, P 0.05% max, S 0.10% max, C 0.10% max, Pb 0.01% max.

Molybdic Oxide

Known throughout the trade as Moly Oxide it is primarily available for arc and AOD furnace additions. It comes packed in a variety of ways most commonly in the UK in cans containing 10kgs of Oxide which in turn are stacked onto pallets (600kg of Oxide per pallet) these are then shrink wrapped to ensure safe handling and transportation to the customers works. Other options include drums containing 400kgs of Oxide and bottom pouring big bags containing 1000kg of Oxide both on pallets for ease of handling.

If required moly oxide can be made available in the form of carbon free briquettes.

A typical specification would be: Mo 57% min, Cu 0.50% max, Pb 0.05% max, P 0.05%max, S 0.10%max, C 0.10%max.

FERRO PHOSPHORUS

Melting Range	1250-1350°C
SPECIFIC GRAVITY	6.4

Used in the production of phosphoric irons and certain free cutting steels, supplied in lumpy or crushed form, typically 25% P with controlled Si contents 1% and 2% max.

FERRO SELENIUM

Melting Range	480-940°C
SPECIFIC GRAVITY	6.35

Available as the 50/50 alloy, normally in the lumpy or crushed form. Used in the production of free cutting stainless steel.

FERRO SILICON MAGNESIUM

Melting Range	1210-1250°C

SPECIFIC GRAVITY	4.9

We can supply ferro silicon magnesium for ductile iron production with various Mg contents from 3-9% with cerium or rare earth additions. Material is available in various size ranges and is packed to customers specific requirements.

FERRO SILICON ZIRCONIUM

Melting Range	1250-1340°C
SPECIFIC GRAVITY	3.5

Ferro silicon zirconium is available in a range of sizes to suit customer requirements. Typical analysis is 50% Si, 35% Zr. Used as deoxidant in steel castings or in certain steels where a low residual aluminium is required.

FERROUS SULPHIDE

We can supply the material in the form of 100 mm lumps or specially sized pieces down to 3 mm. Contains min. 30% sulphur available in drums, sacks or pre-weighed bags down to 5 kgs. Used for accurate charge and trim additions in certain forms to improve the inoculation process. Also used in the production of free cutting steels, or in certain cases where hydrogen embrittlement in steel is a problem.

PRODUCTION OF FERROALLOYS

Ferroalloys are mainly used as master alloys in the iron and steel industry, because it is the most economic way to introduce an alloying element in the steel melt. Besides this, special ferroalloys are also needed for the production of aluminium alloys and as starting material in specific chemical reactions.

As an additive in the steel production ferroalloys improve the properties especially the tensile strength, wear and corrosion resistance.

Primary Processes

Oxidic metal ore + iron ore/scrap + recluctant ® ferroalloy + reductant oxide + slag

Secondary Processes

Metal scrap + iron scrap ® ferroalloy

Today, primary ferroalloys are principally produced either by the carbo-thermic or metallo-thermic reduction of oxidic ores or concentrates. The most important process is the carbo-thermic reduction in which carbon in the form of coke (metallurgical coke), coal or charcoal is normally used as a reducing agent. When a blast furnace is used coke is also needed as an energy source.

Applied Processes and Techniques

Depending on the production rate, ferroalloys can be divided into two main categories, bulk alloys and special alloys. Bulk ferroalloys (ferro-chrome ferro-silicon, ferro-manganese silico-manganese and ferro-nickel) account for about 90% of the total production of ferroalloys in the European Union.

Compared to bulk ferroalloys, the production rate of special ferroalloys is rather small. Special ferroalloys (ferro-vanadium. ferro-molybdenum, ferro-tungsten ferro-titanium ferro-boron and ferro-niobium) are mostly used in the iron, steel and cast-iron industry. Besides this some special ferroalloys are increasingly used also in other industry sectors e.g. aluminium and chemical industries.

Raw Materials

The main raw material to produce ferro-chrome is chromite ore, which is an iron oxide and chromium oxide containing mineral. The ratio between Cr and Fe in the chromite ore determines the chromium content of the alloy produced, e.g. a high Cr/Fe ratio is advantageous for the production of a ferroalloy with high chromium content. Chromite ore and concentrates are used in the form of hard lumpy and friable lump types, as well as chromite fines.

In order to achieve the right metal analysis, a good metal recovery and a satisfactory furnace operation, auxiliary materials such as quartzite, bauxite, corundum, lime and olivine can be added to the burden as fluxing agents.

Pre-treatment Techniques

Chromite is used as a raw material for the ferro-chrome production in the form of lumpy ore, fines and concentrates. It has to be noted that about 70 - 80% of the world's chromite sources are available as fines (< 10 mm). To convert ore fines and concentrates to furnaceable material, they need first to be agglomerated by briquetting, pelletising sintering or sintering.

Agglomeration is necessary to achieve good recoveries and also to give a permeable burden, which allows the gas from the reaction zone to escape.

Briquettes are made by pressing or shaping an ore mix with added binder to a suitable shape and size. The briquettes are used in the furnace after hardening of the added binder, but without thermal treatment. This method can be used for materials with a relatively wide grain size range of less than 5 mm.

PRODUCTION OF FERRO MANGANESE

High-carbon Ferro-manganese

High-carbon ferro-manganese (HC FeMn) can be produced in carbo-thermic reduction of lumpy or sintered manganese ore either in a blast furnace or in a three-phase submerged electric arc furnace.

The blast furnaces that are used for smelting HC FeMn are similar of those used for the production of pig iron, higher temperatures are needed for the reduction of manganese oxides. The reduction of higher manganese oxides (MnO_2, Mn_2O_3 and Mn_3O_4) takes place in the upper part of the blast furnace. The reduction process of higher manganese oxides is exothermic and contributes to maintain a relatively high temperature of the top gas. In some cases additional cooling of the furnace top is introduced to limit the temperature. Further reduction of manganese oxides requires temperatures above 1400°C and takes place in a limited zone above the tuyeres. This reduction process is endothermic and consequently needs high coke consumption.

As a result, the production of HC FeMn in a blast furnace is related to a high generation rate of CO. The quantity of CO produced is much higher than that necessary to heat the blast in the hot stoves. The excess gas is commonly used to produce electric energy.

The CO containing off-gas has to be de-dusted before it can be used to heat the hot stoves or burned to produce steam of the electricity generation. For the off-gas de-dusting a variety of different techniques are available, e.g. electrostatic precipitators, scrubbers, washing towers or bag filter. In order to prevent the hot stoves from damage of the refractory material and to minimise the dust emissions the de-dusting system is designed to work below 10 mg/Nm3 of dust. These techniques are described in detail in section.

