



VARIOUS TECHNIQUES TO PRODUCE LOW CARBON FERROCHROME

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ABSTRACT

Primarily ferrochrome is used to introduce chromium into steels and alloys. Chromium enhances hardness, hardenability, corrosion, abrasion and wear resistance of the steel.

High carbon ferrochrome is one the cheapest sources of chromium, which finds large consumption in foundries and steel plants. However, carbon leads to problems viz. weld decay and sensitization of steels at elevated temperature causing catastrophic failure. Thus high carbon ferrochrome which otherwise enjoys financial edge over its low carbon grade is not suitable for final alloying or adjustment of chromium content.

Subsequently, its addition burdens a steel maker. Hence, metallurgists around the globe have researched on finding out suitable technique for refining of ferrochrome.

Traditional production methods of low carbon ferrochrome have drawbacks i.e. high refractory consumption, losses of chromium in slag and fumes etc-. Later these were overcome by adopting relatively new methods namely, metallothermic reduction, triplex process, vacuum technique to directly produce extra low carbon ferrochrome. Authors have carried SWOT analysis of the aforementioned techniques in the literature.

Key Words: Ferrochrome, carbon content, low carbon grade, chromite, sensitization

1. INTRODUCTION

It is well known that, the chemical and mechanical properties of steels can be greatly improved by introducing certain alloying elements. For all practical purposes, the additions are invariably made in the form of material known as 'ferroalloys'. They are used in preparing special and alloy steels.

Ferrochrome contains chromium as a major alloying element. The chromium is introduced as a constituent into a large number of steels. It makes the steel self-hardening and increases its hardenability and hardness. With low carbon content, high chromium steels ($Cr > 12\%$) are corrosion resistant. With high carbon content, chromium raises the abrasion and wear resistance. Chromium also increases the strength at high temperature [1-5]. Due to these useful contributions ferrochrome finds wide application in steel industries.

2. PROBLEMS OF CARBON

When ferrochrome is produced by the reduction of chromite with carbon (coke) in submerged arc furnace, the product ferrochrome so obtained is basically carbon saturated iron-chromium alloy with typically 6-8-wt % - C. In solid ferrochrome carbon forms solid chromium carbide and complex iron-chromium carbides. Submerged arc furnace is the only mode today to produce ferrochrome economically.

The manufacturing cost of steel depends upon the type of additives incorporated during steel making. Since the breakthrough of AOD (argon-oxygen-decarburization) and vacuum decarburization process for stainless steel mass production in the 1970s, high carbon ferrochrome has become the main source of chromium in

these steels. However, higher percentage of carbon in ferrochrome creates several problems, for many purposes *e. g.* in final adjustment of stainless steel analysis, in extra low carbon alloy steels, special steels *etc.* when it is necessary to have very low carbon content in the alloy. In case of austenitic stainless steels, carbon content is typically limited to 0.02 to 0.05 % higher percentage of carbon causes 'sensitization' *i.e.* at about 810 K excess carbon combines with chromium to form chromium carbide of type $Cr_{23}C_6$. At sensitization temperature the carbide is virtually insoluble and preferentially precipitates along the grain boundaries. This carbide, due to its high chromium to carbon ratio results in impoverishment of chromium in the matrix adjacent to the grain boundaries, this chromium depleted zone, has inadequate corrosion resistance, is anodic to grain matrix and hence gets corroded in a given medium. Thus carbon is indirectly responsible for this type of corrosion, which weakens the material. It also produces similar problem in welded structures and the phenomenon is called 'weld decay' [5].

In austenitic stainless steels, the chromium to carbon ratio is more than 150, while in high carbon ferrochrome it is about 10. Any attempt to add high carbon ferrochrome for final adjustment of stainless steel would inadvertently increase the carbon content. It is hence essential to remove carbon as much as possible from the parent source *i.e.* high carbon ferrochrome as to make it useful as a special alloying element.

3. DECARBURIZATION

To improve the chemical as well as mechanical properties of steels attempts were made to minimize the concentration of the detrimental and undesirable element (*i.e.* carbon) from steel. Chromium being reactive metal any attempt to remove carbon by simple oxidation results in chromium oxidation. Hence the carbon removal techniques followed in steelmaking practice cannot be used for production of low carbon ferrochrome

In fact, carbon removal is indeed a major problem in case of most of the ferroalloys [4]. Use of complex equipment and problems involved during efficient removal of carbon is responsible for significant rise in cost of low carbon ferrochrome.

The conventional decarburization techniques are associated with many disadvantages *i.e.* high refractory consumption, poor metal recovery due to losses of chromium in slag *etc.* However, non-conventional techniques make usage of solid carbon or gaseous reducers for solid-state reduction of chromite to production of low carbon grade of ferrochrome. Authors have done SWOT analysis of the available decarburization technique.

