Calcium Silicide - Methods of production and their technological consideration

D. D. Akerkar
A. K. Vaish
S. S. Dhanjal
G. N. Rao*

ABSTRACT

Three industrial methods of production of calcium silicide have been discussed with their merits and demerits along with technological considerations. Calcium silicide was produced at NML in 500 KVA submerged arc furnace using partial charging method. Based on the results and observations of the smelting trials carried out a model has been proposed to explain the mechanism of formation of calcium silicide. Inoculation trials with calcium silicide produced at NML compares favourably with those obtained from abroad.

Introduction

Calcium silicide is an alloy of Silicon, Calcium and Iron. It is used both in the form of powder and lumps in iron and steel industry as a powerful deoxidiser and desulphuriser, owing to the high affinity of calcium, for oxygen, sulphur and other elements. Since the density of calcium is almost 6 times less than that of iron and its boiling point is close to the melting point of steel, it is generally used as an alloy of silicon, with 28 to 32% calcium and 60 to 65% silicon. This alloy is also extensively used in the foundaries for inoculating grey cast iron and its demand in India is estimated to be in the order of 300 - 400 tonnes per annum. As it is not produced in the country, all its requirements are currently met by imports, involving a large sum of foreign exchange.

This paper (i) discusses the industrial methods of production of calcium silicide, their merits and demerits along with technological considerations, (ii) proposes a model to explain the mechanism of formation of calcium silicide based on the results and observations of smelting trials carried out at NML and (iii) compares the results of inoculation of NML calcium silicide with those obtained from various sources.

Methods of production and their comparison

Three industrial methods of production of calcium silicide are as follows :

Single stage carbothermic process
(Quick lime method)

The process consists of direct reduction of silicon and calcium from their oxides by carbon.

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* Authors are with the National Metallurgical Laboratory, Jamshedpur-7

The furnace is charged with the weighed mixture of calcined lime, silica and carbonaceous material. Calcium silicide analysing roughly 55 to 65% silicon and 25 to 35% calcium can be produced from these materials according to the following reactions :

at 1580°C

$$2\,SiO_2+CaO+5\,C=CaSi_2+5CO$$

$$2\,CaO+2\,SiO_2+6\,C=2\,CaSi+6CO$$

Under proper conditions of an electric submerged arc furnace, the above reactions are not so simple and easy. In reality, the production of calcium silicide proceeds with the formation of certain carbides and gaseous materials, other than CO, which are responsible to complicate the production of this alloy.

Two stage carbothermic process
(Calcium carbide method)

It consists of first producing calcium carbide which is then fed to the sub-merged arc furnace along with silica and carbon to produce calcium silicide.

In this process calcium carbide is used in place of calcined lime. This calcium carbide along with silica and carbon produces calcium silicide according to the following reaction :

At 1520°C

$$2\,SiO_2+CaC_2+2\,C=CaSi_2+4\,CO.$$

This process requires higher power consumption taking into account the power consumed to produce calcium carbide. A modification of the above method is the in-situ generation of calcium carbide in the furnace using partial charging of lime and charcoal followed by addition of quartzite and charcoal to produce Ca-Si.

Silicothermic process

In this process production of calcium silicide takes place by reduction of lime with silicon in the form of ferro silicon according to the reaction :

$$2\,CaO+3\,Si=2\,CaSi+SiO_2$$

The calcium silicide that is formed dissolves in the iron silicon melt. It is assumed that free silicon i.e. not combined with iron, participates in the reaction of calcium reduction. Addition of fluorspar to the charge acts favourably in lowering the melting point and viscosity of slag and accelerating the process of slag formation and increasing the rate of settling of metal droplets. In this process, calcium silicide formed contains less than 20% Ca.

