Physico Chemical Aspects Of Alumino-Thermic Reduction In The Production Of Low Carbon Ferro-Alloys

by

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Introduction

No doubt carbon is the oldest, most extensively used and cheapest reducing agent for the extraction of metals, and ferro-alloys, but due to its high affinity for many metals it results in the formation of undersirable carbides. The growing demand of carbon free alloys has generated considerable interest in aluminothermic reduction of various oxides. A common example of aluminothermic reduction is the thermit welding of rails and repair of steel castings. As early as in 1898, Goldschmidt (1) demonstrated the use of aluminium as a reducing agent in the production of refractory metals. Subscquently, aluminothermic reduction has been extensively used to produce pure metals such as chromium, manganese and master alloys such as carbon free chromium-aluminium, titanium - aluminium, ferro-chrome, ferro-molybdenum, ferro-columbium, ferro-tungsten and ferro-titanium of high purity. Aluminothermic techniques have led to notable developments in the field of high purity special steels. The objective of aluminothermic reduction is to utilise the exothermic heat of the reaction for smelting purposes. Aluminothermic reduction did not generate much interest till 1950's due to various reasons such as high cost of pure aluminium and lack of available means for the removal of residual elements and oxides. The interest in alumino-thermic reduction revived in 1960's and onwards. Since then extensive research work has been carried out on aluminothermic reduction for producing low carbon ferro-alloys by obtaining 95-96% pure metals from their pure oxides and also metallic values from their oxides available as secondary sources.

The various factors that are to be considered in aluminothermic reduction are density, melting point solubility, vapour pressure and viscosity of thereactants and products. Kinetic considerations are relatively less important as the aluminothermic reductions are quite rapid mainly due to the high temperatures involved due to exothermic liberation of heat and the conditions are close to equilibrium. Development of aluminothermic techniques for ferro-alloy production is important under Indian conditions and various low carbon ferro-alloys have been produced by aluminothermic reduction of oxides of respective alloying element along with iron oxide/iron scrap at National Metallurgical Laboratory, Jamshedpur. Aluminothermic reduction technology have been economically trasferred to industry and most of the low carbon ferro-alloys produced in the country in eighties used to come from the NML technology.

During aluminothermic reduction, the ferro-alloys are produced from their oxide ores by reduction with aluminium using the exothermic heat of the reaction. Temperatures of reaction may rise to anywhere between 1800 and 2500°C depending on the exothermicity of the reaction and specific heat of the products. The reduction reaction can be represented as :

$$\text{Metal Oxide} + \text{Al} \dashrightarrow \text{Metal} + \text{Al}_2\text{O}_3$$

If the aluminothermic reactions are extremely fast and heat of reaction is excessive so as to give higher temperature than required, some coolant such as iron scrap or fillings or other inert materials such as lime or crushed slag are added to the charge. It reactions are sluggish and enough heat is not generated during the reaction to give liquid products, the reactants may be preheated to 200-600°C. Sometimes an energiser or booster such as barium peroxide, potassium chlorate, CrO_3 or oxygen rich salt such as $NaNO_3$ etc., are added to increase the heat of reaction. Generally the aluminothermic reduction reaction is spontaneous and the entire reaction gets completed within a few miniutes. It is estimated that for the process to be self sufficient in its heat requirements and good separation of metal and slag, the specific heat effect of the process should be 650-750 K calories per Kgm of reacting substances.

Experimental

Reaction Vessel : Fig. 1 shows the detailed drawing of a reaction vessel and Fig. 2 that of a former for the purpose of monolithic lining of the reaction vessel. The reaction vessel is usually made out of mild steel of 3 mm thickness sheet. The size of the reaction vessel depends upon the capacity of the plant. Usually three fourth of the vessel's volume is utilised for reaction purposes. The lining thickness of the reaction vessel is usually 100 mm. A semi-permanent lining of magnesite bricks of one course is lined by suitable cutting of bricks, on the surface of which a rammed lining is made with dead burnt magnesite powder of -70 mesh bonded with 3 percent sodium silicate. After ramming, the vessel is kept for drying, the former is removed and the vessel is allowed to dry slowly preferably for a day. It is then fired under oil burner and pre-heated. It is of utmost importance that the lining is thoroughly dried as the presence of moisture may create a lot of problems namely the leak out of the metal and slag and even explosion. The higher the degree of preheat, the better will be the results of a reaction.