For the de-carburisation of HC FeMn, oxygen is blown into the molten metal, which is tapped off from the furnace. The oxygen blown into the melt oxidises part of the manganese and increases the bath temperature from about 1350 to 1550°C. With increasing temperatures the carbon present in the HC FeMn also tends to be oxidised and again raises the temperature from 1550 up to 1750°C. The oxidisation of carbon consequently reduces the carbon content of the ferro-manganese. For the production of MC FeMn the de-carburisation process ends when a corresponding carbon content of about 1.3% is reached. The high temperature also leads to the vaporisation of ferro-manganese that leaves the process as fume. The fume can be collected by using hoods and sent back to the HC FeMn smelter.

In contrast to the refining process that uses HC FeMn as a raw material, the silico-thermic production needs manganese ore and lime or a high-grade slag and silico-manganese. The reduction itself is performed in a three-phase electric arc furnace, with electrodes made of graphite. At the end of the cycle, the molten alloy and the slag are cast and separated. The slag is recycled after cooling and crushing as raw material to the silico-manganese production plant. The fumes of the furnaces will be de-dusted in a fabric filter. With the silico-thermic reduction the production of MC FeMn containing 1% of C is possible.

The main advantages of the refining process are the lower operating and capital investment coasts. The advantage of the silico-thermic process is to produce Low-carbon ferro-manganese in the same process.
Production of High Carbon Ferromanganese
Blast Furnace Production

High carbon ferromanganese is produced in blast furnaces in a process similar to the production of pig iron in blast furnaces. But there are some important differences between two processes.

Thus, ferromanganese production in blast furnace needs larger amounts of coke than pig iron production in a blast furnace. Preheating the blast and oxygen enrichment are used to reduce coke requirement. Dolomite or limestone added to the charge raises the activity of MnO for reduction. Small slag volume, basic slag and high blast temperature are required for high manganese recovery. By careful control and a more uniform charge mixture in the shaft, manganese recoveries of over 90% and coke rates of 1530 kg/t are reported.

Electric Furnace Production

In the case of the blast furnace, the thermal energy required for the smelting process is supplied by the combustion of additional coke, which in most countries is a more expensive form of energy than electricity. Capital requirements for a new facility generally favor the electric furnace process. Important furnace design parameters for high carbon ferromanganese production are electrode diameter and spacing, hearth diameter, crucible depth, voltage range, and KVA capacity of the transformer. Because the resistivity of the burden in the electric furnace production of ferromanganese is low, low voltages between the electrodes are necessary to maintain satisfactory penetration of the electrodes in the charge. To obtain the proper power loading for the furnace, higher currents are required. Therefore, to operate within the current carrying capacities of carbon electrodes, the diameter of the electrodes for ferromanganese furnaces is larger than for other ferroalloy furnaces.

Most electric furnaces have sealed covers. The sealed cover is generally preferred because it allows better fume control at lower capital cost and lower energy requirement. The crucibles are steel shells lined with refractor) oxide brick and an inner lining of carbon blocks. The hearth is similar, but has a thicker carbon lining. Electric energy is supplied to the smelting reaction through three carbon electrodes, of the Soderberg, i.e., self-baking, type. An important consideration for a successful smelting operation is the slag composition. The composition of the slag has pronounced effects on furnace resistivity, smelting temperature, recovery of manganese, and the amount of silicon in the ferromanganese. Blending of ores or the addition of fluxing reagents is often necessary to produce the desired slag composition.

Two processes are employed in production of ferromanganese in electric furnace: high manganese slag process and low manganese slag process.
High Manganese Slag Practice

The high manganese slag practice is used by most plants where high grade manganese ores are smelted and silicomanganese is also produced. Manganese content of this slag ranges from 30-42%. Typical slag analyses for the other compounds are 2 to 5% MgO, 10 to 30% Al2O3, 15% CaO and 27% SiO2. These slags

are usually used in silicomanganese production, increasing the overall manganese recovery. Small amounts of fluxes may be used, such as dolomite or limestone, depending on the manganese concentration desired in the slag.

Discard Slag Practice

Although the silicothermic reduction process is more energy intensive than the decarburization of high-carbon ferromanganese, it has the advantage that the final carbon content is limited only by the carbon content of the initial silicomanganese. The silicothermic process can therefore be used to produce low-carbon ferromanganese and industrial manganese metal.

Production of Medium-Carbon Ferromanganese by Oxygen Refining of High-Carbon Ferromanganese

Production of Low-Carbon Ferromanganese

Low-carbon ferromanganese contains 76-92% Mn and 0.5-0.75%C. The production of low-carbon silicomanganese is not possible by the decarburization of high carbon ferromanganese without extremely high losses of manganese. It must accordingly be made of a silicothermic reduction process.

The process is similar to that used in the silicothermic production of medium-carbon ferromanganese. High-purity ores are used and in particular ores containing iron and phosphorus should be avoided. An artificial manganese ore produced as a high-grade slag is particularly suitable because of its low impurity level and because all the manganese is present as MnO. The reduction of the higher oxides of manganese is therefore unnecessary.

Refining of Ferro Manganese

Eramet Research is equipped with a sintering pot, conical to make easier the removal of the sinter cake. The pressure drop between top and bottom of the sintering pot is fixed by a dedicated regulation of the suction fan. Many thermocouples, embedded above, under and in the sinter mix enable to control the firing and gas temperatures, as well as the sintering front location evolution. These measurements enable to assess the productivity of the trial.

Characterization

To evaluate the sinter quality, the sinter cake is then sieved to determine the sinter chemical analysis and mechanical strength according to the ISO 3271 standard. Samples can also be observed through a microprobe analyser to understand more deeply the sintering and dissolution mechanisms and to correlate the microstructure of the product to its mechanical strength.

Performances

Pilot results have been successfully used to define and improve the sinter mix recipe (coke and flux proportion...) of the industrial products, in order to increase their mechanical strength, i.e. reduce the generation of fines during transportation.

Until 2007, the 0-1 mm fines from the mine were dumped. Only the richer 1-8 mm fraction was used to produce sinter. In 2007, Eramet Comilog decided to study the possibility to recover part of the 0-1 mm fraction and use it in the sinter plant.

Before testing industrially the impact of such a fraction on the sintering process, trials were preformed at Eramet Research in order to assess their effect on the product characteristics and on the plant productivity. At pilot scale, trial results showed a sharp decrease in productivity as the proportion of Mn "sand" was increased, due to a lower permeability of the sinter mix. Such results were confirmed at the industrial scale and allowed to find the most adapted proportion of 0-1 mm fraction in order to minimize productivity losses and to maximize the use of such a fraction.

The safety has also always been a concern for all the pilot campaign performed at Eramet Research. As the configuration of the pilot hall always changes from one trial to the other, a risk analysis is performed before each pilot campaign, all the people involved in the project get a safety information and some specific training are organised (e.g. crane driving). After the campaign, a safety debriefing is organised and fault tree analyses are performed if some incidents occurred during the trials. By this way, Eramet Research has improved the safety during pilot campaigns for the last ten years.

