

MANUFACTURE IN INDIA OF FERRO-ALLOYS USED IN ALLOY STEEL INDUSTRY

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Abstract

The paper starts with an outline of established methods of manufacture of different ferro-alloys required for making alloy steels with a comparison of their merits as judged by the products made. The ferro-alloys discussed include those based on manganese, chromium, silicon, tungsten, vanadium and phosphorus and of different qualities and grades. The position of the production of the individual ferro-alloys in India is discussed and the great importance emphasized of expanding production of those required in relation to the expansion of the Indian iron and steel industry. A programme of ferro-alloy production is outlined, with discussion of availability of raw materials, manufacturing capacity and economic factors.

Introduction

A FERRO-ALLOY is an alloy of iron and other special element or elements. Iron merely serves as a vehicle to carry the alloying element. The functions of a ferro-alloy are threefold: (i) to deoxidize and clean the molten bath, (ii) to control the solidification of the metal, and (iii) to give the end product the desired physical characteristics such as tensile strength, toughness, ductility, hardenability, corrosion resistance, etc. The maximum consumption of ferro-alloys in the iron industry is for the purpose of deoxidizing and cleaning the steel.

Methods of Manufacture

There are mainly three established methods of manufacturing ferro-alloys: (1) blast furnace method, (2) electric furnace method, and (3) aluminothermal method.

(1) *Blast Furnace Method* — Spiegel, high-carbon ferro-manganese (containing up to 80 per cent Mn), and low grades of ferro-silicon are mostly manufactured in the blast furnace. Most of the world's supplies of standard high carbon ferro-manganese are from blast furnace. Smelting of manganese ores in blast furnace differs from that of iron ores in many respects. The heat of reduction of manganous oxide is greater than that of ferrous oxide (96.7 K.cal. against 64.3 K.cal. per mol. metal). Thus the blast furnace will have to operate at higher temperatures in order to reduce manganous oxide to manganese. Also, in order to avoid high manganese losses in the slag, the slag is kept more basic. These two factors involve higher coke consumption. Manganese has greater tendency to vaporize, and hence it is imperative that the stack temperature should be low. The charge must, therefore, have uniform gas distribution throughout the furnace area. This is possible only by using lumpy ore and dense metallurgical coke. The phosphorus of the ore goes completely into the metal and cannot be removed by any cheap practical method, and so the phosphorus content in the ore should not exceed 0.3 per cent. The silica of the ore and ash of the coke must be balanced out by extra coke charge, which in turn increases the slag volume and manganese losses in the slag. Thus the silica in the ore and ash content of the coke should be as low as possible.

(2) *Electric Furnace Method* — The use of electric furnace in ferro-alloy production started in 1890, with the discovery of calcium carbide. Development of electric

furnaces by Heroult, Girod and Stassano laid the foundation of the industry, which has been advancing greatly. Practically all ferro-alloys can be manufactured in electric furnaces. Ferro-chrome, ferro-tungsten and others are manufactured exclusively in the electric furnaces. Even ferro-manganese, which was largely manufactured in blast furnaces, is now being made in electric furnaces, in countries where electric power is cheap.

In electric furnaces the temperature required to carry out the reduction is generated by electrical energy; the coke is charged for reduction purposes only. As the electric furnaces are shallow, almost any kind of reducing material and various types of ores can be used. In the blast furnace, on the other hand, only good quality dense metallurgical coke and lumpy ores can be used. The greatest advantage of the electric furnace is its flexibility, i.e. the temperature of smelting can be varied according to the requirements so that any type of ferro-alloy could be manufactured, keeping the volatilization and dust losses to the minimum.

The development of electric furnaces began with the single-phase type furnaces which very soon led to the large three-phase type reduction furnaces. The first three-phase furnaces were of open type. Their three electrodes were arranged in line. The electrodes of the furnaces are buried in the charge so that the electrical energy is converted to heat by the resistance of the charge.

At first amorphous carbon electrodes were used, which were later replaced by Soderberg continuous self-baking electrodes. Because of this development the design of closed-top electric furnace could be made possible. A closed-top furnace offers two principal advantages. First, the heat generated by the burning of carbon monoxide at the top of the furnace can be avoided, and, secondly, the gas can be collected and used for heating, power generation or for chemical processes.

In between these two types (open and closed top), the semi-closed furnace is also

used in the manufacture of ferro-alloys. In this type of furnace, water-cooled gas ducts are embedded in the charge through which carbon monoxide gas is exhausted. Only a part of the total quantity of gas generated during the smelting processes can be obtained in this way.

(3) *Aluminothermic Method* — In this method the reduction of oxide is carried out by aluminium, the oxygen of the ore combining with aluminium to provide heat. The speed of reaction is controlled by adding, to the calculated mixtures of oxides and aluminium, accelerators such as barium peroxide and potassium chlorate, or retardants such as steel turnings, limestone or slag. The requirements for carrying out the manufacture of ferro-alloys by this method are: (1) the charge must be correctly calculated and weighed, (2) all the constituents must be mixed well; naturally these must be in powder form.

The greatest advantage of this method is that it is simple in operation. The thermite pots are either cylindrical or slightly conical. The pots are generally lined with magnesite. For some alloy manufacture, the pot is filled completely with the charge which has been accurately weighed and mixed, and fired from the bottom, but in the manufacture of most of the alloys ignition is started by a mixture of aluminium powder and sodium or barium peroxide, and then charge is fed slowly on top of it.