Preparation of Charge Mixture : The charge mixture consists of ore which must be of uniform size and well dried to drive away the absorbed and combined water. Also any carbonates, if present, should be decomposed. The overheated materials should be cooled to a temperature lower than the fusion point of aluminium (650°)in order to prevent the boiling up the charge before the final mix. After preheating, the charges is mixed with aluminium powder and fluxes in a blender or mixer suitably designed for thorough mixing. In the case of smaller reactions, this can be done by hand on a suitable clean plateform. Only at the end of mixing, the energizer is mixed with the charge. The prepared charge is then fed into the reaction vessel either by of preheat, the better will be the results of a reaction.

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Process for the Production of Low Carbon Ferro-Alloys : Firstly, a small quantity of the charge mix is placed at the bottom of the preheated vessel and the ignition mixture in a paper packet is placed centrally over it and ignited. When the ignition starts, the charge is slowly fed in on the top of it. Care is taken to ensure that it is uniformly spread over the entire area of the reaction vessel and the mixture is fed at a rate that the melt surface is covered with a thin layer of it. If the rate of charging is slow, it will expose the melt surface to the atmosphere and consequently increase the heat losses. Excessivelyrate of charging will slow done the reaction and may result in poor recovery. The advantage of bottom priming method is that the charging can be continued until the reaction vessel is full thereby utilizing the full capacity of the vessel.

After completion of the reaction, the metal is allowed to solidify and cool. When cooled, the solidified mass of slag and metal is separated from the vessel. Further, metal is separated from slag by simple knocking with an hammer. Likewise various low carbon ferro-alloys such as ferro-manganese, ferro-chrome, ferro-vanadium ferro-titanium, ferro-boron, ferro-silico zirco-nium and ferro-tungsten, containing trace to 0.1% carbon can be produced. The compositions for these low carbon ferro-alloys are mentioned in Table I and Figure 3 illustrates various steps of their production.

Thermodynamics : Auminiuum is the best commerical reductant because Al_2O_3 is much more stable than most metal oxides. The aluminothermic reduction reaction can be represented as :

$$3MO + 2Al = Al_2O_3 + 3M \quad \ldots \ldots \ldots \quad (1)$$

The Gibbs energy change associated with the reaction provides the driving force for the aluminothermic reduction process. Figure 4 represents the Gibbs energy changes involved in the reduction of various oxides by aluminium. It is obvious from Fig. 4 that most oxides, except ZrO_2 and TiO_2, can be readily reduced by aluminium.

The equilibrium constant for reaction (1) is given by :

$$K' = [a_{(Al2O3)} \cdot a^3_M]/[a_{3MO} \cdot a^2_{Al}]$$

The equilibrium constant K is a function of temperature and is constant at given temperature. The factors promoting the aluminothermic reduction reaction are :

i) Lower activities of Al_2O_3. This can be done by adding fluxes such as CaO

ii) Lower activities of M. This can be achieved by alloying.

iii) A lower temperature which promotes the reduction reaction since most aluminothermic reduction reactions are highly exothermic.

This enthalpy change is necessary to calculate the thermal balance of the reaction and to predict whether the heat generated will be sufficient to melt the metal and the slag and to separate them into two layers without the use of a furance. The amount of heat released per unit mass of reactants can be calculated as follows :

$$\Delta H^0_{298} = \Delta H^0_{Al2O3} - \Delta H^0_{MO} \quad \text{.. .. ..} \quad (4)$$

Tabel II shows 4, 5 and 6 heat of reaction, calories per Kg of reactants, for various reactions producing low carbon ferro-alloys. The heat of reactions involving these boosters are also presented in figure - Preheating of the charge to a temperature of 500°C has also been found to give encouraging results in alumino-thermic reduction. Aluminothermic reduction reactions which produce excess heat may be violent and they may be controlled by adding thermally inert materials e.g., lime is used in some aluminothermic reactions. These inert materials are also called as "heat sinks".