4. DECARBURIZATION TECHNIQUES

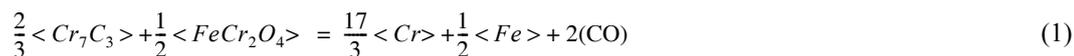
Depending upon type and state of oxidizer, the methods of decarburization are grouped as Conventional and non-conventional techniques.

4.1 CONVENTIONAL TECHNIQUES

Conventional methods of decarburization have been further classified as follows.

4.1.1 Refining of Ferrochrome by Chromium Ore

To determine the thermodynamic characteristic of this process Y.P. Elyutin [4] assumed that the liquid high carbon ferrochrome is a solution in which chromium exists in the form of carbide *i.e.* Cr_7C_3 . In such case the decarburization reaction can be written:



$$\Delta G^\circ = 612 - 0.323 T \quad \text{kJ}$$

Hence at $P_{CO} = 1$ atm, the theoretical initial temperature of the decarburization reaction is 1890 K. However, in actual practice, the temperature should be higher than this, to ensure a sufficiently high process velocity [4].

One of the real substantial difficulties encountered in the practical realization of this process are; the considerable high melting point and the viscosity of the high chromium refining slag, which prevents the growth of chromic oxide concentration in the slag and thus limits the possibility of increasing the oxidizing capacity of the slag. The decarburization process should be conducted at a temperature of about 2175 K for obtaining 2% C in the alloy while very low carbon grade might be obtained only at a temperature higher than 2375 K. Therefore, the production of low carbon ferrochrome by this process is associated with considerable difficulties.

4.1.2 Refining of Ferrochrome by Blowing Oxygen

Here the carbon is removed by blowing O_2 through ferrochrome melt in a converter. The process is used where chromium ore is costly. Yazikov [4] brought carbon below 1 % by using air as an oxidizer. For this he used an enclosed furnace, equipped with tuyeres for blowing air. This method did not give satisfactory results because the amount of heat generated in decarburization reaction was insufficient to compensate the heat losses due to the heating of the large amount of nitrogen in air. Hence the bath temperature could not be elevated above 1935 – 1985 K. Also the formation of a refractory slag containing chromium oxide caused additional heat losses. The process was further complicated due to nitrogen pick up in the alloy. The thermal disadvantages could be eliminated to a great extent when ferrochrome is blown with oxygen [6].

Decarburization at lower temperature is possible by lowering the external pressure. As difficulties there were insufficient durability of the converter lining and, particularly that of the tuyeres under the high temperature conditions of the process.

4.1.3 Refining of Ferrochrome with the Presence of Silica

The essence of this process consists of the refining of ferrochrome by oxygen in the presence of silica, under high vacuum. Since the reaction is accompanied by the formation of gaseous product, the use of vacuum displaces the equilibrium of the system sharply to the right and facilitates the process of decarburization. In practice, it is carried out in the electric resistance furnace. The alloy so obtained contains 0.02 to 0.04 % C. The disadvantages of the process are contamination of the alloy with unreduced silica, high silicon content of the product and lengthy time of production.

4.1.4 Silicothermic Process for the Production of Low Carbon Ferrochrome

Increasing silicon content in an alloy decreases the solubility of carbon, correspondingly. Low carbon ferrochrome can be obtained by reduction of chromite using silicon as a reducer in the form of silico-chrome.

The smelting is done in shaft type electric furnace lined with magnesia [7]. Furnace should be dry because moisture causes oxidation of silicon, and thus reduces chromium recovery and raises the electrical power consumption. Size of chromium ore should be less than 50 mm and of ferrochrome less than 10 to 15 mm. Also chromium ore should contain less phosphorus and sulphur. Ferrosilico-chrome should be free from slag inclusions because slag contains carbon in the form of entrapped silicon carbide particles. Use of higher voltage minimizes carbon pick up from the electrodes.

Main advantage of the process is, that it can produce an alloy with carbon less than 0.03 %. But at the same time metal recovery is low and as it needs, totally, three furnaces, which makes it uneconomical.

4.1.5 Production of Carbon Free Ferrochrome by Aluminothermic Method

This technique is good for *in situ* production of carbon free ferrochrome on a small scale. The reduction reaction proceeds as per reaction equation no. (2). The amount of the heat generated per unit mass of the reactants for the aforesaid reaction is 2649 kJ/kg. It is sufficiently higher than that required by 'Zhemchugney's Law' [1]. Aluminothermic reduction will be easier than silicothermic. High refractory slag ($Al_2O_3 + Cr_2O_3$) having high melting point can be kept fluid by making use of booster mixture ($NaNO_3 + Al$) in the charge. This will improve the recovery of metal. Excess use of pyrophoric aluminum should be avoided.



$$\Delta G^\circ = -309 + 0.004 T \quad \text{kJ}$$

4.2 Non Conventional Techniques

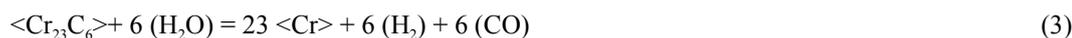
Development of AOD and VOD established the status of these processes in stainless steel industries. But problems of high refractory and argon consumption still exist. Hence upon studying several difficulties and limitations of conventional decarburization methods, attention was focused on non-conventional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