Transfer of the Pilot Results to the Plants

For each campaign, 3 shifts made of 4 people ran the furnace under the control of a research engineer and of the head of the pyrometallurgy department. Each junior engineer will be in charge of the organization of a pilot campaign while working in Trappes, as we consider this mission as his/her first industrial experience, and therefore an essential part of his/her education for his/her future position in a plant. Many results will be transferred this way eventually.

As many people coming from the different plants of Eramet Mn division (i.e. Norway, U.S., France) as possible have been integrated into the pilot teams to take advantage of their experience of the process (i.e. furnace behaviour, tapping etc.). They will also be the main vectors to transfer good practices from Trappes to the plants.

In the following sections, 3 examples of pilot campaigns that led to changes in Eramet plants or that were at least followed by industrial tests are presented.

In 2001, Eramet Research pilot campaign focused on the optimum lining in the scope of HC-FeMn production. Both slag and ore smelting situations were studied and the monitoring of the lining temperature all around the furnace stressed that the high heat flows experienced at the slag level were due to convective heat transfer between the liquid slag and the inner sidewall whereas the heat transfer was mainly convective at the metal level leading to lower heat flows. To cope with such a situation, it appeared that a conductive lining combined with shell water cooling was much more efficient than an air cooled insulating lining. Eramet Norway Sauda was the first plant within the group to use the "freeze lining" concept to reline one of its HC-FeMn furnaces in 2002.

A second example of relevant result from a pilot campaign consists in burden optimisation. Actually, the HC-FeMn 2003 pilot campaign aimed to study the parameters responsible for eruptive phenomena in submerged arc furnaces. Different burden compositions were tested and it appeared that the moisture content of the charge was a first order parameter leading to mix bridging and then possible eruptive phenomena when collapsing. A maximum moisture content was thus

determined to limit the risk of blowing conditions, which is today applied in Eramet safety standard.

The third example of results from pilot campaign deals with the power increase through resistance increase in the scope of HC-FeMn production. As industrial furnaces are operated at a rather low resistance, most of them are limited by the current that the electrical system can sustain. Therefore, increasing the resistance operating point is the most efficient way to increase the power. Different parameters were tested at a pilot scale and it appeared that the size of the coke bed and the grain size of the reducing agent used were first order parameters to manage to increase the resistance. Operating with a small coke bed and using small coke enabled to increase the power at a pilot scale. Industrial tests were then performed by Eramet Norway using small coke to produce HC-FeMn, which confirmed the above results.

PRODUCTION OF FERRO MOLYBDENUM

Technical grade molybdenum trioxide (MoO3) is the main raw material in the production of ferro-molybdenum as well as the starting compound for a number of other molybdenum containing products such as ammonium dimolybdate, sodium molybdate and molybdenum metal. Roasting as it is shown schematically below performs the conversion of concentrated molybdenite (molybdenum sulphide ore) into technical grade molybdenum trioxide for the metallurgical or chemical industry.

Metallo-thermic Production of Ferro-molybdenum

As mentioned before, today the metallo-thermic reduction is the most common process that is used for the production of ferro-molybdenum, due to the higher Gibbs live energy of aluminium compared with silicon, ferro-silicon is the preferred reducing agent in order to assure safe process conditions. However, to obtain the required heal balance for the reaction, it is necessary to use a small amount of aluminium.

The metallo-thermic process requires dry raw material for the process. Mill-scale that arrives wet is stored in a covered bunker prior to screening and drying in order to prevent fugitive losses. Steel scrap that also arrives in bulk is offloaded and packed into containers prior to be Stored. Smooth efficient smelting reactions require a blend of suitably sized raw material, this is of particular importance with respect to the oxides and the reducing agents. Fluorspar is sometimes added to improve the slag and metal separation.

PRODUCTION OF FERRO NIOBIUM

Introduction

In less than two centuries niobium has evolved from being an unknown metal to a rare and high-priced material in the market, and then to the opposite extreme, becoming readily available, with an excess of supply and reduced price.

Applications of niobium began around 1925 when it was added to tool steels as a partial substitute for tungsten, and later in 1933 when it was first used to stabilise interstitial in austenitic stainless steels. In the 40's niobium was added to super alloys for use in gas turbines. Interest in using niobium in plain carbon steels dates back to the late 30's. However, due to its high cost, more than US $ 25 per kg niobium ctd, and lack of availability, the use of niobium in plain carbon steels did not materialise until the late 50's and early 60's. During this period, the source of niobium was the mineral columbite-tantalite, mainly processed for the production of tantalum through a costly separation process.

The raw materials were weighed and mixed. An open reactor was charged with the aluminothermic mix which was ignited with magnesium turnings. After the reaction was complete (approximately 15 min) all the components had melted, and the slag was separated from the ferro-niobium by gravity. The slag was tapped from the reactor and the ferro-niobium was left to solidifx and cool down.

Approximately 11,000 kg of ferro-niobium containing about 65 per cent niobium were produced per batch.

In 1991, CBMM began a new metallurgical operation - the FeNb semi-continuous autothermic reduction process in a closed vessel. This process had the main objective of introducing and developing improvements in environmental control and working conditions.

In 1994, CBMM introduced a submerged electric arc furnace, to the ferro-niobium production, incorporating all the advantages developed in the previous step, and allowing a 25 per cent saving in aluminium consumption by the replacement of iron oxide (hematite) with metallic iron powder.

Since 1994 more than 150,000 tons of ferro-niobium have been produced in a 4,25 MVA electric arc furnace at CBMM. The furnace, initially designed to produce 15,000 tpy reached a capacity of 30,000 tpy in 1998. The present production capacity of the electric arc furnace is 39,000 tpy of ferro-niobium.

The figure below shows the evolution of CBMM's ferro-niobium sales compared to total world demand. It also shows CBMM's ferro-niobium production capacity.

Recent Developments in Ferro-niobium Manufacturing

Because of its relatively high phosphorous, sulphur and lead contents (1.0, 1.0 and 0.2 per cent respectively), the floated concentrates must be refined before conversion into ferro-niobium.

PRODUCTION OF FERRO TITANIUM

Ferro-titaniurn can be produced either from primary and secondary raw material and is used for a variety of different purposes. As an alloying element it increases yield strength and reduces the cracking tendency. In the production of stainless steel with a high chrome and nickel content, ferro-titanium is used to bond the sulphur.

For the production of ferro-titanium the primary raw material titanium oxide containing minerals such as ilmenite are used. The reduction occurs commonly by the metallo-thermic process because the carbo-thermic reduction produces an alloy that contains too much carbon and is therefore not interesting as an alloying element in the steel industry. The production takes place as a batch process in a refractory lined crucible or in an electric furnace depending on the process variation.

In recent years the availability of titanium scrap on the market increased and therefore the production of ferro-titanium from secondary raw material is more important. The production of ferro-titanium is achieved by melting ferrous scrap and titanium in an electric induction-melting furnace. The alloying process is a slag free process.