From the above a generalised statement may be made as follows :

For a controlled reaction to take place, between 600 to 1100 Kcal/kg of total charge are required. Above 1100 Kcal, the reaction is violent and below 600 Kcal it is very slow and booster or energizer may be added or preheating of the charge may be necessary.

Melting Point : In an aluminothermic reduction, the melting point of the metal and slag produced should be such that both of them are clearmelted during the process. The refractory metals like molybednum, tungsten, vanadium etc., may present difficulties during melting. When the ferro-alloys of these metals are to be produced, the melting points are usually lowered and the problem of melting is less severe. The alumino-thermic reactions may present some difficulty during ferro-alloy production when the thermal load is high. The melting point of metallic oxides may be lowered by suitable flux additions. In this connnection lime has been found to be the most effective flux as small amount of lime helps to decrease the melting point of alumina considerably. Lime addition, besides lowering the melting point of slags, also reduces the overall reaction temperature, as a part of heat generated in the procss is consumed in fusing CaO. Therefore, only the optimum amounts of CaO should be employed so as to conserve the heat balance of the reaction and also minimize the losses of metal oxides in some cases.

Density : The density of the liquid slag and the liquid metal play significant role in the separation of two phases after the completion of the aluminothermic reaction. Larger the difference between the densities of liquid slag and liquid metal, better the separation of two phases. Generally most of the liquid slags have a low density of around 3 gm/cm^3 while most of the liquid metals have much higher densities. Therefore the separation of the two phases does not usually present any difficulty. Slag metal separation depends upon aluminium to metal ratios also. Higher A/M ratios although decrease the melting point of metallic phases but result in poor separation due to decrease in the densities of metallic phases.

Solubility and Chemical Affinity : The solubility and chemical affinity of the metals and compounds involved in aluminothermic reduction with other metals and compounds affect the reduction reaction significantly. The chemical affinity between the reductant and the reduced metal may decrease the thermodynamic activity of the reduced metal in such a way as to provide extra driving force for the aluminothermic reaction to proceed in the forward direction. Also when the reductant and the reduced metals have high mutual solubility or chemical affinity, the production of pure reduced metal will not be possible as it will be contaminated by the reductant. This happens in the aluminothermic reduction of titanium dioxide, TiO_2 by aluminium. Sometimes the reaction between the compound to be reduced and the compound formed in aluminothermic reaction affects the reaction in an adverse way e.g., aluminothermic reduction of chromic oxide, Cr_2O_3 is the case where interaction between alumina and chromium oxide limits the progress of the reaction, and a high metal recovery becomes difficult. On the otherhand, the presence of a compound which reacts with product compound in aluminothermic reaction facilitates the reaction in the forward direction by decreasing the activity of the product compound. Thus lime can be used in alumino-thermic reactions to decrease the activity of alumina.

Vapour Pressure and Viscosity : The vapour pressure of the metal and slag phases at the reaction temperature significantly influences the separation between the two. Lower the viscosities of metal and slag phases, better is the sepration. Generally the viscosities of liquid metals and alloys are much lower than those of liquid slags. Therefore the viscosity of the slags is to be considered seriously. Usually the slags produced during aluminothermic reduction processes are highly viscous and their viscosity can be considerably decreased by suitable flux additions. Lime and fluorspar have been suitably used as fluxes in order to reduce the viscosity of such slags.

References :

1. Thermit Welding by Hans, D. Fricke, Metals Handbook, 9th edition, 1983, Vol. 6, p.692.

2. Symposium on ferro-alloy industry in India, Organized by the National Metallurgical Laboratory, Jamshedpur, 1962, p.174-186.

