DEVELOPMENT OF A THERMO-CHEMICAL MODEL FOR THE PRODUCTION OF CALCIUM-SILICON ALLOYS

ASHOK KUMAR VAISH

National Metallurgical Laboratory
Jamshedpur - 831 007, INDIA

Calcium silicon alloys are used in iron and steel industry as powerful deoxidisers and desulphurisers. A thermo-chemical model has been evolved to predict the grade of the alloy, slag and gas composition and heat losses from the furnace.

INTRODUCTION

Calcium silicon alloys are extensively used in the steel industry for the process of deoxidation and desulphurization and in foundries for inoculation of cast iron to alter the morphology of graphite. Volkert[1] has briefly outlined the principles underlying the process of production of CaSi alloys. The criticality of the charge composition, scheduling of the charging conditions and the crucial importance of the electrical operation schedule for the success of the process have been emphasizd in the Russian studies[2-6]. The technical know-how of the process for the production of calcium-silicon alloys is presently restricted to a few advanced countries. Presently, the entire demand of calcium silicon alloys is met by imports. National Metallurgical Laboratory, Jamshedpur has successfully developed the process for the production of standard grades of calcium silicon alloys under TATA-NML interactive programme in its pilot scale 500 KVA submerged arc furnace. In order to understand the pocess in depth and also to determine the behaviour of unknown parameters in the operation of simultaneous reduction process, a thermo-chemical model has been evolved.

PROCESS OF SIMULTANEOUS REDUCTION OF SILICON AND CALCIUM

The process consists of direct reduction of silicon and calcium from their oxides by carbon. Calcium silicon alloys analysing roughly 55 to 65% Si and 25-35% Ca are produced. The charge mix for the production of calcium silicon alloys consists of quartz, calcined lime and

reductant in excess of their stoichiometric requirements. Firstly, the smelting of ferro-silicon was conducted in order (i) to heat up the furnace hearth and lining so that high temperature is attained prior to the smelting of calcium silicon alloys and (ii) to clear the taphole for easy flow of the alloy. Before changing over from ferro-silicon to calcium silicon alloys, the furnace bath was cleaned by lime melting. A charge containing calcined lime, quartz and charcoal was added gradually around each electrode and three charge compositions were tried during the smelting campaign so as to produce the calcium silicon alloys of the desired grade. All the carbides formed on the furnace hearth were destroyed by adding quartz and scrap iron. The formation of calcium silicon alloys during smelting trials was insured by (i) homogeneous mixing of charge constituents (ii) accurately feeding the charge mix into the smelting zone (iii) varying the proportion of the calcined lime in the charge mix (iv) feeding the extra quantity of charcoal or quartz or both and (v) varying the temperature of the smelting zone.
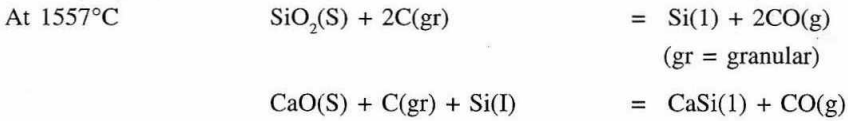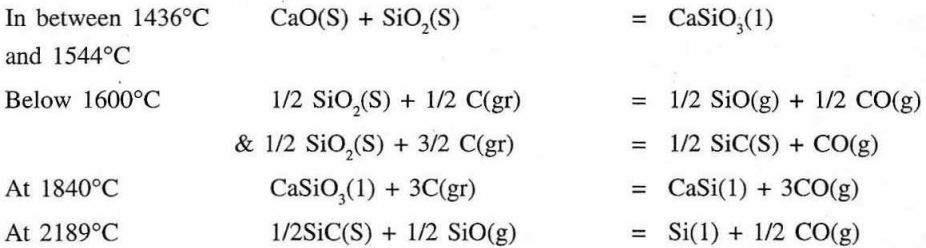
MODEL OF CALCIUM-SILICON ALLOY FORMATION

During the smelting of calcium silicon alloys, several reactions take place in a close temperature range through some intermediate stages. The mechanism of all such reactions has been studied and a simplified model has been proposed for the formation of calcium silicon alloys as shown in Figure 1.
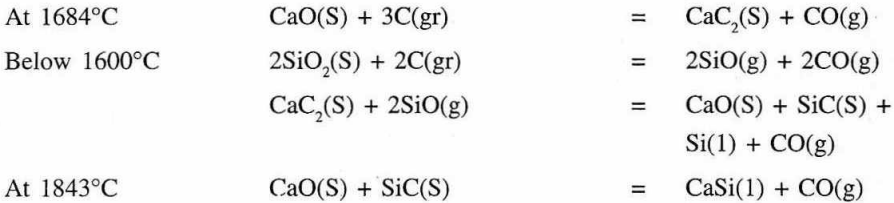
DEVELOPMENT OF THERMO-CHEMICAL MODEL

The thermo-chemical model for the production of calcium-silicon alloys is developed based on material and energy balance. In order to simplify the model, the following assumptions have been made :

(1) The slag and gas composition are in equibilrium with CaSi alloys.