Ferrous units are purchased to a specification in the form of mild steel solids. Titanium scrap is delivered to site in container trucks. The feedstock includes lump scrap metal castings, wrought products and turnings (swarf) from machining processes. Upon receipt, materials are checked to ensure that are not contaminated with radioactive materials. Large lumps of scrap are reduced in size by oxy-flame cutting. Swarf is chipped using a swarf pulveriser and then fed through a centrifuge to remove oil and moisture.

The Reduction of TiO2

Compared with other, mora expensive reactive metals, aluminium is the most practical agent for the reduction of titanium dioxide to titanium metal. The use of carbon results in the formation of carbide, and the Gibbs free energy, G°, for carbide formation is more favourable, at all practical temperatures, than that for the formation of titanium metal. Reduction by silicon is not possible since the G° for the reaction is positive at all practical temperatures.

The free-energy change for the further reduction of this oxide is positive at the reaction temperatures and therefore the yield of titanium metal will be diminished to some degree.

Enthalpy Considerations

A number of metals are produced by alumino-thermic reductions. The term 'aluminothermic' is usually taken to mean self-sustaining aluminium reduction reactions. In these processes, the enthalpy of reaction is high enough, i.e. at a level such that, after the reaction has been initiated in one part of the charge, sufficient thermal energy is liberated to heat progressively the rest of the reacting materials to a suitable reaction temperature and to superheat the metal and resulting slag to a temperature such that good separation of these two phases is achieved without the need of any other heat source.

Reasons for the Choice of a d.c. Transferred-arc Plasma Furnace

Initially, attempts were made to produce ferro-titanium in a 60kW single-phase submerged-arc furnace. The operation was very difficult because of the very high conductivity of the titaniferous slag. The penetration of the electrode into the bath could not be maintained at a constant level, and violent fluctuations occurred in the current drawn from the transformer.

Although an alloy contained 61.6 per cent titanium, 9.0 per cent iron, and 15.1 per cent aluminium was produced in one test, it was felt that an arc-smelting operation would not be commercially viable, since it would be too erratic to be easily controlled, and that some other heating system, in which there would be no contact between the electrode and the charge, should be used. The transferred-arc plasma furnace appeared to offer an attractive alternative and, as a preliminary study, four tests of short duration were carried out in a 100 kVA furnace using ilmenite and the titania-containing slag as a source of titanium.

Small-scale Batch Tests in a 50 kVA Water-cooled Furnace

The preliminary large-scale tests were done before the small-scale tests were started. However the investigations were done in parallel at a later stage, and modifications to equipment and lessons learned in the small-scale tests were applied, wherever possible, in the large-scale tests.

Interpretation of Results of the Small-scale Tests

The substantial decrease in the slag-to metal ratio that occurred when no lime vas added to the smelting charge resulted in mora efficient heat transfer to the lower regions of the bath.

In the particular furnace configuration used in these-tests, most of the arc energy is dissipated on the surface of the bath at the point of arc attachment. As Titania slags have high electrical conductivity, it may be assumed that the degree of resistance heating in the slag is negligible. This improved energy transfer ensures that the metal in the lower regions of the bath remains fluid and is therefore able to participate in the reactions throughout a run. This effect, coupled with the higher reaction temperatures that prevail during operation with more refractory slags, is believed to be one of the reasons for the improvement in the ratio of titanium to aluminium in the alloy as the lime additions to the charges were decreased. Another factor may be the increased activity of the titanium dioxide in the slag, which is suppressed at high concentrations of lime.

Smelting with substoichiometric quantities of aluminium leads to a decrease in the residual aluminium in the alloys produced due to the more favourable reaction equilibria that are established under these conditions. However, it appears that a thermodynamic barrier is encountered that does not allow ferrotitanium alloys with a titanium-to-aluminium mass ratio higher than about 7 to be produced. It appears that attempts to improve this ratio by further decrease of the aluminium contained in the charge result only in a corresponding increase in the oxygen content of the alloy.

FURTHER EXPERIMENTAL WORK

A further campaign was then mounted so that this modification could be tested, and some of the operating conditions were changed. Because the higher-powered thyristor drive was being used at that stage, a higher feed rate and an increased prorated power were used in an attempt to shorten the time of reaction and, hence,

to minimize the time for reaction between the alloy formed and the air.

It is obvious from the wide fluctuations in composition of the slags that this campaign suffered from a lack of metallurgical control despite careful monitoring of the feed rate and rate of energy input. The titanium content of the metal dug out of the hearth was low, except for sample 1, but the titanium-to-aluminium ratio vas encouragingly high in some cases. The oxygen content of the metal was also high, but it was felt that this could have been partly due to slag entrainment as well as to the effect of a reduced aluminium addition.

SMALL-SCALE SEALED FURNACE

A small-scale (50kW) sealed plasma furnace, which had been developed from the pot-test facility, was available, and it was decided that tests should be conducted in that furnace before the 200kW facility was modified.

Figure 3 shows the design of the furnace, which uses the same type of magnesia crucible as that used in the other small-scale experiments. The aim in these tests was: determination of the oxygen and nitrogen contents of the alloy produced under air-free conditions as well as the effect of iron additions on the concentrations of these elements. Table 10 compares the composition of the metal produced in three tests in the sealed furnace with that of three alloys produced in the unsealed furnaces but having similar titanium and iron contents.

PRODUCTION OF FERRO TUNGSTEN

Ferro-tungsten as well as Tungsten Melting Base (TMB) which is made from secondary raw material is mainly used to improve the properties of steel. Tungsten as an alloying element forms stable carbides and therefore increases the hot strength and wear resistance of steel. Such steel (high-speed steel) is needed to produce high speed cutting tools that can be used up to temperatures of about 600°C. Besides this the tungsten will increase a number of other properties like the hardness, yield strength and the ultimate tensile strength.

A combination of the carbo- and metallo-thermic process using both carbon and ferro-silicon as a reducing agent are used to produce a ferroalloy with high tungsten content. The process is carried out in three successive stages in an electric are furnace. In the first stage, a tungsten trioxide slag is produced that is furthering reduced with ferro-silicon in the following stage. The third and final stage is needed to increase the tungsten content by refining the low-tungsten metal from the second stage by adding tungsten concentrates.

The metallo-thermic process is less valid from an economic viewpoint because the process requires very pure and therefore expensive raw material. In order to keep the process self-sustaining a mixture of silicon and aluminium is normally used as a reducing agent. The metal can be recovered from the furnace vessel after cooling and removing of the furnace linings. According to the economic disadvantages the metallo-thermic production of ferro-tungsten is today only suitable if there arc special customer requirements.

Tungsten Melting Base (TMB)

Tungsten Melting Base (TMB) is a tungsten alloy that is produced from secondary raw material. The main sources are different kinds of tungsten metal scrap. The TMB production is only a re-melting and alloying process, which can take place in an electric arc furnace. The fact that more and more tungsten scrap is available on the market increases the importance of the re-melting process that requires less energy as the primary smelting process.