3. Richardson & J.H.E. Jeffes, Journal of Iron and Steel Institute, 160, 1948,

4. Ibid 163, 1949.

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TABLE-1 : ANALYSIS OF VARIOUS LOW CARBON FERRO-ALLOYS

FERRO-CHROME

INDIAN STD.	PRODUCED AT NML
Cr - 65-75%	Cr - 69.58%
Si - 1.5 max	Si - 1.57 %
C - 0.03 Max	C - 0.03%
S - 0.05 "	S - 0.03%
P - 0.03 "	P - 0.004%

FERRO-VANADIUM

INDIAN STD.	PRODUCED AT NML
V - 50% Min.	V - 52.37%
Si - 1.25% Max.	Si - 1.3%
C - 0.1% "	C - 0.06 %
S - 0.1% "	S - 0.06%
P - 0.1% "	P - 0.07%
Al - 1.5% "	Al - 1.14%

FERRO-SILICO-ZIRCONIUM

INDIAN STD.	PRODUCED AT NML
Zr - 35-40 Min	Zr - 35.68%
Si - 47-52% Max	Si - 15.93%
C - 0.3% Max	C - 0.45%

FERRO-TUNGSTEN

INDIAN STD.	PRODUCED AT NML
W - 70% Min	W - 76.86%
Si - 1% Max	Si - 0.97%
C - 1% Max	C - 0.08 %
Mn - 0.8% Max	Mn - 0.34%
Al - 0.3% Max.	Al - 0.4%
S - 0.06% Max.	S - 0.02%
P - 0.06% Max.	P - 0.04%

FERRO-MANGANESE

INDIAN STD.	PRODUCED AT NML
Mn - 80-85%	Mn - 81%
C - 0.06% max	C - 0.04%
S - 0.05% Max	S - 0.04%
P - 0.06% Max	P - 0.05%
Si - 1.0% max	Si - 0.8%

FERRO-TITANIUM

INDIAN STD.	PRODUCED AT NML
Ti - 35-40 Min	Ti - 40.6%
Si - 3% Max	Si - 3.1%
C - 0.1% Max	C - 0.07%
Al - 20% Max	Al - 11.1%
S - 0.06% Max	S - 0.04%
P - 0.1% Max.	P - 0.08%

FERRO-MOLYBDENUM

INDIAN STD.	PRODUCED AT NML
Mo - 60-70% Min	Mo - 70.02%
Al - 0.5% Max.	Al - 0.10%
Si - 2% Max.	Si - 0.23%

FERRO-BORON

INDIAN STD.	PRODUCED AT NML
B - 17% Min	B - 17-18%
Si - 1.5% Max	Si - 0.95%
C - 0.5% Max.	C - 0.35%
Al - 0.5% Max.	Al - 0.55%

TABLE-II

THERMOCHEMICAL DATA AND SPECIFIC HEAT OF THE PROCESS IN ALUMINO-THERMIC REACTIONS (3,4,5,6)