As large quantities of aluminium are required for the production of alloys, this method proves expensive except, of course, when very small quantities of ferro-alloys are required or the alloys are required to be carbon-free. Ferro-alloys of vanadium, molybdenum, tungsten and titanium are usually manufactured by this method.

Manufacture of Ferro-manganese

Next to carbon, manganese is the most important element in the smelting of iron; without manganese no steel could possibly

be made. In the steel melting process, manganese prevents excess oxygen uptake in the melt. Also, at the end of the refining process, the oxygen absorbed and the sulphur present in the melt are converted into less harmful forms, and thus the steel becomes forgeable. Besides, manganese is an important alloying element in various alloy and special steels. Manganese additions in the steel melting processes are generally made in the form of ferro-manganese, which is manufactured in various grades as standard ferro-manganese, medium-carbon ferro-manganese and low-carbon ferro-manganese.

Ores used in the manufacture of ferro-manganese are graded as follows: 48 per cent Mn and above as I grade, 45-48 per cent Mn as II grade and below 45 per cent Mn as III grade, and the price of the ore is governed by this grading of the ores. The established manganese deposits of the world would be about 500 million tons; of this, U.S.S.R. has 250 million tons, India 100 million tons, Brazil 50 million tons and Gold Coast 30 million tons. Thus India occupies the second position as regards manganese ore deposits. The deposits at present being worked are in Singhbhum (Bihar), Panchmahal (Bombay), Balaghat, Bhandara, Chhindwara and Nagpur (Madhya Pradesh), Indore (Madhya Bharat), Visakhapatnam, Sandur (Madras), Shimoga (Mysore State), Bonai, Keonjhar and Koreput (Orissa), and Banswara (Rajasthan). India is at present exporting manganese ore at the rate of approximately 1 million tons per annum. The total value of these exports is approximately Rs. 14 crores. Instead of exporting the ore, if India builds up her own ferro-manganese industry, about 300,000 tons of ferro-manganese could be produced from the ore which is being exported. At present only the Tata Iron & Steel Co. Ltd. are producing ferro-manganese for their own consumption. They are using higher grades of ores from Orissa. The ferro-manganese produced is low in manganese and too high in phosphorus,

so that it cannot be exported. The composition of Indian-made ferro-manganese is:

| | <i>Per cent</i> |
|------------|-----------------|
| Manganese | 70.0-75.0 |
| Carbon | 6.0-8.0 |
| Phosphorus | 0.5-0.6 |
| Sulphur | 0.027 |
| Silicon | 0.550 |

The permissible maximum phosphorus in high-grade ferro-manganese is 0.35 per cent. The high phosphorus content in the Indian product is mainly due to the high phosphorus content in the Indian coke. The low percentage of Mn in the ferro-alloy is due to the low manganese/iron ratio, and the iron content in the coals (1.25-2.30 per cent Fe) which dilute the ferro-manganese. The Mn/Fe ratios of manganese ores of the major production centres of the world are: U.S.S.R., 4.0-6.0; India, 5.5-7.5; Gold Coast, 10-13; and Brazil 12-13.

Factors that govern the making of standard grades of ferro-manganese acceptable for export are:

(a) *Manganese ore*

1. The manganese/iron ratio should be as high as possible.
2. The phosphorus content should not exceed 0.10-0.13 per cent.
3. The silica and alumina contents should not exceed 8 and 10 per cent respectively.

(b) *Coke*

1. The fixed carbon content should be 77 per cent minimum.
2. The iron and silica contents should be 1 per cent and 10 per cent maximum respectively.
3. The phosphorus content should be 0.65 per cent maximum. With the types of coke now used in the production of pig iron, it is not possible to manufacture a high-grade ferro-manganese in the blast furnace. If the Giridih coal which is low in phosphorus (0.02 per cent) is exclusively utilized

for the production of ferro-manganese, it will be possible to produce ferro-manganese of required standard.

By trying out various blends of Jamadoba coal and other grades such as Bararee, it may be possible to produce a coke suitable for ferro-manganese production.

At the present rate of consumption about 18-20 thousand tons of ferro-manganese (manganese content being 70-75 per cent) are required per annum. When the Rourkela and Bhilai plants go into production, and when the expansion programmes of the Indian Iron & Steel Co. Ltd. and the Tata Iron & Steel Co. Ltd. are completed, the country's demand for ferro-manganese will go up to 40,000 tons per year. If the target of the steel production by the end of the next Five Year Plan is fixed at 4.5 million tons of ingot steel, the quantity of ferro-manganese required for the production of the above quantity of steel would be about 67,500 tons per year.

At present only the Tata Iron & Steel Co. Ltd. are producing ferro-manganese in blast furnace for their own consumption using higher grades of ores from Orissa. The average annual production is about 15-17 thousand tons per year.

The other method of producing ferro-manganese is by electric furnace. For producing high-carbon FeMn, the three-phase low-shaft furnace with round hearth is generally used. The burden consists of ore, coke or bituminous coal and lime in the form of limestone, with an addition of about 20 per cent burnt lime. The ratio of coke to ore is about 1:3. The furnace operation is continuous. The energy consumed per ton of 80 per cent FeMn amounts to 3000-3500 kWh./ton. In the electric furnace about 1500 lb. of coke are used against 2.25 tons in the blast furnace for the production of 1 ton of ferro-manganese. Since more than 60 per cent of the phosphorus in the ferro-manganese made in the blast furnace comes from coke (Indian coals are very high in

phosphorus), the manufacture of ferro-manganese in the electric furnace is of great interest to India. In electric furnace only one-third of the coke used in blast furnace is required for the reduction of the ore. If coke of suitable quality is not available, any other suitable form of 'carbon' could be employed. The cost of electric power is the most important factor. Norway, Sweden and Canada manufacture ferro-manganese in electric furnaces for export from imported manganese ores.