Ferro-titanium

Ferro-titanium can be produced either from primary and secondary raw material and is used for a variety of different purposes. As an alloying element it increases yield strength and reduces the cracking tendency. In the production of stainless steel with a high chrome and nickel content, ferro-titanium is used to bond the sulphur.

For the production of ferro-titanium the primary raw material titanium oxide containing minerals such as ilmenite are used. The reduction occurs commonly by the metallo-thermic process because the carbo-thermic reduction produces an alloy that contains too much carbon and is therefore not interesting as an alloying element in the steel industry. The production takes place as a batch process in a refractory lined crucible or in an electric furnace depending on the process variation.

PRODUCTION PROCESS OF FERRO SILiCON

In order to achieve good process results the selection of the raw material is due to some quality requirements. The thermal strength of the quartzite for example is of special importance, because it is connected to the gas permeability of the charge where too much fine sized material may prevent gas flow. The carbon quality is important for the environmental performance of the process, because the coal and coke contains normally sulphur and some other unwanted elements. If for instance carbon contains mercury or other vaporous elements, they will evaporate in the process and will be transferred as part of the off-gas into the environment.

Production of Ferro-silicon, Silicon Metal and Silico-calcium

Raw material is normally supplied to or closed to the plant by truck and train. Several ferro-silicon and silicon plants are located near the sea or a river where boats are mainly used for transportation of raw materials and products. The loading and unloading of raw material is done with the use of crane grips, front-end loaders or dumper trucks.

The different raw materials that are used for the Si, FeSi and SiCa-production are preferably stored on hard surfaces in order to prevent contamination. The reductants are normally stored indoors, to avoid the material from humidity caused by rain. Some of the reductants can have self-igniting characteristics. In these cases, appropriate ways of surveying have to be implemented to avoid self-combustion, e.g. charcoal or coal with a high content of volatile matter and woodchips.

Ferro-silicon, silicon metal and silicon-calcium are commonly produced in low-shaft three phase submerged electric arc furnaces. The electric arc furnaces can be of the open or semi-closed type. The furnace normally rotates e.g. once a week, in order to connect the reaction areas around each electrode tip. This homogenises the molten metal in the furnace and saves 5 to 10% of electric energy. The rotation gives rise to some difficulties in obtaining good capture efficiency of the fugitive emissions at the tap-hole as the location of the tap-hole will rotate with the furnace. A typical electric arc furnace for the production of ferro-silicon is shown in the following figure.

Oxidising Treatment with Gaseous Oxygen/Enriched Air

The limitations of the process are that the impurities, such as, aluminium and calcium in 74 to 76 percent ferroalloy should not be more than 0.45 percent and 0.20 percent respectively. Because of the patented nature of the process the information is not available in detail. However the patent claimed that there is no substantial silicon loss.

Refining with Chlorine Gas

Wise reported in 1960 the refining of ferro-silicon by injecting chlorine deep inside the ladle of molten bath. Chlorine injection was carried out by hydraulically operated dispenser tubes. The author reported that chlorine requirement was of the order of 30 parts per 1000 parts by weight of the melt. During the process the silicon level got reduced because of volatilisation to silicon tetrachloride and calcium chloride level thus formed cannot be removed completely. Silicon level had to be replenished for adhering to the required composition. Further removal of aluminium level to less than 0.1 percent was not possible.

The Oxygen Injection Method

One kg melt of FeSi-75 was refined in an induction furnace by the addition of 20-25gms of lime powder followed by the injection of oxygen at the rate of 80-90 litres per hour for about 40 minutes at 1450-1500°C. The slag of composition $CaO.Al_2O_3.2SiO_2$ was formed and floated at the top of the melt. The slag was removed and refined metal was separated. Mere the aluminium level in FeSi-75 was brought down from 1.4% to 0.20%. Graphite dispenser tube was used for the injection of oxygen gas and silicon loss was about 3 to 5%.

Types of Slag

The term SLAG for the molten oxide is analogy from the production of other metals, where the ore normally contains more of impurity elements that are less nobler than the metal that is to be produce. The main metal is extracted as metal phase and the less noble impurities are left as slag which is normally the mix of impurity oxides and being in molten form can easily be separated from the metal phase.

SiC with Si at the Bottom

When sufficient heat is available, all the oxygen in the bottom deposit will evaporate, while pure Si-SiC will be left to form deposits at the furnace bottom at normal operating conditions. An optimum carbon content in the burden gives a maximum silicon recovery at operational conditions. If the carbon content is lower than the optimum, all the SiC intermediate is consumed, but the loss as SiO is higher than at the optimum. Some SiO is lost even all the optimum carbon content. If the carbon content is increased beyond the optimum, the loss as SiO will decrease, but the silicon loss as SiC more than balances the gain. This SiC is deposited at the furnace bottom and when deposit becomes too large it will obstruct the operation severely. The optimum carbon content depends on the state of the furnace. Operation needs to be observed continuously to determine the carbon input close to optimum.

Controlled solidification of Ferrosilicon

INTRODUCTION

Work on process optimisation has illucidated the problem of fines generation during this crushing process. Fines, defined as having a particle size under 10mm, are likely to be trapped in the slag, while coarser materials would need a longer dissolution time. Thus fines resulting from any crushing process can be sold only to a limited extent or at a low price.

EXPERIMENTAL WORK

Equipment

A Bridgman furnace has been used in order to allow for a certain uncoupling of the growth rate and the temperature gradient. Such a furnace has a hot and a cool zone as seen in figure 1. The distance between these zones and their temperatures determines the temperature gradient. A crucible is translated through this temperature field at a uniform rate (growth rate).

The heater is made of an induction coil connected to a 12 kW high frequency generator. The frequency varies from 500 kHz to 1,3 MHz depending on the dimensions and the physical properties of the workpiece and has not been measured in this study. Indirect induction heating has been achieved by surrounding the sample by a susceptor. The susceptor consist of a $MoSi_2$ tube with the same length as the coil inside which it is placed. It is believed that the susceptor absorbs all the power of the induction field thereby efficiently shielding the sample as it is heating it. The penetration depth of the induction field has been calculated to be 0,5mm and the thickness of the susceptor is about 12 mm.

Casting

The sample is molten in the hot zone of the furnace and solidifies before it enters the cold zone. Samples are typically 20 cm long and have a diameter of 8 mm. They are prepared from a mixture of solar-grade silicon and pure iron that are molten by induction heating in a graphite crucible, and then cast by sucking into quartz glass tubes by vacuum. Pure calcium and pure aluminium are added for the impurity containing ferrosilicon. The carbon contamination of the sample is estimated to be below 0.012wt% C at 1820°K according to previous work.