Sl. No.	Metal Oxide	Heat of formation of metal oxide Cals./gm. mole of oxide (25°C)	Chemical reaction for the reduction of one gm. mole of oxygen from the oxide with aluminium	Heat of reaction in calories	MOL wt. of metal oxide	Specific heat effect /kg of oxide K. cals	Specific heat effect/kg of reacting substances K.cals.
1.	2	3	4	5	6	7	8
1.	Al_2O_3	-399,600	-	-	-	-	-
2.	B_2O_3	-305,300	$2/3\ B_2O_3 + 4/3\ Al - 4/3B + 2/3\ Al_2O_3$	67,867	46.43	1354.0	762.8
3.	Cr_2O_3	-272,650	$2/3\ Cr_2O_3 + 4/3\ Al - 4/3Cr + 2/3\ Al_2O_3$	84,633	101.30	835.6	616.5
4.	CrO_3	-140,000	$2/3Cr\ O_3 + 4/3Al - 2/3Cr + 2/3\ Al_2O_3$	173,067	66.7	2595.0	1686.0
5.	FeO	- 63,800	$2\ FeO + 4/3Al - 2\ Fe + 2/3\ Al_2O_3$	138,800	144.0	963.8	771.1
6.	Fe_3O_4	-267,800	$1/2Fe_3O_4 + 4/3Al - 3/2Fe + 2/3\ Al_2O_3$	132,500	116.0	1142.0	871.9
7.	Fe_2O_3	-196,800	$2/3Fe_2O_3 + 4/3Al - 4/3\ Fe + 4/3\ Al_2O_3$	135,200	106.7	1268.0	947.3
8.	MnO	- 92,000	$2MnO + 4/3Al - 2Mn + 2/3\ Al_2O_3$	82,400	142.0	580.2	462.9
9.	Mn_3O_4	-331,400	$1/2Mn_3O_4 + 4/3Al - 3/2Mn + 2/3\ Al_2O_3$	100,700	114.5	879.2	669.1
10.	Mn_2O_3	-229,400	$2/3Mn_2O_3 + 4/3Al - 4/3Mn + 2/3\ Al_2O_3$	113,467	105.3	1078.0	803.5
11.	MnO_2	-124,300	$MnO_2 + 4/3Al - Mn + 2/3\ Al_2O_3$	142,100	87.0	1533.0	1155.0
12.	MoO_3	-178,200	$2/3MoO_3 + 4/3Al - 2/3Mo + 2/3\ Al_2O_3$	147,600	96.0	1537.0	1118.0
13.	$NaNO_3$	-111,250	$4/5NaNO_3 + 4/3Al - 2/5Na_2O + 2/5\ N_2 + 2/3\ Al_2O_3$	217,067	68.0	3192.0	2087.2
14.	Nb_2O_5	-170,200	$2/3\ Nb_2O_5 + 4/3\ Al - 4/5Nb + 2/3\ Al_2O_3$	81,200	106.3	764.0	570.0
15.	SiO_2	-218,500	$SiO_2 + 4/3\ Al - Si + 2/3\ Al_2O_3$	47,900	60.0	798.2	498.9
16.	TiO_2	-225,500	$TiO_2 + 4/3\ Al - Ti + 2/3\ Al_2O_3$	40,900	80.0	511.2	352.6
17.	TiO_2 -TiO	-123,900	$2\ TiO_2 + 4/3\ Al - 2TiO + 2/3\ Al_2O_3$	63,200	160.0	395.0	322.4
18.	TiO_2-Ti_2O_3		$4\ TiO_2 + 4/3\ Al - 2Ti_2O_3 + 2/3\ Al_2O_3$				
19.	V_2O_3	-371,800	$2/5V_2O_3 + 4/3Al - 4/5\ V + 2/3\ Al_2O_3$	117,680	72.8	1617.0	1081.0
20.	WO_3	-200,000	$2/3WO_3 + 4/3\ Al - 2/3W + 2/3\ Al_2O_3$	133,067	154.6	861.0	698.4
21.	ZrO_2	-259,500	$ZrO_2 + 4/3\ Al - Zr + 2/3\ Al_2O_3$	6,900	123.2	56.0	43.3