A comparative study of these three processes reveals that single stage carbothermic process is preferable compared to two stage carbothermic process because the later one is likely to accumulate more calcium carbide on the hearth leading to lower yield and higher power consumption. In the case of silicothermic process while the furnace operation is comparatively easy and free from the carbide formation with lower energy consumption, the calcium content in the calcium silicide produced is of much lower grade in comparison to that obtained by the quick lime method.

Technological considerations in the production of calcium silicide

Smelting of calcium silicide requires a great excess of reductant. As a result, the furnace hearth gets rapidly crusted with the carbides of silicon and calcium. If lot of carbides are formed, penetration of electrodes and tapping become difficult. The symptoms of the furnace crusting are (a) high calcium content in the alloy (b) absence of slag during tappings, (c) tapping difficulties, (d) high positioning of electrodes and buzzing of electric arcs and (e) the decrease in burden movement and frequent blow outs. When the crusting of the furnace is rapid, quartzite is charged in large portions. In extreme cases, apart from the addition of the extra quartzite to destroy the carbides, the quantity of reductant is also reduced to improve the furnace run.

Reductant with low ash content, large reactive surface, low volatile matter content, high electric resistance and sufficient mechanical strength should be used. The moisture contained in the reductant is undesirable. Quartzite should consist of minimum 98% silicon, less than 0.02% P_2O_5, with minimum of alumina, magnesia, and lime. Its moisture absorption should not exceed 5% and it should not loose its mechanical strength when crushed or heated. Lime with minimum 90% of CaO and free from fines should be properly calcined as the poorly calcined lime raises power consumption, lowers furnace efficiency and causes operational problems. Proper care should be taken in the preparation of charge mixture for the furnace. If the quantity of reductant is less, there will be continuous fluctuations in the current the burden will move fast, the calcium content in the alloy will decrease, the slag quantity will be more with less calcium carbide content and plugging of tap hole will be difficult. If the quantity of lime in the mixture is less, the calcium content in the alloy will be less and the running qualities of slag will get deteriorated while with excess lime in the mixture leads to high slag volume.

To compensate the stack losses of calcium, silicon and charcoal, generaly two times the stoicheometric lime, 1.5 times the required quartzite and 1.3 times the charcoal are to be maintained in the charge. If slag formation is more, more reductant should be added. The slag from each heat should be tested for the calcium carbide content. The density of slag is higher than that of calcium silicide of 30% Ca content. The quality of the calcium silicide can be judged roughly by examining the character of the fracture of the ingot. An alloy (i) with less than 25% Ca content has a uniform fine grained structure, (ii) with 28-29% Ca content has microcrystalline fracture and (iii) with 30% or more Ca content has columnar structure.

Experimental trials in the 500 KVA submerged arc furnace at NML

Smelting trial for the production of Calcium silicide was successfully carried out in NML's 500 KVA submerged arc furnace using Partial Charging method. The furnace is open top rotating type, provided with a fume extractor system and fitted with suitable temperature measuring devices at different levels. The furnace has an outer shell dia 245 cm and the inside dia being about 180 cm. The inside height of the furnace after lining is 145 cms, with 45 cms deep tapered hearth. The furnace is provided with 3 tap holes. The lining is of fire bricks backed by 5 cms of insulating bricks. The electrodes used are 20 cm dia spaced at the corners of an equilateral triangle of 62 cms side. Power to furnace is supplied from an electric-substation equipped with a circuit breaker, furnace transformer, amplidyne controller and low tension distribution system.

The raw material used and their analysis are given in Table-1. The chemical analysis of calcium silicide along with slag and the smelting operation parameters are given in Table - 2 and 3 respectively.