No ferro-manganese is being produced in electric furnaces in India. Recently schemes have been sanctioned and licences issued under the Industries Act for setting up ferro-manganese plants to produce standard ferro-manganese of 78-80 per cent Mn and phosphorus not more than 0.35 per cent.

| <i>Name</i> | <i>Capacity (tons p.a.)</i> | <i>Location of plant</i> |
|---|---------------------------------|------------------------------|
| 1. Jeypore Mining Syndicate | 12000 | Jeypore |
| 2. Mysore Iron & Steel Works | 1800 | Bhadravati |
| 3. Cambata Industries, Bombay | 30000 | Tumsar (M.P.) |
| 4. Indian Ferro-alloys Ltd., Samastipur | 20000 | Comharria (Bihar) |
| 5. Tata Iron & Steel Co. Ltd.* | 30000 | Joda (Orissa) |
| 6. Electromet Works Ltd., Bombay* | 12000 | Dandeli (Dharwar) |

It is expected that all the above schemes will be completed at the latest by 1956. Ministry of Commerce & Industry have fixed for the time being a target production of 100,000 tons of ferro-manganese per year, most of which will have to be exported as the present internal demand, as stated above, is only 18-20 thousand tons per annum. They have also decided not to issue licences for further schemes unless any of the parties mentioned above fail to take effective steps to implement their proposal.

*Schemes approved but licences not so far issued.

With the completion of hydro-electric projects, especially Hirakud and Damodar Valley Corporation, which are near the main manganese ore deposits, it will not be difficult to start ferro-manganese production by electric furnaces.

Methods for Manufacturing Ferro-manganese from Low-grade Ores

Extensive investigation work is being carried out, in countries deficient in manganese resources, to beneficiate low-grade manganese ores. Besides, attempts have been made to manufacture high-grade ferro-manganese from Spiegeleisen and manganese-rich slags. So far no attention has been paid in India to utilize the low-grade ores. For every ton of high-grade manganese ore mined, about equal or more tonnage of low-grade manganese ore is discarded. Large dumps of ore wastes have been accumulated at the manganese mines. This waste material, if utilized, will lead to the conservation of our high-grade manganese ores.

Preliminary experiments for the thermal beneficiation of low-grade manganese ores conducted at the National Metallurgical Laboratory have provided useful clues for pursuing the work on pilot plant scale. The process of manufacture has to be carried out in two stages: (1) Production of Mn-rich slag having a minimum Mn/Fe ratio of 6:1 under acid condition at low temperature. The iron oxide is reduced by coal or coke to get pig iron containing all the phosphorus of the ore and the reducing agent. (2) The Mn-rich slag is used as synthetic ore for the production of ferro-manganese.

Krupp-Renn type rotary kiln will be useful for carrying out the first stage. For the second stage closed-top electric furnace will be ideal.

Manufacture of Ferro-chrome

Chromium imparts resistance to oxidation and is used extensively for the production of

stainless steels of various grades. Besides, it is used for high-speed steel manufacture. It is a useful element in the construction of high-strength low-alloy steels.

The main chromium ore deposits occur in Turkey (more than 50 per cent Cr_2O_3), Union of S. Africa (about 45 per cent Cr_2O_3), Philippines, Cuba (low-grade ore 33-43 per cent Cr_2O_3), Yugoslavia, New Caledonia, India, Soviet Union, Sierra Leone, Bulgaria, Brazil and U.S.A.

The chief Indian chromite deposits are situated in the Singhbhum district of Bihar, the Mysore State, in Ratnagiri and Sawantwadi area of Bombay, Krishna and Salem districts of Madras and in the Seriakela and Keonjhar district of Orissa. Amongst these, the deposits at Singhbhum, Mysore and Keonjhar are being worked at present. No reliable estimates of reserves are available; the following figures give only a general indication:

| | <i>Tons</i> |
|----------------|------------------------|
| Mysore | 135,000 |
| Bombay | 67,000 |
| Orissa | 200,000 (20 ft. depth) |
| Salem (Madras) | 200,000 (20 ft. depth) |

The suitability of chromite ores for the manufacture of ferro-chrome depends on chrome content and Cr/Fe ratio. Ore suitable for smelting into FeCr has the composition:

| | <i>Per cent</i> |
|-------------------------|-----------------|
| Cr_2O_3 | 33-56 |
| FeO | 10-20 |
| Al_2O_3 | 10-30 |
| MgO | 3-20 |
| CaO | up to 10 |
| SiO_2 | up to 10 |

For the production of high-grade FeCr the ratio of Cr to Fe in the ore should not be less than 2.8:1, preferably 3:1. Only sufficiently high-grade ore is marketed, without dressing except for handpicking; with disseminated ores, table concentration can be used to produce concentrate containing about

50 per cent Cr_2O_3 . It is not a common practice to beneficiate the chrome ores since, although this may improve the Cr_2O_3 content, it generally does not improve the Cr/Fe ratio. For the production of high-carbon ferro-chrome, a hard and lumpy ore is preferred; for low-carbon ferro-chrome grades, crushed ore is generally preferred.