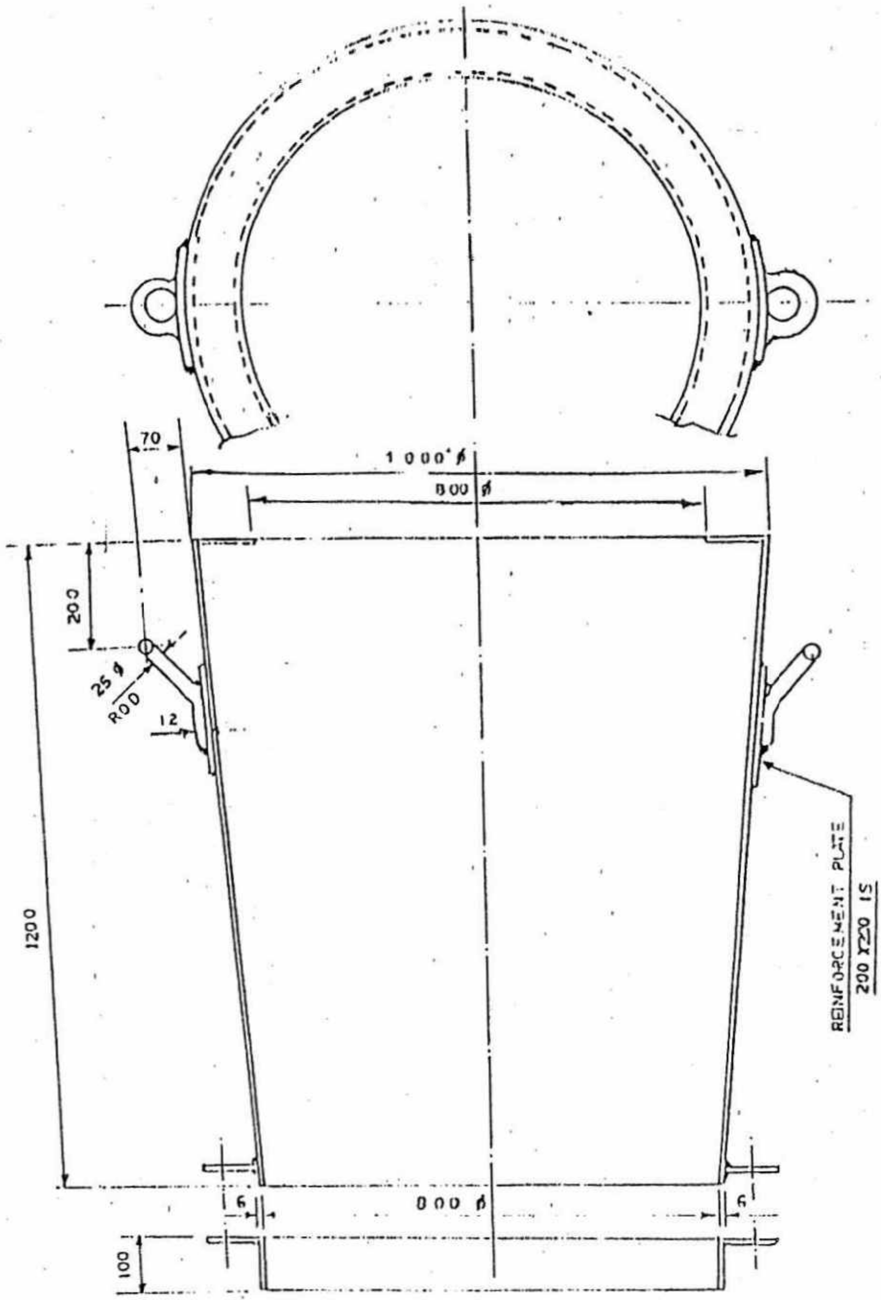

FIG 1 REACTION VESSEL

MATERIAL: M. S.