TABLE—1

Raw materials analysis

Constituents in %	Raw materials Charcoal	Calcined Lime	Quartzite
F. C.	67.2	—	—
SiO_2	0.9	1.0	98 4
FeO	0.18	trace	1.14
Al_2O_3	0.36	1 4	0.35
CaO	3.2	93.5	trace
MgO	—	1.0	trace

TABLE—2

Chemical analysis of calcium silicide and slag in%

Calcium silicide		
	Ca	28 32
	Si	59-62
	Fe	4-6
	Al	1.9 (Average)
	C	0.5-0 7,
	$CaSiO_3$	0.7
	P	0.07
	S	Trace
Slag		
	CaO	46-50
	SiO_2	28-33.
	Al_2O_3	11 Average
	FeO	1
	C	2.5 - 4
	Residue	4.5 to 5

TABLE—3

Smelting operation parameters

1 Period - 4
2 Duration 27 hours
3 Average KwH/Hr - 400
4 Arc voltage in volts - 50
5 Arc current in Amps - 4000 to 4500
6 Electrode current density - 12 to 14 amps/Cm^2
7 Charging rate in Kg/Hr-99.3
8 KwH/100 Kg of charge - 421
9 Alloy weight in Kgs - 638
10 Slag weight in Kgs - 130
11 Alloy recovery - 56%
12 Power consumption - 16500 kwh/ton
13 Average calcium content in the alloy - 30%
14 Average silicon content in the alloy - 60%
15 Heat Utilization - 52%
16 Electrode power density in $Kw/Cm^2 = 0.5$

Discussion of results

Calcium silicide containing an average 30% Ca was produced in successive tappings in four periods of 27 hour duration by partially separate charging of lime and quartzite into the furnace in order to reduce the possibility of contact between the pieces of lime and quartzite, Figure-1, with 56% alloy recovery. One lime charge-consisting of lime and charcoal was followed by a quartzite charge consisting of quartzite and charcoal after half an hour interval. The flow diagram for the formation of calcium silicide by partial charging method is shown in Figure-2. A model has been proposed to explain the mechanism of formation of calcium silicide by partial charging method after envisaging the results and observations of these smelting trials.

The following assumptions have been considered in developing the model :

1. Almost all calcium in the partial charge forms calcium carbide.
2. This calcium carbide reacts with the mixture of silica and carbon or only with silica to produce calcium silicide depending upon the temperature conditions.
3. Some silica is reduced by carbon to form silicon carbide in the other partial charge.
4. The silicon carbide formed is destroyed to some extent by the unreacted lime of the previous partial charge to form calcium silicide.
5. The loss of silicon and calcium takes place by evaporation due to side reactions in the arc zone adjacent to reaction zone.

A MODEL OF CALCIUM SILICIDE FORMATION
BY
PARTIAL CHARGING METHOD

FORMATION OF CALCIUM SILICIDE

AT 1437°C $SiO_2 + 3C = SiC + 2CO$

AT 1625°C $CaO + 3C = CaC_2 + CO$

AT 1520°C $CaC_2 + 2SiO_2 + 2C = CaSi_2 + 4CO$

AT 1791°C $CaC_2 + SiO_2 = CaSi + 2CO$

AT 1843°C $SiC + CaO = CaSi + CO$

LOSS OF SILICON

AT 1554°C $SiO_2 + 2C = Si + 2CO$

AT 2023°C $SiC + SiO_2 = SiO + CO + Si$

AT 2091°C $2SiC + SiO_2 = 3Si + 2CO$

AT 2190°C $SiO + SiC = 2Si + CO$

LOSS OF CALCIUM

AT 2154°C $CaO + C = Ca + CO$.