Distribution of Aluminium and Calcium

Elemental mapping in an electron micro-probe has been carried out to determine the distribution of the additional elements Al and Ca. The calcium distribution could not be analysed probably because of a too low concentration. The aluminium distribution has been found to be dependent on the growth rate and is probably related to the growth of the intermetallic cells. In the samples containing very clear intermetallic cells, aluminium is segregated on the boundaries of these cells. At low growth rate, aluminium seems to be more soluble in the intermetallic. In any case, the solubility in silicon is very low and not detected by this method.

PRODUCTION OF FERRO NICKEL

Raw Materials

Ferro-nickel (FeNi) as well as ferro-chrome is the major alloying agent in the production of stainless steel. Laterite ore is the main raw material. Laterite ore is characterised by a relatively low nickel content (1.2-3%) and a high moisture content (up to 45%) together with chemically bound water in the form of hydroxide. Besides laterite ore, coke or coal is the second raw material that is needed in the ferro-nickel production. Coke or coal is used as a reducing agent because the ferro-nickel production takes place by a carbo-thermic process. FeNi can also be produced from secondary raw materials, such as spent catalysts and sludge from the galvanising industry.

Production of Ferro-Nickel from Primary Raw Material

The production of ferro-nickel from primary raw material is carried our exclusively by the rotary kiln-electric furnace process. As mentioned before the raw material carries a significant amount of water, therefore the first step of the process is a drying operation. Drying normally takes place in a directly fired rotary dryer where the moisture content can be reduced from about 45 to 15%. Further drying below 15% should be avoided in order to keep the dust generation in the subsequent calcining and smelting process as low as possible.

The next process step is homogenisation where the different ores are mixed with coal and pelletised dust, which is recycled from the main process. The dry feed mix is then fed to a rotary kiln. The rotary kiln is used to de-hydrate the ore by calcination and to pre-reduce the nickel and iron oxide. The process takes place at about 900-1000°C. The calcining and pre-reducing process results in a furnace feed which contains about 40% of the nickel as a metal and the iron content in form of iron (II)-oxides.

The hot pre-reduced calcine can be introduced directly to the smelting furnace or by insulated containers. The containers may be used for two reasons, first to conserve the heat and second to add coke or coal required for complete reduction before they are discharged into the electric furnace, where or melting and final reduction occurs.

Ferro-nickel smelting today only takes place in electric arc furnaces. In the electric furnace the reductive smelting operation occurs by the combined action of carbon electrodes and added solid carbonaceous reductant. The slag melting temperature in the ferro-nickel smelting process is strongly dependent on the FeO-content. The operation mode of the furnace therefore changes if the slag melting temperature is above or below the melting temperature of the metal. If the melting temperature of the slag is higher than the melting point of the metal the furnace can easily be operated with a covered bath. In this case the electrode tips are not immersed in the slag and the final reduction of the nickel and iron oxides takes mostly place in the hot charge which covers the slag layer. If the melting temperature of the slag is below the melting temperature of the metal the furnace is more difficult to operate. In order to reach the melting temperature of the metal the electrodes should penetrate deep in to the slag layer. The highest bath temperature will then be around the electrode tips where smelting takes place in the slag-metals interface. These operating conditions result in a high generation rate of CO-gases, which requires an open bath surface around the electrodes.

To reduce a high content of nickel oxides commonly the burden contains an excess proportion of carbon. These also increase the amount of iron that will be reduced and the final carbon content of the crude ferro-nickel. To reduce the iron and carbon content a further refining step is necessary. To avoid further refining several process improvements had been made. For instance in the "Ugine Ferro-nickel Process" no reductant is added. The electric furnace produces a molten ore, which is reduced to ferro-nickel by using ferro-silicon in a further ladle furnace. In the "Falcondo Ferro-nickel Process" a shaft furnace is used instead of a rotary kiln. In the shaft furnace a briquetted ore is reduced with a reducing gas (low sulphur naphta). The subsequent electric furnace is then only used to melt the metal and to separate it from the slag.

Ferro-nickel produced by the conventional process needs further refining. Besides the reduction of iron and carbon, the impurities like sulphur, silicon and phosphorus should be removed. For ferro-nickel refining a variety of equipment is available e.g. shaking reaction ladle, induction furnace, electric arc furnace and oxygen blown converters. The purified ferro-nickel is cast into ingots or granulated under water.

The dust containing off-gas from the rotary kiln, the electric arc smelting furnace and the refining step is treated by an appropriate abatement system. The dust content can be pelletised and recycled to the raw material blending station. A flow sheet of a ferro-nickel production is presented in the above figure.

Production of Ferro-Nickel from Secondary Raw Material

FeNi can also be produced from nickel containing residues used as secondary raw material. These residues, mostly spent catalysts from the grease production, are burned in a rotary kiln in order to concentrate the Ni-content as Ni-oxide in the flue dust. The flue dust containing off gas is cleaned in a membrane bag filter, where the collected dust is used as the raw material for the smelting process. The production of FeNi then takes place in a submerged electric arc furnace. The molten alloy is tapped, granulated in water and packed in drums or big-bags for supply.

"Ferronickel Ladle Furnace Refining Process"

Experiences in FeNi-Smelters and Rectangular Furnaces

To this date, SMS DEMAG has supplied most of the large-scale Ferro nickel furnaces world-wide. These furnaces are in Venezuela, New Caledonia, Greece and Macedonia. During the last 4 decades, we supplied around 40 furnaces.

It should be mentioned that the furnace in New Caledonia represents the best available technique for producing FeNi. The customer has already announced his intention to purchase a second furnace with an identical power rating of 99 MVA.

CALCINE TRANSPORT SYSTEM

The availability of two container transfer cars and two hoists for each bin line ensures interchange ability of these components and therefore allows uninterrupted furnace operation even if one of the transfer cars or hoists fails.

The solution provides the highest flexibility and allows a clear definition of the paths for incoming raw materials and outgoing products.

This system has proved its effectiveness on a large scale in several of our reference plants and yields the best flexibility.

ADDITIONAL TECHNOLOGICAL HIGHLIGHTS

SMS DEMAG Tapping Machines

The tapping machines are of great importance. SMS DEMAG supplies reliable combined tapping machines (drilling and tapping). We provide a 30-liter and a 50-liter machine. The machines will also be installed in the new rectangular furnaces for Onca Puma in Brazil.

Off-gas System

The process gas produced in the electric furnaces is completely combusted inside the furnace and at the same time by the addition of diluting air cooled down 10 approx. 1,000ºC.

This concept avoids any formation of an explosive mixture of carbon monoxide and air inside the furnace and the build-up of accretions in the off-gas duct due to post combustion. To minimize the capacity of the de-dusting plant, the off gas is routed through a water-cooled duct. After leaving this part of the duct, further cooling of the off gas is effected by hair-pin coolers. Before entering the filter bag house, the off gas temperature is decreased to the allowable entrance temperature by quenching with the secondary fumes collected via hoods above the metal and slag tap holes.