SCALE: 1:10

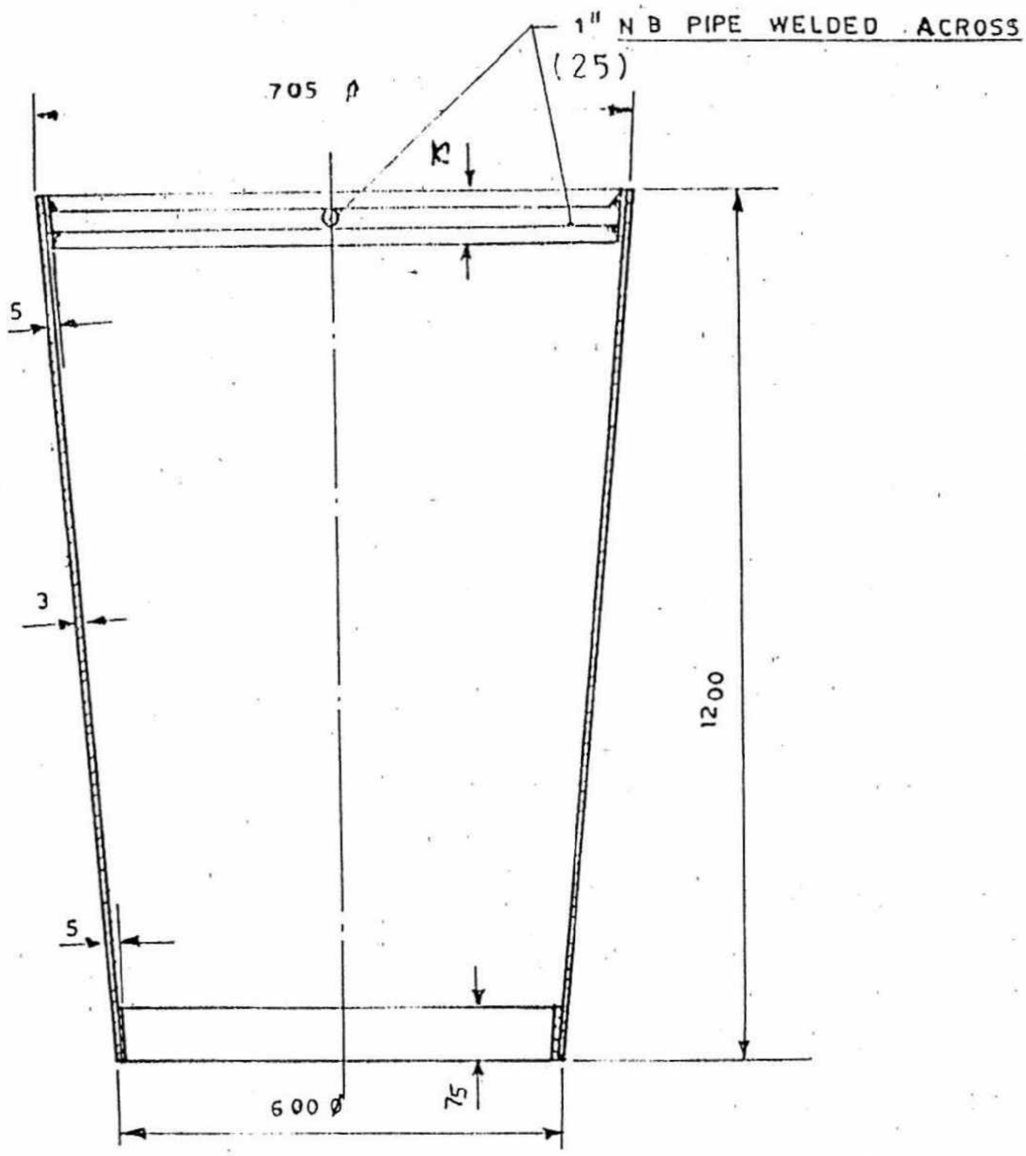

FIG. 2 FORMER

MATERIAL : M. S.

SCALE :- 1:10

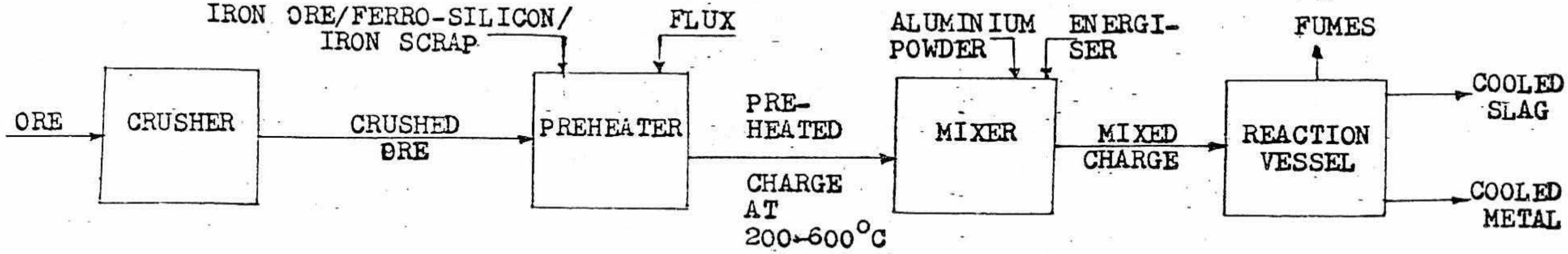

FIG. 3 FLOW DIAGRAM FOR THE PRODUCTION OF LOW CARBON FERRO-ALLOYS.