AT 2236°C $2CaO + CaC_2 = 3Ca + 2CO$

FIG.—1

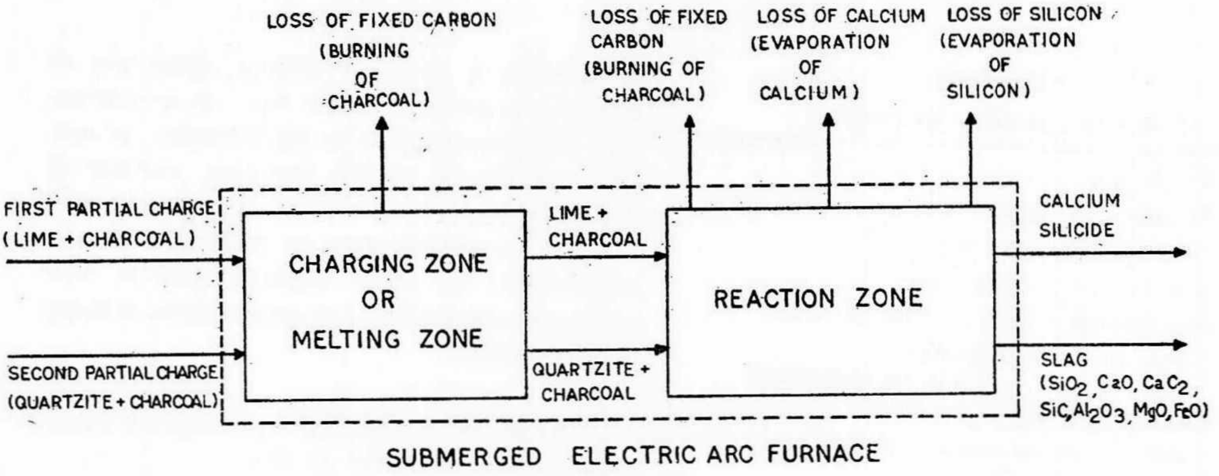


FIG.—2. FLOW DIAGRAM FOR THE SMELTING OF CALCIUM SILICIDE USING PARTIAL CHARGING METHOD AT NML.

The model illustrates the chemical reactions at different temperatures which are responsible for (i) the formation of calcium carbide and silicon carbide, (ii) the destruction of these carbides to form calcium silicide and (iii) the losses of silicon and calcium by evaporation. The model has been verified experimentally and it has been well established that the reaction between calcium carbide and silica is the main reaction to form calcium silicide. However, some quantity of calcium silicide is also formed by the reaction of silicon carbide with unreacted lime depending upon the situation

The model concludes that the major amount of calcium silicide is produced due to the reaction between calcium carbide and silica, inspite of some overall losses of charcoal, silicon and calcium.

A comparative chemical and sieve analysis of NML produced CaSi with that imported by H. M. T. Bangalore is given in Table-IV. It may be seen that both the chemical and sieve analysis of NML produced calcium silicide are at par with the imported one used by H. M. T. in their foundries.

Inoculation experiments with NML calcium silicide

Experiments were carried out to study the effectiveness of NML calcium silicide as an inoculant by comparing the results obtained with imported varieties under identical conditions.

Cast iron of the following composition was used for the inoculation.

C—3.1, Si — 1.7, Mn — 0.15
S—0.02, P — 0.25

The iron was melted in induction furnace for subsequent treatments by following uniform melting procedure and pouring temperature. The molten metal was inoculated with NML produced Ca Si and those obtained from France, Japan and Premier Automobile of India Ltd. The inoculation was done with 0.1, 0.15, 0.2, 0.25 and 0.3 percent of CaSi. In all cases a-10 mesh CaSi was used. The treated metal was poured into standard tensile specimen sand moulds and wedge moulds. The specimens for hardness measurements and microstructure examination were taken from a particular place in all cases. The results of tensile test and hardness measurements are given in Table - 4.

TABLE—4

Data on mechanical properties of cast iron inoculated with calcium silicide

Percentage addition	NML CaSI		French CaSi		Japanese CaSi		Premier Automobile CaSi	
	Tensile strength ton/sq. In	Hardness BHN	Tensile strength ton/sq. in	Hardness BHN	Tensile strength ton/sq. in	Hardness BHN	Tensile strength ton/sq. in	Hardness BHN
0.10	20.7	209	19.7	214	—	—	—	—
0.15	20.5	202	21.0	204	11 0	200	20.7	204
0.20	21.1	210	20.7	210	18.5	200	18.8	199
0.25	18.7	203	18.7	201	23.2	202	20.5	198
0.30	22.95	213	21.47	212	22.65	213	—	—

It has been observed that NML produced calcium silicide is equally effective as compared to imported varieties and optimum properties are obtained with 0.25 to 0.30 percent additions A comparison of the tensile strength and hardness of cast iron inoculated with calcium silicides of various sources is illustrated in Figures - 3 and 4 respectively. The microphotographs of cast iron inoculated with CaSi are shown in Figure - 5.