(2)   The condensed phases are

    (i) Slag containing CaO and SiO_2 in equimolar proportions.

    (ii) Solid CaC_2 and SiC

    (iii) liquid alloy consisting of Ca, Si, Fe, Al and C and

    (iv) Gas phase comprising of CO, CO_2, SiO and Ca.

(3)   The slag consists of CaC_2 and SiC also apart from CaO, SiO_2, Al_2O_3 and FeO. About 73.68% of Ca present in slag is in the form of CaO and the rest in the form of CaC_2. Similarly about 89.4% of Si present in slag is in the form of SiO_2 and the rest in the form of SiC. Aluminium present in slag is in the form of Al_2O_3 while Fe present in slag is in the form of FeO.

(4)   The silicon present in gas is in the form of SiO. The gas phase is mainly comprised of Ca., SiO and CO. Since the equilibrium oxygen partial pressure for alloy-slag equilibrium is of the order of 10^{-25} atm and the corresponding p_{CO}/p_{CO_2} ratio is of the order of 10^{17}, the presence of CO_2 in the gas phase is neglected.

SIMULTANEOUS REDUCTION OF CaO AND SiO_2 BY CARBON

At 1557°C	$SiO_2(S) + 2C(gr)$	$=$	$Si(1) + 2CO(g)$
			(gr = granular)
	$CaO(S) + C(gr) + Si(I)$	$=$	$CaSi(1) + CO(g)$

SLAG FORMATION AND ITS REDUCTION BY CARBON TO FORM $CaSi_2$

In between 1436°C and 1544°C	$CaO(S) + SiO_2(S)$	$=$	$CaSiO_3(1)$
Below 1600°C	$1/2\ SiO_2(S) + 1/2\ C(gr)$	$=$	$1/2\ SiO(g) + 1/2\ CO(g)$
	& $1/2\ SiO_2(S) + 3/2\ C(gr)$	$=$	$1/2\ SiC(S) + CO(g)$
At 1840°C	$CaSiO_3(1) + 3C(gr)$	$=$	$CaSi(1) + 3CO(g)$
At 2189°C	$1/2SiC(S) + 1/2\ SiO(g)$	$=$	$Si(1) + 1/2\ CO(g)$

The Overall Reaction is

| $CaO(S) + 2SiO_2(S) + 5C(gr)$ | $=$ | $CaSi_2(1) + 5CO$ |

CARBIDE FORMATION AND ITS REDUCTION TO FORM $CaSi_2$

At 1684°C	$CaO(S) + 3C(gr)$	$=$	$CaC_2(S) + CO(g)$
Below 1600°C	$2SiO_2(S) + 2C(gr)$	$=$	$2SiO(g) + 2CO(g)$
	$CaC_2(S) + 2SiO(g)$	$=$	$CaO(S) + SiC(S) +$ $Si(1) + CO(g)$
At 1843°C	$CaO(S) + SiC(S)$	$=$	$CaSi(1) + CO(g)$

The Overall Reaction is

| $CaC_2(S) + 2SiO_2(S) + 2C(gr)$ | $=$ | $CaSi_2(1) + 4CO(g)$ |

LOSSES OF SILICON AND CALCIUM

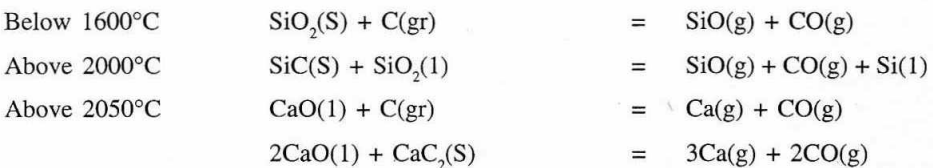| Below 1600°C | $SiO_2(S) + C(gr)$ | $=$ | $SiO(g) + CO(g)$ |
Above 2000°C	$SiC(S) + SiO_2(1)$	$=$	$SiO(g) + CO(g) + Si(1)$
Above 2050°C	$CaO(1) + C(gr)$	$=$	$Ca(g) + CO(g)$
	$2CaO(1) + CaC_2(S)$	$=$	$3Ca(g) + 2CO(g)$

Figure 1 : Model of Calcium-Silicon alloy formation

(5) Some amount of air is leaked into the furnace per tonne of alloy production.