PRODUCTION PROCESS OF FERRO CHROME

The submerged arc furnaces use Soderberg electrodes where the electrode may be formed by hot paste, briquettes, blocks or paste cylinders. The electrode paste is charged on top of the electrode in accordance with its consumption. The material is subject to increased heat as it moves downwards in the electrode column. It melts at about 80°C and bakes at 500°C. To control the smelting process the furnace operation can be based on resistance or current control, so that the electrodes are lifted and lowered when necessary to keep resistance or current constant. This means certain requirements to the electrode sealing to prevent air leakage into the furnace. As an alternative another practice is commonly used where the electrode moves only during slipping and otherwise stand in place.

During the smelting process the metal oxides are reduced by the coke, with metal carbides as the final product. The reduction produces large volumes of CO gas from the reaction zone under the electrode tips. In an open furnace the CO gas is burned at the surface of the furnace. By using a closed, sealed furnace the volume of the off-gas can be reduced by a factor of 50-75 and by the factor of 10-20 in case of a semi-closed furnace. The investment cost for the off-gas cleaning systems for closed furnaces are much lower than for open furnaces. The cleaned CO-gas can be used as fuel for raw material preheating, coke drying and similar processes, substituting oil or other fossil fuels. Energy can be recovered from semi-closed furnaces in the form of steam or hot water.

LC FeCr can also be produced by the so-called Simplex process. In the Simplex process HC FeCr is crushed in a ball mill in order to get a ferroalloy powder. After briquetting the HC FeCr-powder together with Cr_2O_3, Fe_2O_3 the mixture can be de-carburised by annealing at about I350ºC in a vacuum furnace.

Silico-Chromium

Silico-chromium is also used as an alloying element in the steel industry. It can be produced in the same kind of three phase submerged electric arc furnaces as used for HC FeCr production. The reduction of SiO_2 to Si is combined with the generation of huge amounts of CO gas. The high generation rate of CO makes it important to use a porous burden (e.g. gas coke), a semi-closed or closed furnace with an appropriate energy recovery system.

Ferro-Silicon and Silicon Alloys

Ferro-silicon, silicon metal and silico-calcium (SiCa) are used as additives in different industrial activities. As an alloying element, ferro-silicon increases the strength of steel and is therefore used to melt steel that is needed to produce for instance wire-cords for tyres or ball-bearings. High purity FeSi is used to produce high permeability steel for electric transformers. Silicon metal is important as alloying element in aluminium and for the production of chemicals.

DECARBURIZATION TECHNIQUES

Depending upon type and state of oxidizer, the methods of decarburization are grouped as Conventional and non-conventional techniques.

Non Conventional Techniques

Development of AOD and VOD established the status of these processes in stainless steel industries. But problems of high refractory and argon consumption still exist. Hence upon studying several difficulties and limitations of conventional decarburization methods, attention was focused on non-conventional techniques.

Decarburization of Solid Ferrochrome

Ferrochrome with 0.01 to 0.03% carbon is produced from high carbon ferrochrome (6 to 8%) by vacuum heat treatment with an oxidant e.g. iron oxide. In the former U.S.S.R, oxidized ferrochrome was mainly used as oxidant. High carbon ferrochrome is ground to a size of 0.16 mm. Oxidized ferrochrome is obtained by oxidizing

roasting of high carbon ferrochrome with the particle size of up to 1 mm in a rotary furnace at 1475-1525 K. Upon oxidation the product contains over 5% oxygen.

TAPHOLE OPERATION

Temperature Monitor and Control

Monitor—Thermo couples are provided in the refractory during the installation at various places for continuous monitoring of lining condition by recording the temperatures. These temperatures are basis for control of the operations and process.

Control—Increase in the furnace shell bottom temperatures is co-related with penetration of the electrodes, composition of slag and that of the metal. Corrective action consists of controlled slipping and changes in the mix to attain desired composition of the metal and slag, to keep the temperatures under control.
SKIMMING SYSTEM

It was found that inspite of pouring out some metal with the top slag in the first ladle the metal cast in the casting machine had traces of slag. Hence a hydraulic skimming machine was installed to skim away the floating slag from the surface of the metal before casting in the casting machine.

PRODUCTION OF FERROALLOY FROM SECONDARY RAW MATERIALS

Due to the large amount of available secondary raw materials, especially metal oxides from the production of stainless steel, the recovery of ferroalloys, mainly ferro-chrome has become an important part of the ferroalloy industry. The development of the various processes followed the increasing need of the stainless steel manufacturers to treat their waste product in order to reclaim the valuable metal content and to limit or prevent dumping of waste.
Mixing and Drying (Plasma Dust Process only)

After screening, the slag forming agents are analysed in the raw materials in order to determine how much sand or lime has to be added to balance the basicity of the slag. The necessary amount of slag formers are added-predominantly silica sand-together with a approx. 1-10% of water in a high turbulent batch mixer in order to obtain enough free flowing micro pellets.

Submerged arc Furnace Process

The recovery process that uses a submerged electric arc furnace is very similar to the production of ferro-chrome in an electric arc furnace. One installation in the U.S. employs a rotary hearth furnace for the pre-reduction, followed by melting in a submerged arc furnace.

The furnace off gas is dry filtered in a conventional bag filter. The gas is diluted by the ambient air in the open top furnace where the combustion of CO is complete. Typical composition is 90% air (18 to 20% excess O_2), 7% CO_2, and 3% H_2O.

Off-gas cleaning is done in a two-stage bag house. After cooling below 200°C, furnace dust is separated in the first stage and collected for recycling or further processing. In the second stage, absorbent granules (activated carbon or lignite coke) is injected. Volatile metals notably mercury and to a lesser extent cadmium and lead is chemisorbed on the surface of the carbon. The absorbent also traps chlorine compounds including dioxin. This second stage operates below 130ºC. The same bag filter collects the fumes from the tapping process.

A limited amount of water is injected and vaporised in the off gases for temperature control. Process and cooling water are close circuited, the net consumption being released as steam in the furnace flue gases and by evaporative coolers.

Therefore, the process does not produce liquid effluents. About 60% of the water consumption is insured by the collection of rainwater falling on the industrial site (ground and buildings).

The liquid slag is separated from the metal by gravity. The use of multiple cascades affords virtually complete separation. The low basicity of slag (0.7 to 0.8) insures the formation of stable silicates, which are non-leaching. Prior to shipment, chemical composition and leaching tests are performed to qualify each production lot. The slag is used in various construction applications after the appropriate down sizing.

The alloy is cast in iron moulds. The pigs weight 2 to 4 tonnes each. The free flowing slag is collected in an open pit where is solidifies. After the solidification of the metal, the ingots are broken in a few large pieces with a hydraulic hammer in order to facilitate shipment and remelting. Because of its nickel content, the metal is relatively tough (not brittle) contrary to most ferroalloys. It requires no further processing and is apt to bulk transport by truck or rail cars.
Plasmadust Process

After the pre-processing steps secondary raw material as it is also used for the submerged arc process is pneumatically transported by means of a closed vacuum system from the raw material preparation building to the furnace building.