4.2.1 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. Oxidized ferrochrome is mixed with non-oxidized ferrochrome in the ratio 100:15. Chromium anhydride is also used as binder. This mixture is pressed into briquettes of dimensions W = 65 mm, L = 130 mm and B = 265 mm. They are dried at 425 to 675 K for 3 hours. Then they are transferred to a vacuum furnace where temperature is around 1675 K and pressure is 0.6 mm of Hg. The decarburization process takes 800 to 1000 hours. Upon end of decarburization *i.e.* end of gas evolution; the charge is cooled in vacuum for 30 hours. A typical composition of ferrochrome obtained by this method is 60 to 70 % Cr, 0.01 to 0.03 % C

4.2.2 Decarburization using Oxidizing Gas Mixture

(a) Water Vapor: The oxidation of carbon from ferrochrome takes place according to reaction equation (3) S. Shimmizu [8] did experiment using water plus calcium compound to get dense ferrochrome. But due to the endothermic nature of the reaction and requirement of hard vacuum actual mechanism of decarburization was left unknown.



$$\Delta G^\circ = 1890 - 0.296 T \quad \text{kJ}$$

(b) Carbon Dioxide: In this method decarburization can be carried out by subjecting ferrochrome pellet to carbon dioxide flow. Decarburization proceeds by reaction (4).



$$\Delta G^\circ = 1436 - 1.012 T \quad \text{kJ}$$

It is basically a solution reaction, which is endothermic. Thermodynamically high temperature and low partial pressure of CO can help in feasibility of reaction [10].

4.2.3 Production of Low Carbon Ferrochrome from Chromite Ore

Unlike liquid state decarburization of high carbon ferrochrome to produce low carbon grade, following processes can be viewed as reduction of chromite by solid carbon (graphite), or H₂ to get metallic chromium or an alloy of iron and chromium in solid state. It was studied by W.F. Chu [11] with H₂ and J.W. Rankin [12] who made reduction experiments of chromite by CO. He observed X-ray diffraction pattern of the product at

various stages at different temperature. N.S. Sundermurti [13] carried out chromite reduction in Stanton Redcroft thermo-gravimetric balance under argon. He studied kinetics of the process. Also fractional reduction of Iron and Chromium Oxide were reported by Hiroshi G [14]. He did not notice carbide formation. Synthetic chromite reduction was studied by Sheshadri [15]. Various mechanisms were explored to derive the rate-controlling step. However, they found that these processes were kinetically slow. Also the separation of metal beads from the unreduced oxide and gangue material seems problematic.

4.2.4 Khalafala's Method

Pahlman J.C. [16] designed a direct method to prepare low carbon ferrochrome. This work was followed up by S.E. Khalafala [17] bringing direct method to prepare low carbon ferrochrome alloys containing less than two per cent carbon in a single vacuum furnace reactor. This method can conserve chromium and should reduce the capital and energy requirement relative to chromite electrothermal reduction.

Reduced products containing less than 2 % carbon and as low as 0.01 % carbon were obtained by reacting pellet of chromite and carbonaceous reductant mixture at pressure of 0.1 to 1 torr and temperature of 1500 to 1600 K. The extent of reduction increased with rising temperature and decrease in pressure. But in these conditions vaporization losses of chromium increase as well. Foundry coke, anthracite and carbon black were found to be superior to graphite as reductant. The reduction of chromite to metallic product was found to proceed via formation of intermediate carbides *i.e.* $\text{Fe}_3\text{C} + \text{Cr}_3\text{C}_2$. Lime accelerates rate of solid state reduction of chromite and can shorten the furnace time at 1573 K under vacuum from 13 hours to less than 3 hours. Soaking the charge for about 20 minutes gave button of low carbon ferrochrome alloy [17].

4.2.5 Other Methods

Also attempts of using prereduced chromium ore for low C ferrochrome are made by J.E. Stress [14]. Pre-reduction decreases the power consumption and increases the production of ferrochrome. K.Suzuki studied decarburization of liquid Fe-Cr-C alloys by rotating Cr_2O_3 cylinder in the melt [18]. For medium carbon content he found that decarburization rate increases with rotation speed of cylinder.

5. CONCLUSION

Chromite ore is an efficient reagent in removal of carbon from ferrochrome. It also increases the grade of ferrochrome. Traditional production methods of low carbon ferrochrome have drawbacks *viz.* high refractory consumption, losses of chromium in slag and fumes *etc.* These drawbacks were overcome by adopting other methods *e.g.* metallothermic reduction, triplex process, and vacuum techniques. Use of these methods helped in direct production of extra low carbon ferrochrome.

Solid-state production of low carbon ferrochrome using non-conventional technique might have an advantage of executing the operation at comparatively lower temperature, without formation of slag and fumes. The process is, however, slow and the product is not free of oxidic residues.

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