High-carbon Ferro-chrome — High-carbon ferro-chrome is produced by electrothermal method by reducing chrome ore with carbon. However, in Germany, during the war FeCr was made in blast furnace. The product was low-grade, containing 30-40 per cent chromium with carbon content up to 12 per cent and silicon content up to 7.5 per cent. Only by special working conditions such as very high furnace campaign, extreme crushing of ore and lining the hearth with carbon it was possible, in blast furnace, to produce FeCr with 65 per cent Cr. Tapping of the metal was difficult due to the extreme viscosity of the metal. In recent years experiments have been conducted in low-shaft furnace with oxygen-enriched blast. The oxygen content in the blast was 55-80 per cent. The blast was not preheated.

For electrothermal smelting of chrome ore both single-phase and three-phase furnaces are used. In the Continent three-phase furnace with suspended electrodes is generally used, but in America single-phase furnaces are preferred as it is easier to tap the viscous slag from these furnaces. Composition of the charge depends on the ore quality, carbon content desired in the metal and the yield. Silicon (more than 20 per cent) lowers the carbon content in the ferro-chrome and also reduces the yield of Cr; lime and fluorspar increase the Cr yield, but at the same time the carbon content in the product is also increased. The ore/coke ratio in the charge is 3:4. Furnace lining is generally of carbon, but in Germany magnesite lining is extensively used.

Low-carbon Ferro-chrome — To produce ferro-chrome with less than 2 per cent C high-

carbon ferro-chrome is refined further to reduce the carbon content. Highly refined ferro-chrome is made in two or three steps. The final refining stage consists of oxidizing the Si in low-carbon Si-Cr alloy produced in the earlier stages. Carbon in high-carbon ferro-chrome is reduced by chrome ore in an electric furnace. Silico-chrome method, though tedious, is preferred. In the latter method, for the required low carbon content, the greater part of chromium also is oxidized along with carbon. As such the method becomes more expensive.

The high-silicon metal required in the second stage is produced from chromite ore, quartz and coke. The product obtained has general composition of 10-14 per cent Fe, 40-45 per cent Cr and 40-45 per cent Si. The carbon content does not exceed 0.1 per cent. The higher the silicon content in the intermediate product, the lower will be the carbon content. This product is refined with chrome ore, if necessary with very small additions of lime or limestone. Production of low-carbon ferro-chrome is possible if low-carbon silico-chrome, high-grade chromite ore and electrodes of high purity are available.

In a patented process by Perin a mixture of chrome ore and lime is melted in an arc furnace. This molten mixture is brought into intimate contact with liquid silico-chrome alloy in a ladle. An exothermic reaction between oxides and silicides takes place producing low-carbon ferro-chrome.

In the National Metallurgical Laboratory low-carbon ferro-chrome was produced from Keonjhar chrome ore containing 53 per cent Cr, about 0.8 per cent C and 5-8 per cent silicon. These experiments showed that low-carbon ferro-chrome can be manufactured in India from existing chrome ore deposits.

Low-carbon ferro-chrome finds its main use in the production of stainless steels. In these steels carbon has to be controlled to prevent excess C from precipitating along the grain boundaries and leading to corrosion.

If extra-low-carbon (0.01-0.0025 per cent C) ferro-chrome could be manufactured in India, the costly stabilizers like tantalum and columbium could be dispensed with for the manufacture of stainless steels.

The present requirement of ferro-chrome is very very small as there is still not much production of alloy steel in the country. However, with the expansion of engineering industries such as automobiles, industrial plant and machinery, etc., the requirements of chrome alloy steel would increase. The requirements of standard ferro-chrome containing about 60 per cent chromium for the next few years may not exceed 200-250 tons per year even on a liberal estimate. This estimate is arrived at on the basis that about 4000 tons of chrome steel averaging 2 per cent chromium and about 200 tons of stainless steel bars and rods containing about 18 per cent chromium would be manufactured in the country. If stainless steel sheets, which are getting popular for the manufacture of household utensils and for industrial uses, are planned to be produced in the country, the requirements of low-carbon ferro-chrome would increase further.

At present there is no plant regularly manufacturing ferro-chrome although Mysore Iron & Steel Works had manufactured in the past small quantities of ferro-chrome.

As our requirements of ferro-chrome for the next five years are not large, it may not be economical to put up a plant only for the manufacture of ferro-chrome. It would be advisable to put up a plant for the combined manufacture of ferro-chrome, ferro-tungsten and ferro-vanadium. Bhadravati might be a suitable location for putting up such a plant.

Manufacture of Ferro-silicon

Ferro-silicon is used in the manufacture of all grades of steels and special steels like silicon steels and also in grey iron foundries for making high-silicon acid-resistant cast-

ings. In steel melting silicon serves as a deoxidizing and scavenging agent.

Ferro-silicon includes alloys of silicon and iron containing 10-97 per cent silicon; about 98 per cent Si the alloy is termed as silicon metal.

FeSi containing 10-15 per cent silicon is made in the blast furnace and is used exclusively in grey iron foundries. For steel-making, two grades are in general use, one containing 50 per cent silicon and other containing 75 per cent silicon.

The raw materials for the production of FeSi are quartz, coke or charcoal and steel scrap.