The material balance and energy balance expressions for the process of simultaneous reduction of calcium oxide and silica by carbon were formulated as follows :

Material Balance

Ca in the charge = Ca from calcined lime + Ca from quartz + Ca from charcoal.

Si in the charge = Si from quartz + Si from charcoal + Si from calcined lime

Al in the charge = Al from quartz + Al from calcined lime + Al from Charcoal

Fe in the charge = Fe from quartz + Fe from calcined lime + Fe from charcoal

C in charge = C from charcoal

The overall material balance can be formulated as follows :

Kg-atoms [basis : 1000 Kg of CaSi alloy]

	Charge	*Alloy*	*Slag*	*Gas*
Ca	M_1	$0.5\ M_1$	$0.475\ N_1$	N_2
Si	M_2	$0.65\ M_2$	$0.475\ N_1$	N_3
Fe	M_3	$0.73\ M_3$	$0.025\ N_1$	N_4
Al	M_4	$0.14\ M_4$	$0.050\ N_1$	N_5
C	M_5	0.083	$0.030\ N_1$	N_6
O	M_6	—	$1.300\ N_1$	$(N_3 + N_6)$

The material balance equations will be as follows :

$$0.475\ N_1 + N_2 = 0.50\ M_1 \qquad \ldots (1)$$
$$0.475\ N_2 + N_3 = 0.35\ M_2 \qquad \ldots (2)$$
$$N_4 + 0.025\ N_1 = 0.27\ M_3 \qquad \ldots (3)$$
$$N_5 + 0.05\ N_1 = 0.86\ M_4 \qquad \ldots (4)$$
$$N_6 + 0.30\ N_1 = (M_5 - 0.083) \qquad \ldots (5)$$
$$N_3 + N_6 + 1.30\ N_1 = M_6 \qquad \ldots (6)$$

With the known values of M_1, M_2, M_3, M_4 and M_5, these equations were solved to determine the values of N_1, N_2, N_3, N_4, N_5 and N_6. The composition of Calcium-silicon alloy, slag and gas can be determined by following expressions :

Composition of Alloy (kg)	*Composition of slag* (kg)	*Composition of Gas* (kg)
Ca - $20 M_1$	SiO_2 - $25.5\ N_1$	Ca - $40 N_2$
Si - $18.2\ M_2$	CaO - $19.6\ N_1$	SiO - $44 N_3$
Fe - $40.88\ M_3$	CaC_2 - $8 N_1$	CO - $28 N_6$
Al - $37.8\ M_4$	SiC - $2 N_1$	Al - $27 N_5$
C - 0.996	Al_2O_3 - $2.55\ N_1$	Fe - $56\ N_4$
	FeO - $1.8\ N_1$	

Energy Balance

Basis : 1000 kg of alloy, tapping temperature of slag and metal - 1700°C and temperature of off-gases - 500°C

Enthalpy input	=	Sensible heat in the solid charge + charcoal heat equivalent + heat input through electrical power supply

$$H_{solid} + H_{charcoal} + H_{electrical} \qquad \text{... (7)}$$

Enthalpy output = Sensible heat in the alloy + sensible heat in the slag + sensible heat in the off-gases + Chemical heat in the off gases + heat absorbed by reactions + heat losses

$$H_{Alloy} + H_{slag} + H_{gases} + H_{gases\ (c)} + H_{Reactions} + H_{Loss} \quad \text{... (8)}$$

$$H_{Alloy} = H[Ca, Si, Fe, Al, C] \qquad \text{... (9)}$$

$$H_{slag} = H\,[SiO_2, CaO, CaC_2, SiC, Al_2O_3, FeO] \qquad \text{... (10)}$$

$$H_{gases} = H[Ca, SiO, Ca, Al, Fe] \qquad \text{... (11)}$$

$$H_{gases[C]} = H[CO] \qquad \text{... (12)}$$

$$
\begin{aligned}
H_{Reactions} =\ & H[<CaO> + <C> = (Ca) + (CO)] \\
& + H[<SiO_2> + 2<C> = (Si) + 2(CO)] \\
& + H[<SiO_2> + <C> = (SiO) + (CO)] \\
& + H[<CaO> + 3<C> = (CaC_2) + (CO)] \\
& + H\,[<SiO_2> + 3<C> = (SiC) + 2(CO)] \qquad \text{... (13)}
\end{aligned}
$$