Coke is charged from the top of the furnace in regular intervals. The coke column acts as reductant and filter for the gas being led out of the furnace. Due to the equal heat distribution in the furnace and its height a high yield can be achieved in terms of the reduction of the valuable elements Ni, Cr, Mo, Fe and a comparatively low carry over into the gas-cleaning step. Before tapping is reached, raw material feed is injected in the shaft. In regular intervals the furnace is tapped by drilling a hole at the bottom of the furnace similar to the procedure on blast furnaces.

About 50% of the process gas is re-circulated into the plasma generators through a compressor and used as heat transfer gas. Since a short time also the mercury emissions in the gas stream after the flare are measured continuously on-line.

The slag is separated from the metal by gravity and skimming the slag from the metal. The inert slag flows into a pit where it is regularly dug out and crushed at the same time. Then, the slag is separated externally from metal pieces. By experience, the basicity is approx. 1.0 (CaO, SiO2) so that this kind of slag product can

be sold as a non leaching material useful for road construction. Long term large scale leaching tests have been made, in which slag from the production was exposed to rain water during 1.5 years.

PRODUCTION TECHNIQUES OF FERROALLOYS

General

Ferroalloy is an alloy of iron with some element other than carbon. Ferroalloy is used to physically introduce or "carry" that element into molten metal, usually during steel manufacture. In practice, the term ferroalloy is used to include any alloys that introduce reactive elements or alloy systems, such as nickel and cobalt-based aluminium systems.

Chromium provides corrosion resistance to stainless steels. Manganese is essential to counteract the harmful effects of sulfur in the production of virtually all steels and cast iron. Silicon is used primarily for deoxidation in steel and as an alloying agent in cast iron. Boron, cobalt, columbium, copper, molybdenum, nickel, phosphorus, titanium, tungsten, vanadium, zirconium, and the rare earths impart specific characteristics and are usually added as ferroalloys.

Exothermic (Metallothermic) Process

The exothermic process is generally used to produce high-grade alloys with low-carbon content. The intermediate molten alloy used in the process may come directly from a submerged electric arc furnace or from another type of heating device. Silicon or aluminum combines with oxygen in the molten alloy, resulting in a sharp temperature rise and strong agitation of the molten bath.

ALUMINOTHERMIC REDUCTION OF OXIDES WITH LIQUID START

Description

The aluminothermic reduction process (ATR) has efficient application in several metallurgical melting processes for production of alloys and ferroalloys with usage of the oxidized raw materials including the secondary ones as the basic charge components.

The melts were done without adding of expansive titanium metallic compounds according to the current ATR technology with a solid start. As the result the produced ferroalloy has lower content of the dissolved gases (%, 0.8 O and 0.001 N) then that is produced by the traditional ATR (%, 2.O and 0.5 N) or even from the metallic compounds (%, 2.O and 0.12 N).

Process Selection

The selection of the optimum process for a given product demands a lot on experience. Many factors must be considered including scale of operation, product quality demands, alloy reactivity etc. Unless the equipment vendor has previous experience of the precise alloy and product in question, trials of different processes are highly desirable.

ARTIFICIAL VISION SYSTEM

The artificial vision system consists of two cameras (one working and another stand-by) that control the vibration of the casting machine. The operation can be explained this way: when the metal covers the rectangular area that it is shown in the figure 5, the vibration is activated and after few seconds this area is ready for receiving new metal.

NEW IMPROVEMENTS OF THE CASTING MACHINE

We continuously develop new ideas to keep this machine as cutting-edge technology and make it even more cost effective. One of these ideas is the installation of a grinder at the end of the second iron table to achieve lower granulometries.

In the next installation we have proposed to set up a new grinding system which would permit to automate in one machine the process of casting, cooling and crushing of ferroalloys.

ADVANTAGES OF THE CASTING MACHINE

The main advantages of the casting machine are the following ones:

From the Metal Quality Point of View

It is well known that the solidification processes are very important for the alloy structure and hence the qualities of the alloy. Normally, rapid solidification leads to small grains and high alloy strength. In the Ferroatlantica's Casting Machine, the solidification occurs fast. Such fast cooling results in a very homogeneous product that could improve the performance of the same in certain downstream processing.

APPLICATION OF FLUID BED IN FERROALLOY INDUSTRY

INTRODUCTION

Some time ago Mintek identified a trend in the mineral industry, one of increasing use of finely sized (less than 3 mm) concentrates rather than huge chunks (greater than 50 mm) as feed in pyrometallurgical operations. This trend reflects the need to process ore deposits of ever-lower grade. Fluidized beds are ideally suited to the processing of these finely sized raw materials.

Atomisation of Ferroalloys

THE ATOMISATION PROCESS

Atomisation is the breaking up of liquid into droplets if a molten material is atomised into droplets, these normally cool rapidly to produce solid panicles. Thus one could say that granulation and atomisation are conceptually identical, differing only in the size of particles produced.

POLLUTION CONTROL IN FERROALLOY PRODUCTION

Introduction

Industrialisation and pollution control measures go hand in hand for the socioeconomic progress of a country since pollution is a sign of inefficiency in industrial production. In recent years, environmental aspects with respect to air and water pollution have assumed special significance in ferroalloys production both in developed and developing countries. The stringent environment pollution control legislation in developed countries have necessitated the development and adoption of appropriate pollution control systems in the plants, and greater awareness has been created in developing countries for pollution control in ferroalloys production.

Process of Pollution Control in Ferroalloys Production

The air pollution control in the ferroalloy industry is carried out by adopting the application of pollution control equipment, either singly or in combination, depending on the plant and other considerations. Various processes of pollution control are as follows :

1.   The smoke gas from a ferroalloy plant is cooled in ambient air coolers and the coarse particles are taken out in a cyclone placed before the main fans. Then the smoke gas is cleaned in standard bag house filters. The filters have proven to be very effective. The dust collected is pelletised with water. In the case of ferro-silicon and silicon metal plant, the silicon dust pellets so formed can be used in a cement plant.

2.   In high carbon ferro-manganese and silico-manganese production, where the furnaces are closed type, the gas is cleaned with venturi scrubbers usually in two stages for either drying off the ores and carbon reductants or preheating the laddles and power generation. The collected dust of manganese ore in the slurry is recovered, pelletised and recycled into the furnace and the clarified water is fed to the existing water circulation system or let out.

Conclusions and Remarks

During last three decades there is increased awareness of pollution hazards among the people and various measures are being taken to effectively protect ecology by pollution control from ferroalloy plans also. It is extremely essential to have the knowledge of the process of ferroalloy production, that produces pollutants, for an efficient selection of the control equipment. Emissions from ferroalloy furnaces can be extracted by various ways. Fumes can be captured right at the source or when they come out of the furnace.

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