Low-grade FeSi can be made in the usual iron blast furnace. The operation differs in that the blast furnace under FeSi production is worked under higher temperatures, the slag is kept highly acidic, and coke consumption is 2-3½ times more than that for pig iron production.

The composition of blast furnace ferro-silicon is given below:

| | <i>Per cent</i> |
|----|-----------------|
| Si | 10-15 |
| C | 1-2 |
| Mn | 1-2 |
| P | 0.10 |
| S | 0.05 |

As the low-grade FeSi is used only in foundries, its consumption is quite small. All the high-grade FeSi is manufactured in electric furnaces, so that the economic production of high grades of FeSi is linked with the availability of cheap electric power. The main raw material quartz or quartzite is available everywhere in India in sufficient purity. Single and three-phase electric furnaces are used. The modern practice is to use three-phase furnace with three to six electrodes, depending on the size of the furnace. In Norway rotary hearth furnaces are being used which are of 2000-12,000 kVA. capacity. The lining is generally of fireclay bricks, but in modern practice at the melting

zone carbon electrodes are used; for large furnaces Soderberg electrodes are also being used.

Maximum purity of charge is essential for making metallurgically suitable ferro-silicon, quartz should not decrepitate and should contain minimum of alumina, lime, magnesite and alkalies. It should have at least 93 per cent SiO_2 . Ash content of coke should be minimum and phosphorus should be low. Presence of 0.05 per cent P and over 3 per cent aluminium in the FeSi will cause it to disintegrate to powder on cooling and exposure to moisture. Wood charcoal has proved to be best for operation and purity of product. It is said that the use of charcoal brings down the electrode consumption. Steel turnings are used for iron additions. Iron ore has been used by some manufacturers, but it is not generally used for the production of higher grades. Proper sizing and mixing of the charge is essential for good working of the furnace, otherwise due to uneven distribution of the charge the furnace efficiency will go down markedly, and in some cases the charge at the bottom may not be heated up at all. Also heat and volatilization losses increase rapidly. In a good furnace, volatilization losses of silicon should not be more than 12 per cent, and 75 per cent silicon of the charge should enter the alloy. The energy consumption depends on the silicon content required in the alloy, local raw material conditions, operating factors and above all furnace efficiency.

During the Tariff Commission Enquiry in 1953, the country's demand of ferro-silicon was estimated at 4500 tons per annum for the next three years. By the time the Rourkela and Bhilai steel plants go into production and the expansion programme of the Tatas and Indian Iron & Steel Co. are completed, the demand will rise to about 7500 tons per annum.

The only manufacturer of ferro-silicon in India is the Mysore Iron & Steel Works, Bhadravati, whose installed capacity as

accepted by the Tariff Commission is 5570 tons of 70-75 per cent grade per year. They have three electric furnaces, but it is understood that only one big furnace is working on ferro-silicon and the other two furnaces (small) which were installed at Mysore have been shifted to Bhadravati and they propose to utilize them for the manufacture of ferro-manganese in future. It would thus be seen that the installed capacity of Mysore Iron & Steel Works for the manufacture of ferro-silicon will not be sufficient to meet the total demand of the steel industry when the present expansion programme is completed. It is, therefore, suggested that it should be planned to raise the capacity of the Mysore Iron & Steel Works so that it will be in a position to manufacture and supply about 6500 tons per annum of ferro-silicon by the end of 1957. There is scope for this expansion as the quartz, iron scrap and charcoal are readily available. Cheap electrical power is also necessary and no difficulty is envisaged in future when the various hydro-electric schemes now under execution are completed.

If by the end of 1960-61 a production of 4.5 million tons of steel ingots is aimed at, about 12,000 tons of ferro-silicon will be required. Installation of more plants for the manufacture of ferro-silicon should, therefore, be included in the next Five Year Plan. Probably Hirakud Dam area or Bhakra Nangal area would be suitable for this purpose when cheap electric supply becomes available in these areas. Quartz, which is the principal raw material, is available in large quantities in various parts of India.

Manufacture of Ferro-tungsten

Tungsten is used for the production of high-speed steels. It is the only alloying element which gives the 'red hardness' and strength to the cutting tool; though attempts have been made to replace it by molybdenum and vanadium, it has not been possible to

replace tungsten completely by these alloying elements. Tungsten is also an important alloying element in the manufacture of hot-die and cold-die steel for permanent magnets and hacksaw steels.

Tungsten content in the ore is mostly low and rarely exceeds 2 per cent WO_3 or 1.6 per cent W. The most important deposits of the world are in Southern China. The other workable deposits are situated in South Burma, Bolivia, Portugal, Indo-China, Malaya, Australia, Korea, Japan, Spain and South Africa. In the U.S.A. there are small deposits in California, Colorado and Nevada.

India has no tungsten deposits of any great economic interest. The Degana wolfram mines (Jodhpur) which were worked during World War II have been suspended since 1947. The deposits are again being worked by the Government of Rajasthan; 2 metric tons of concentrates containing 60 per cent WO_3 were produced.

The tungsten ore is concentrated by hand-picking, magnetic separation, roasting and finally leaching till 60-65 per cent WO_3 is obtained in the concentrate. This concentrate is used for the manufacture of ferro-tungsten.

High-grade ferro-tungsten is produced by:

(1) *Electrothermal process* — In this process carbon is used as a reducing agent. The product contains about 1 per cent carbon and 75-85 per cent tungsten.