Therefore heat losses can be determined by the following expression

$$H_{Loss} = H_{Solid} + H_{charcoal} + H_{Electrical} - H_{Alloy} - H_{Slag} - H_{gases} - H_{gases(C)} - H_{Reactions} \qquad \text{... (14)}$$

Thus with the known composition and quantities of input materials· and specific power consumption, the model can predict the composition of the alloy, slag composition, off gas composition, sensible heat in the alloy, sensible heat in the slag, sensible and chemical heat in the off-gases and heat losses from the furnace.

VERIFICATION OF MODEL

The proposed model was verified with the input data of the smelting trial conducted in NML's pilot scale 500 KVA submerged arc furnace.

Inputs

Calcined lime — 742 kg [CaO = 679.74 kg]

Quartz — 2252 kg [SiO_2 = 2230.60 kg]

Charcoal — 1994 kg [F.C. = 1398.59 kg]

Specific power consumption — 20340· KWh/T CaSi

Chemical Analysis :

Calcined Lime			*Quartz*		
CaO	-	91.61%	SiO_2	-	99.05%
FeO	-	0.20%	Fe_2O_3	-	0.76%
MgO	-	1.03%	Al_2O_3	-	0.03%
Al_2O_3	-	5.13%	CaO	-	0.02%

Charcoal			*Charcoal Ash*		
F.C.	-	70.14%	SiO_2	-	59.62%
Ash	-	8.4%	Al_2O_3	-	15.94%
V.M.	-	16.32%	CaO	-	9.85%
Moisture	-	5.14%	MgO	-	3.6%
			FeO	-	10.84%

Therefore M_1 - 12.13, M_2 - 37.17, M_3 - 0.4866, M_4 - 1.283, M_5 - 116.540 and M_6 - 132.60

With these input values, the model's predictions are as follows :

Composition of Alloy (kg)			*Composition of Slag (kg)*		
Ca	-	250	SiO_2	-	111.84
Si	-	700	CaO	-	85.96
Fe	-	20	CaC_2	-	35.08
Al	-	5	SiC	-	8.772
C	-	1	Al_2O_3	-	11.18
			FeO	-	7.89

Composition of Gases (kg)

Ca	-	164
SiO	-	517
Fe	-	1.11
Al	-	23.72
CO	-	3223.94

Sensible heat in the alloy = 385.33 x 10^3 Kcal [2.2%]

Sensible heat in the slag = 151.76 x 10^3 Kcal [0.867%]

Sensible and Chemical heat - 674.47 x 10^3 Kcal [3.853%]
in the off-gases

Heat absorbed by reactions - 7540.06 x 10^3 Kcal [43.07%]

Heat losses from the furnace - 8751.72 x 10^3 Kcal [$\cong$ 50%]

The predicted composition of the alloy and slag was found to be in close range of actual furnace composition and about 50% of heat is lost from the furnace. Due to high value of heat

losses, the power consumption in the present situation was found to be one and a half times more than the commercial furnaces.

CONCLUSION

The proposed model can predict the composition of the alloy, slag composition, off-gas composition, sensible heat in the alloy and slag, sensible and chemical heat in off-gases and heat losses from the furnace.

REFERENCES

1. Durrer R. and G. Volkert, Die Metallurgie der Ferrolegeirungen, Springer - verlag (1953)

2. Elyutin V.P. Yu. A. Pavlov, B.E. Levin and E.M. Alekseev, Production of Ferroalloys, Electrometallurgy, 2nd ed., The state Scientific and Technical Publishing House for Literature on Ferrous and Nonferrous Metallurgy, Moscow (1957)

3. Riss A and Y. Khodorovsky, Production of Ferroalloys, Foreign Languages Publishing House, Moscow.

4. Akhmetshin I, I. V. Zhukov, Yu, S. Maksimov and A. N. Rabukhin, STAL (1966) 545

5. Topil' skii V.P., G. S. Belyaev, T. A. Zelenetskaya, Yu. M. Maslenikov, V. N. Lyubimov, A. S. Mikulinskii and A. F. Filippov, STAL, (1967) 224

6. Mikullinskii A. S. and I. V. Ryabchikov, Izvest VUZ Chernay, Met. **6** (1962) 44.