Discussion

Dr. Venkatadri, SAIL (R&D), Ranchi

Q. What would be the cost of CaSi produced ?

A. The price of CaSi is Rs 40-50,000 / tonne.

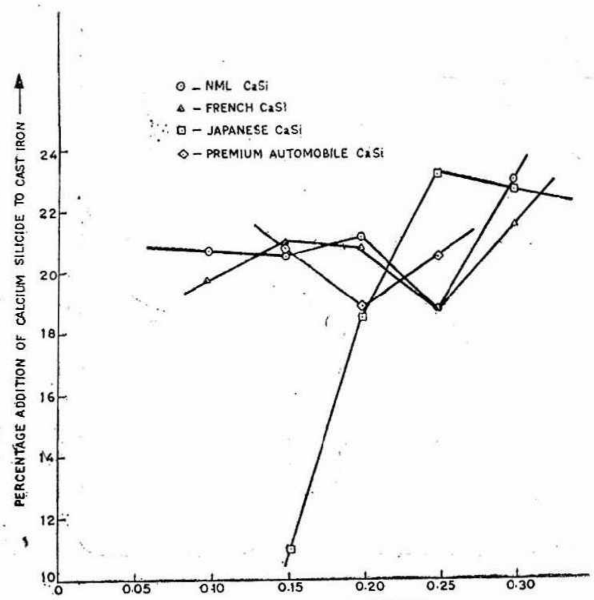


FIG:3. A COMPARISON OF TENSILE STRENGTH OF CAST IRON INOCULATED WITH CALCIUM SILICIDES OF VARIOUS SOURCES

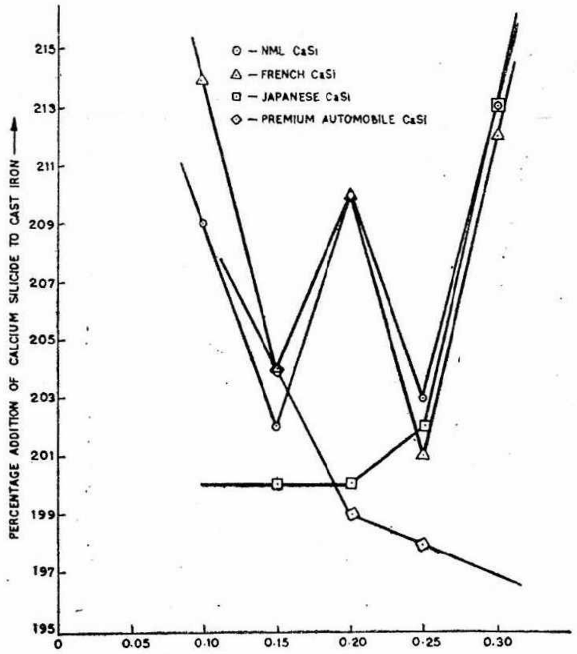
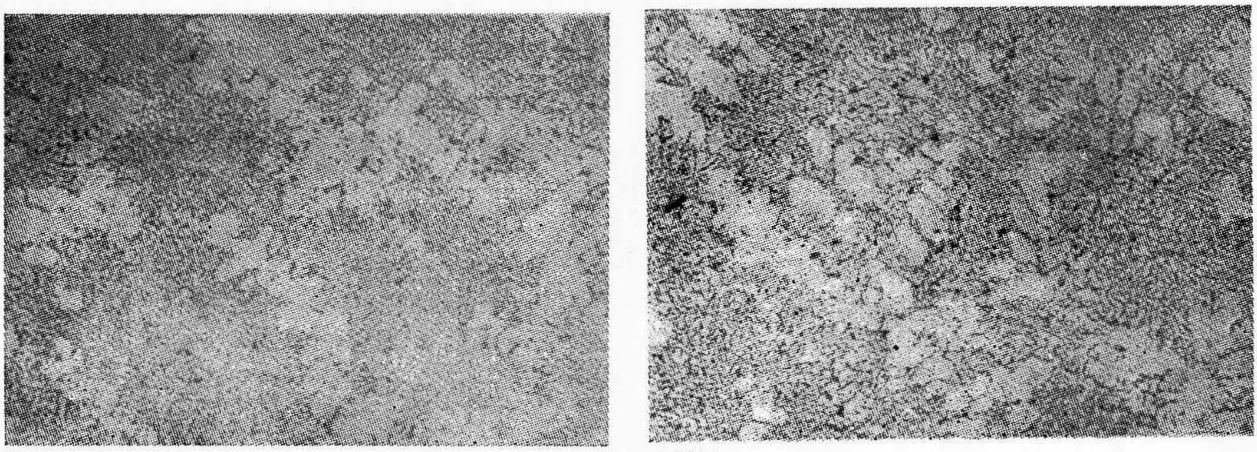
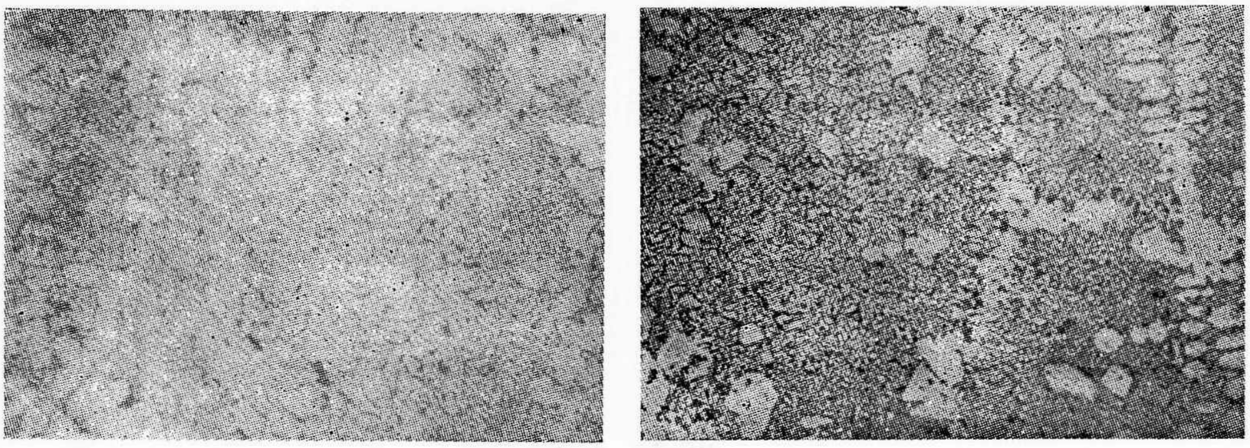


FIG:4. A COMPARISON OF HARDNESS OF CAST IRON INOCULATED WITH CALCIUM SILICIDES OF VARIOUS SOURCES



As Polished 0.20% x 100 — As Polished 0.25 x 100

Photomicrograph showing structure of cast iron inoculated with NML calcium silicide with 0.20 and 0.25 percent additions in cast iron.



As Polished 0.25% x 100 — As Polished 0.25% x 100

Photomicrograph showing structure of cast iron inoculated with Premier Automobile Calcium Silicide with 0 20 and 0.25 percent additions.

Fig. — 5