(2) *Aluminothermic process* — The ore is reduced by aluminium and silicon. By this process ferro-tungsten with 0.1 per cent C maximum can be obtained.

Out of these two processes the electrothermal is by far the most widely used wherever there is availability of cheap electric power. However, aluminothermic process is very simple in operation and is used in America where aluminium is quite cheap. In the United Kingdom the process is adopted because there is shortage of electric power.

The melting point of ferro-tungsten is very high. The melting point of iron is lowered

slightly on additions of very small quantity of W and increases rapidly with further additions, at 40 per cent W it reaches 1600°C. Therefore, only up to this limit ferro-tungsten can be manufactured by the melting method in the electric furnace. But in high-speed steel melting FeW containing 80 per cent W is generally used; the melting point of this alloy is about 2500°C. Due to the high melting point of high-grade W alloy, the ferro-tungsten cannot be tapped but is allowed to solidify in the furnace. At the end of the heat the furnace bottom is knocked down and a new furnace bottom is provided for the next campaign.

The furnace charge consists of tungsten concentrate (about 65 per cent WO_3), coke breeze, burnt lime and sand.

The bottom of the furnace (called 'crucible') which is removable is lined with a mixture of powdered graphite, tar and hard pitch. When dry, the crucible is carried under the electrodes. Furnaces used are either single-phase or three-phase.

The bigger furnaces have a capacity of 1000-2000 kVA. The fumes and dust from the furnaces are collected by means of Cottrell type dust collectors. The fumes collected generally contain 5 per cent WO_3 . In modern furnaces the campaign lasts from 72 to 90 hr., with average charges of 1500 lb. The yield is above 90 per cent. When the furnace is completely full, the steel shell is removed, the lining material chipped off, and the block of metal is broken into small pieces after cleaning.

Slag from the ferro-tungsten operation contains 25-30 per cent WO_3 . Tungsten is recovered from the slag by reducing it with coke breeze in another furnace where low-grade ferro-tungsten containing 50 per cent tungsten is obtained. This product is again mixed with high-grade concentrates to get 80 per cent W.

The production of ferro-tungsten by aluminothermic process is easier. The raw material must be pure. Impurities like

arsenic, antimony and molybdenum will be reduced in the smelting operations in total. The charge consists of concentrates and aluminium powder of 20-30 mesh size. The ignition mixture consists of aluminium metal powder and barium peroxide. The process is carried out in a crucible made from foundry sand or in a cylindrical reaction pot lined with magnesite. The charge is generally from $\frac{1}{2}$ to 2 tons. The loss of tungsten in the slag varies between 0.5-1.0 per cent.

The process is further modified by the use of silicon. Eighty per cent of aluminium is replaced by silicon. This reduces the cost of operation.

India has no wolfram deposits of any economic importance. The only possibility for the present is to import the concentrates from the Eastern and Far-Eastern countries like Burma, Malaya, Indo-China, China and Korea and smelt them at such locations where electric energy will be available cheaply. Aluminothermic process can also be worked, but due to high price of aluminium, this will not be an economic proposition.

It has been estimated by the Tariff Commission that the country's annual demand of high-speed steel would be about 150 tons while the demand of hot-die steel containing about 10 per cent tungsten was estimated at 125 tons per year. The demand for ferro-tungsten containing about 50-60 per cent tungsten is, therefore, not likely to exceed 150 tons per year even on the assumption that the above quantity of high-speed steel and hot-die steel is manufactured in the country. At present, there is no production of high-speed steel and hot-die steel as Messrs Tatas have discontinued the manufacture of all types of alloy steels.

As a scheme of the Mysore Iron & Steel Works to manufacture tool and alloy steels including high-speed steels has already been approved in principle by the Government, it would be advisable to start the manufac-

ture of ferro-tungsten at Bhadravati. A plant for the exclusive manufacture of ferro-tungsten will not be justified as our requirements are very small. However, a furnace can be installed at Bhadravati for the manufacture of ferro-chrome, ferro-tungsten and ferro-vanadium one after the other at successive intervals.

Manufacture of Ferro-vanadium

Addition of vanadium to steel removes oxygen and nitrogen and also increases its tensile strength, toughness and elastic limit. Vanadium was first used in U.S.A. as additional deoxidizer for high-grade structural steels. Amount of vanadium added to general engineering steel is not more than 0.10-0.25 per cent. It is often used in combination with other metals, particularly Mn and Cr, in making special alloy steels. The high-speed tool steels contain 1.5 per cent vanadium.

The greater part (about 90 per cent) of the vanadium extracted is used in the form of ferro-vanadium. Ferro-vanadium is generally added in the ladle in basic open-hearth practice as it oxidizes the melt very rapidly; ferro-vanadium is made in several grades. The commonly used variety contains 35-55 per cent V as this type favours its solution in the steel bath. The higher grades dissolve in steel bath with difficulty, because of low density and higher melting point.

Vanadium is obtained from many sources from which it is chemically extracted. It can be recovered from soot and from petroleum oil refining process. In Germany it is recovered from iron ores. When vanadium-bearing iron ores are smelted, 80-90 per cent of V enters pig iron. This is blown in converters to get vanadium-bearing slag, which is again charged in the blast furnace, and the cycle repeated to get a slag rich in vanadium. This slag is further treated to get V_2O_5 . Countries producing vanadium concentrates in appreciable amounts are U.S.A., Mexico,

Peru, North Rhodesia and S.-W. Africa. In India vanadium-bearing titaniferous magnetic ores are found in Singhbhum district of Bihar.