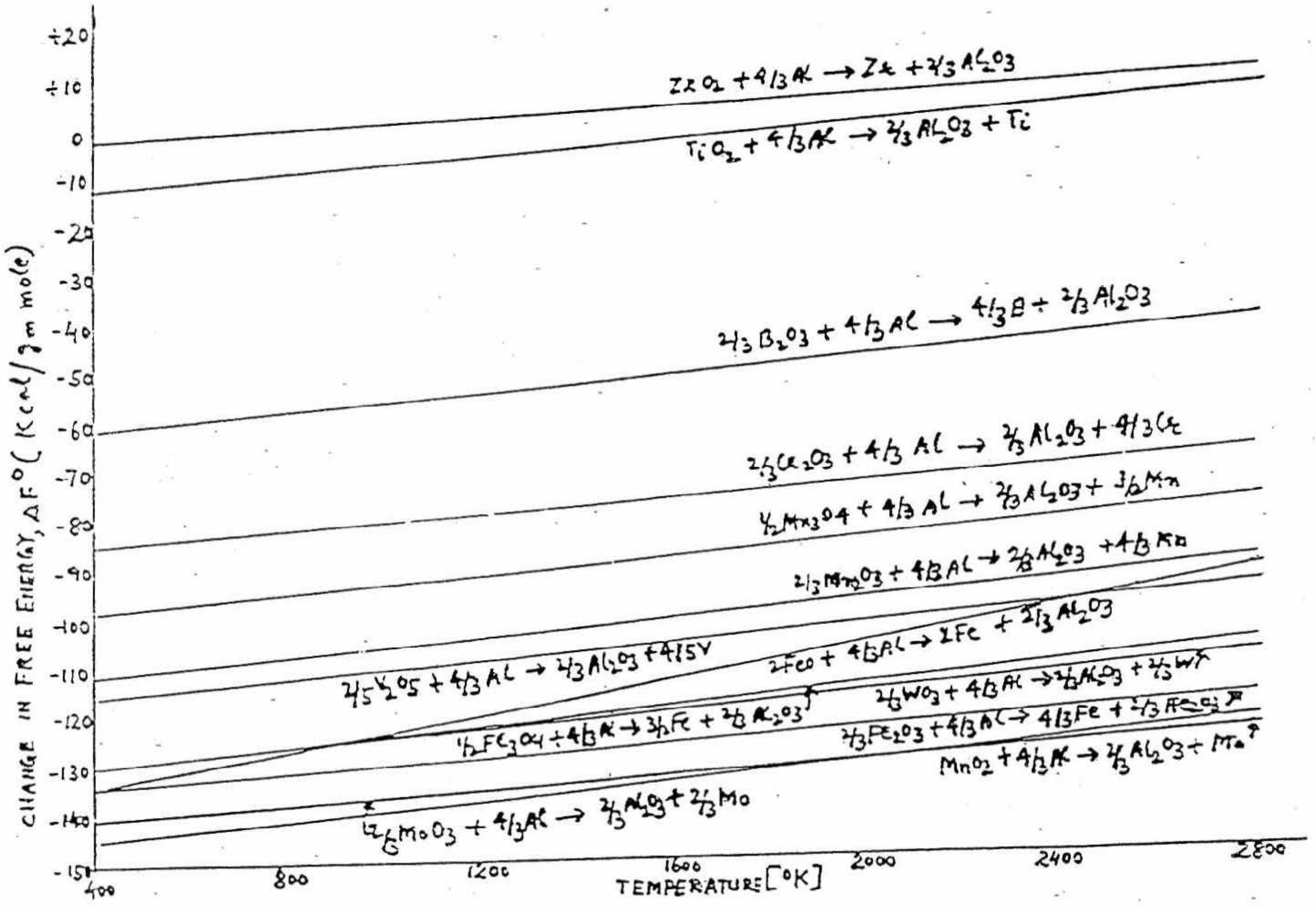

FIG 4 STANDARD FREE ENERGY CHANGE FOR ALUMINO-THERMIC REDUCTION OF OXIDES: (REF.-2.)