The raw material for the production of FeV is V_2O_3 or iron vanadate ($FeVO_4$). The material should contain at least 90 per cent of these vanadium compounds. Vanadium pentoxide is obtained from the vanadium-bearing material by chemical extraction. Ferro-vanadium is produced by aluminothermic method or by carrying out the aluminothermic reaction in three-phase electric furnace. Vanadium has high affinity for oxygen, carbon and nitrogen. Therefore, it is very difficult to reduce V_2O_5 by carbon. In spite of this, reduction of oxide of vanadium by carbon is carried out by Vanadium Corporation of America. In a 4000 kVA. three-phase furnace lined with carbon bricks, crushed concentrate is reduced. The product contains 7-8 per cent carbon. This product is refined by the addition of V_2O_5 to the melt. Vanadium from the slag is recovered by additions of aluminium.

Vanadium pentoxide is also reduced by silicon metal. Extraction is carried out in an electric furnace lined with magnesite bricks. An intermediate product containing 8 per cent Si is obtained, which is refined to 1 per cent silicon by additions of vanadium oxide. For getting fluid slag, limestone and fluor-spar are added. The energy consumption is 7500-9000 kWh./ton of alloy — 4000-5000 kWh./ton for melting and 3500-4000 kWh./ton for refining.

Aluminothermic Process — The reduction reaction is carried according to the equation:



The charge consists of vanadium concentrates, aluminium powder, iron scrap and slag from previous melts. The pot walls are lined with crushed vanadium slag and the hearth is lined with magnesite. The charge is slowly fed to the pot in such a way that

no violent reaction takes place; no retardants are used.

The same method is carried out in an electric furnace lined with magnesite. The charge is first filled in the furnace crucible and ignited. The reaction proceeds at a temperature of 2000°C. Heating is continued by lowering the electrodes into the slag. More aluminium granules are added at this stage to reduce the vanadium content in the slag. Towards the end of the process more V_2O_5 is added to reduce the aluminium content of the alloy. For producing one ton of ferro-alloy by this method the consumption of raw materials is: vanadic acid, 1000 kg.; scrap, 320 kg.; Al turnings, 590 kg.; burnt lime, 275 kg.; burnt magnesite, 55 kg.; coke, 11 kg.; electrodes 8.25 kg., and the energy consumed is 1100 kWh.

In India the Tata Iron & Steel Co. Ltd. have taken a patent to manufacture ferro-vanadium from vanadium-bearing magnetite ores. The ore which contains about 3 per cent V_2O_5 is treated to get a vanadium compound. This concentrate of vanadium is smelted in an electric furnace lined with magnesite or dolomite.

A factory was established by the Vanadium Corporation of India at Rairangpur (Orissa) to get V_2O_5 from magnetite ores by crushing and leaching methods, but due to economic reasons the factory did not start work though the pilot plant experiments were a success.

Assuming that 150 tons of high-speed steel and some quantity of alloy structural steel will be required per year, it is estimated that the requirement of ferro-vanadium will not exceed 10 tons a year.

Manufacture of Ferro-phosphorus

Ferro-phosphorus is primarily used as an addition in the manufacture of certain open-hearth steels to prevent sticking of sheets on pack rolling. It is sometimes used for the

manufacture of high-strength low-alloy steels which do not require quenching or tempering. Incorporation of small amounts of P to steel is said to increase strength. The ferrite phase is steel. Additions of ferro-phosphorus are made in iron foundries when very intricate castings are desired.

The chief raw material for ferro-phosphorus is phosphatic rock which comes from the mineral apatite. In India only a small amount of phosphate is obtained from Tiruchirapalli in Madras and Singhbhum in Bihar. The Tiruchirapalli deposits contain 20-30 per cent P_2O_5 and are estimated at 2 million tons up to a depth of 50 ft. The P_2O_5 content of Singhbhum deposits averages 20-25 per cent. The reserves are estimated at 700,000 tons. The entire production from these deposits is used for the manufacture of fertilizers.

Ferro-phosphorus is made in two grades containing 17-19 per cent P and 22-25 per cent P. It is manufactured in electric furnace though the low-grade ferro-phosphorus can also be manufactured in blast furnace. It is not considered desirable to run a blast furnace on ferro-phosphorus, as it will always result in phosphorus contamination after the furnace is switched back to regular iron production. Also, the output of the alloy is very low because of the large amount of phosphorus carried off with the top gases.

Ferro-phosphorus is mainly a byproduct of the phosphorus industry and the phosphoric acid industry. The FeP is formed by reduction of iron compounds present in the rock, silica and coke; the higher the Fe content of charge to the furnace, the more FeP is formed. By adding more iron to the charge the production of FeP can be increased.

The charge consists of phosphate rock, quartz and coke or anthracite coal. The furnace is totally enclosed. Phosphorus vapour and carbon monoxide are drawn off and phosphorus is condensed as a liquid.

The furnace has two tap holes, the lower one for tapping FeP, the higher one for slag.

The furnace is of three-phase type working on 200-300 volts. The electrode consumption is generally 15 lb. per thousand tons of phosphorus produced. Unless there is enough demand for elemental phosphorus in India, the production of ferro-phosphorus cannot be visualized.

Manufacture of FeTi

Ti, considered for long as undesirable accompanying element in Fe, was first used as alloying element in steel-making around 1930. Hence it has a relatively narrow but important field of application for preventing the diffusion of C and as age-hardening element. The former is attributed to its high affinity for C and the insolubility of TiC in solid iron at practically all the possible temperatures of thermal treatment. The latter use is in view of decline in solubility of the compound Fe_3Ti in alpha iron at decreasing temperature. Besides, it has high affinity for N_2 and hence it is a second denitration agent (weaker than Zr), and also for O_2 . The heat of formation of TiO_2 is between that of SiO_2 and Al_2O_3 .

Because of its high affinity and high m.p. ($1727^\circ C.$), production of metallurgically useful FeTi is difficult and costly, and is possible only by electrothermic or metallothermic means. Only low C varieties can be used in the steel industry. FeTi produced aluminothermically gives smudgy surface in cast Ti steels, as the Al content is unavoidable. Because of high affinity alloying is fairly uncertain. Unless appropriate deoxidation and denitration are carried out before Ti addition, the distribution of Ti content in the steel is more or less uncertain.

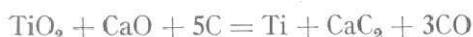
For the production of FeTi, only the following Ti minerals are of interest:

Rutile (TiO_2) (60 per cent Ti)

Ilmenite ($FeOTiO_2$) (31.6 per cent Ti)

FeTi is produced electrothermically and aluminothermically. It is possible to produce in blast furnace a pig iron containing up to 2 per cent Ti. This is used in grey iron foundries. The furnace must be run hot and other conditions must be favourable.

In the electrothermic process, titanitic acid is reduced by C in electric arc furnace, and subsequently refined with TiO_2 if necessary. In an earlier method, iron shavings are first melted and a mixture of Ti ore, coal and slaked lime is added to the Fe bath. The reduction proceeds according to the equation:



The FeTi contains 10-25 per cent Ti and 5-8 per cent C. It is called ferro-carbotitanium and is exclusively used in grey iron foundries.

According to a different electrothermic process, TiSi is first made (50 per cent Ti, 40 per cent Si, 7 per cent Fe and 3 per cent C) and this is refined with iron oxide to get Si-free FeTi containing about 30 per cent Ti and 2 per cent C.

In an electro-alumino-thermic process, Fe shavings are melted together with Al and Ti ore. A part of the Al is used up in Fe reduction. The Al content of melt is lowered by refining with Fe ore.

The disadvantage of all refining processes is that the Ti yield is low.

The major part of FeTi is produced aluminothermically. The charge consists of ilmenite, Al powder, pot. perchlorate and caustic lime. The addition of pot. perchlorate effects an increase in the exothermic character of the reaction by introducing O_2 and thus the reaction in the crucible is completed. Oxidation of Al by titanitic acid gives a heat excess of 26.5 K.cal./g.-atom Al, while in the reaction with KClO_4 , 174 K.cal. are liberated/g.-atom Al.

The charge is mixed well and put in the crucible, made of iron plate with a lining of

graphite plates, over which is provided a layer made up of powdered Ti slag and water glass.

The charge is ignited, and the reaction is over in 15 min. The crucible is removed and cooled for two days. Metal and slag are separated.

The Ti content of FeTi produced aluminothermically can be increased by the addition of Ti-rich slag concentrate to burden. The concentrate is produced by smelting ilmenite with limited carbon in the electric furnace. A concentrate containing 60-75 per cent TiO_2 and 10-15 per cent FeO is obtained.

Using rutile or chemically prepared titanitic acid, we can produce FeTi containing up to 80 per cent Ti and 8 per cent Al.

It would be advantageous to work with a deficit in Al of 94 per cent of the amount theoretically required for the complete reduction. Addition of caustic lime (30 per cent) and preheating the mix to $400^\circ\text{-}430^\circ\text{C}$. are also desirable. In this way, the Al content of 27 per cent FeTi can be brought below 7 per cent and the Si content below 2.7 per cent.

FeTi produced aluminothermically (37 per cent) has a density of 6.2 and melts at 1400°C .

The greater part of FeTi produced is used for alloying corrosion and heat-resistant steels, especially weldable steels.

Ferro-cerium

The only important ore of Ce is monazite sand, and orthophosphate of the rare earths and thorium. Nearly all the world's production of monazite sand is from the beach sands of Travancore and Brazil.

Mischmetal is an alloy of 50-70 per cent Ce, the rest being La and Nd, with traces of other elements.

FeCe consists of mischmetal or Ce with 10-65 per cent Fe and traces of other impurities or intentional additions.

Ce alloys are used as refining and cleaning agents in metallurgy. In steel, Ce is a deoxidizer when used in very small amounts as FeCe.

Mischmetal is successfully used in basic electric or open-hearth steels. Steels properly made and with 1.5 lb. Al, 2 lb. mischmetal and 3 lb. Ca-Mn-Si per ton have good low temperature impact resistance. In cast iron mischmetal is added for the production of 'nodular cast iron'. It also improves the fluidity, hot-workability, oxidation resistance and strength.

The hot-workability of austenitic steels (4-40 per cent Ni) is improved by adding mischmetal up to 0.2 per cent. The Ni content determines the amount of mischmetal required, and in some cases better high temperature strength and increased corrosion resistance are obtained.

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