

PREPARATION OF ALUMINIUM-SILICON ALLOYS BY ALUMINOTHERMIC REDUCTION*

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Abstract

Alloys of aluminium-silicon have today attained considerable commercial importance in their wide use for multifarious applications and as much as 80 per cent of the world's production of light alloy castings have been estimated to belong to the family of these alloys.

Based on thermodynamical data, the reduction of silica by aluminium is feasible. It was observed that substantial reduction of quartz depends upon a number of factors, the chief of which are: particle size of quartz, amount of cryolite in the charge, temperature of the reactants and holding time. Physical properties of the alloys made by this method have been compared with the physical properties of corresponding alloys produced by direct alloying of the two metals. This comparison yielded identical results in the two cases. It has finally been stressed that this method can be usefully exploited for commercial applications in countries dependent on silicon imports and rich in bauxite and quartz such as India.

Introduction

ALTHOUGH alloys of aluminium-silicon have been mentioned in literature since 1854, it was from 1920 that these alloys were developed for industrial use following the classic discovery of the modification process by Pacz¹. Within the last few years, these alloys have gained considerable commercial importance. At present in U.S.A. alone it has been estimated that 50 per cent of the aluminium alloy castings produced are from these alloys while conservative estimates show that as much as 80 per cent of the world production of light alloy castings belong to this group.

These alloys possess excellent fluidity, castability, machinability, resistance to corro-

sion, freedom from hot-shortness and enhanced mechanical properties after modification. The ternary, quaternary and other complex alloys of this group lend themselves to solution treatment and ageing. In recent times, a number of these alloys have been developed which are characterized by high yield strength, ductility, resistance to deformation, shock and wear, with low coefficient of expansion and excellent frictional properties. Castings subjected to complex stresses and corrosion and particularly those having thin sections are specially made from these alloys. Pistons for internal combustion engines and castings for service at high temperatures such as cylinder blocks, crank-cases and cylinder heads are some of their latest applications.

With the combination of such versatile properties and lightness, the aluminium-silicon alloy and its group find today an extensive use in automobile, general engineering, ship-building, food, chemical and aircraft industries. In a country like India having inadequate resources of copper, the potentialities of these alloys are very high and the need for their development requires no emphasis.

A Review of the Early and Existing Methods of Preparation

Before the year 1900, preparation of these alloys was only of academic interest and the aim of the different workers was only to get a silicon-rich aluminium alloy. Thus, Wholer² and St. Claire Deville³ obtained an alloy with 10 per cent silicon by treating

*Abridged version of the process for which application covering the invention by patents in India, U.K. and U.S.A. has been filed.

potassium silicofluoride with liquid aluminium. From the beginning of this century alloys of composition beyond the eutectic range have been prepared from aluminium, silicon virgin metals or by simultaneous electrolytic reduction⁴ of alumina and silica from molten fluoride baths. In 1920, Pacz invented the famous modification process for enhancing the physical properties of cast aluminium-silicon alloys of eutectic composition and this marked the beginning of the industrial development of these alloys. The modification accomplished by treating the liquid melt just before casting with certain fluorides, especially that of sodium, caused a profound refinement in the structure and considerable improvement in their physical properties. Since then, great efforts have been made to understand its mechanism which afforded a substantial degree of control over the process and the properties attainable in these alloys.

Commercial Methods

The manufacture of aluminium-silicon alloys on a commercial scale received an impetus following the experiments of Pacz on electrothermal reduction of aluminium silicate with carbon. High-grade kaolin mixed with 15-50 per cent of the alumina obtained from Bayer's process formed the main raw material while charcoal with petroleum coke was used as reducing agent. During World War II, this process was widely practised on a tonnage basis in Germany, and was conducted in three stages. The first stage involved pure reduction of kaolin and alumina by carbon in an electric arc furnace resulting in a primary alloy of the following analysis:

	<i>Per cent</i>
Silicon	39.0
Aluminium	58.0
Iron	>0.8
Titanium	>0.5
Calcium	>0.5
Carbon and oxygen	1.2

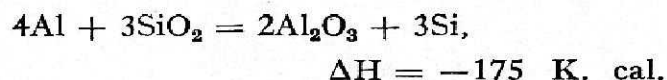
During the second stage, this primary alloy, contaminated with various impurities, was refined through suitable fluxing to yield an alloy containing about 40 per cent silicon. In the third stage it was diluted with pure aluminium to yield 13 per cent silicon (silumin) or alloyed with other alloying elements for use as ternary and quaternary alloys.

The other method which is generally used in all foundries consists in direct melting and alloying with pure silicon to get a suitable master alloy containing 20 or 30 per cent Si in the first instance. From this master alloy, alloys of the required composition are then made subsequently.

Thus it may be observed that the above two methods require either costly reduction furnaces consuming much electrical energy with the necessity of skilful operation or the availability of pure silicon, for both of which India is not well placed.

Aluminium-silicon Alloys by Aluminothermic Reduction

The principle of this process is based on the high free energy of formation of alumina (FIG. 1) in respect of silica. The reaction is, therefore, essentially aluminothermic and takes place as follows:



Aluminium thus reduces silica to silicon and the reduced silicon directly alloys with excess of the reductant to yield an alloy of aluminium-silicon of the desired composition. By adding cryolite to the charge, the activity of Al_2O_3 , which is formed as a final reaction product, is minimized by its removal by cryolite from the sphere of reaction. This alumina-cryolite slag offers a possibility of its use in the aluminium reduction cells—a factor which may favour the economics of this process.

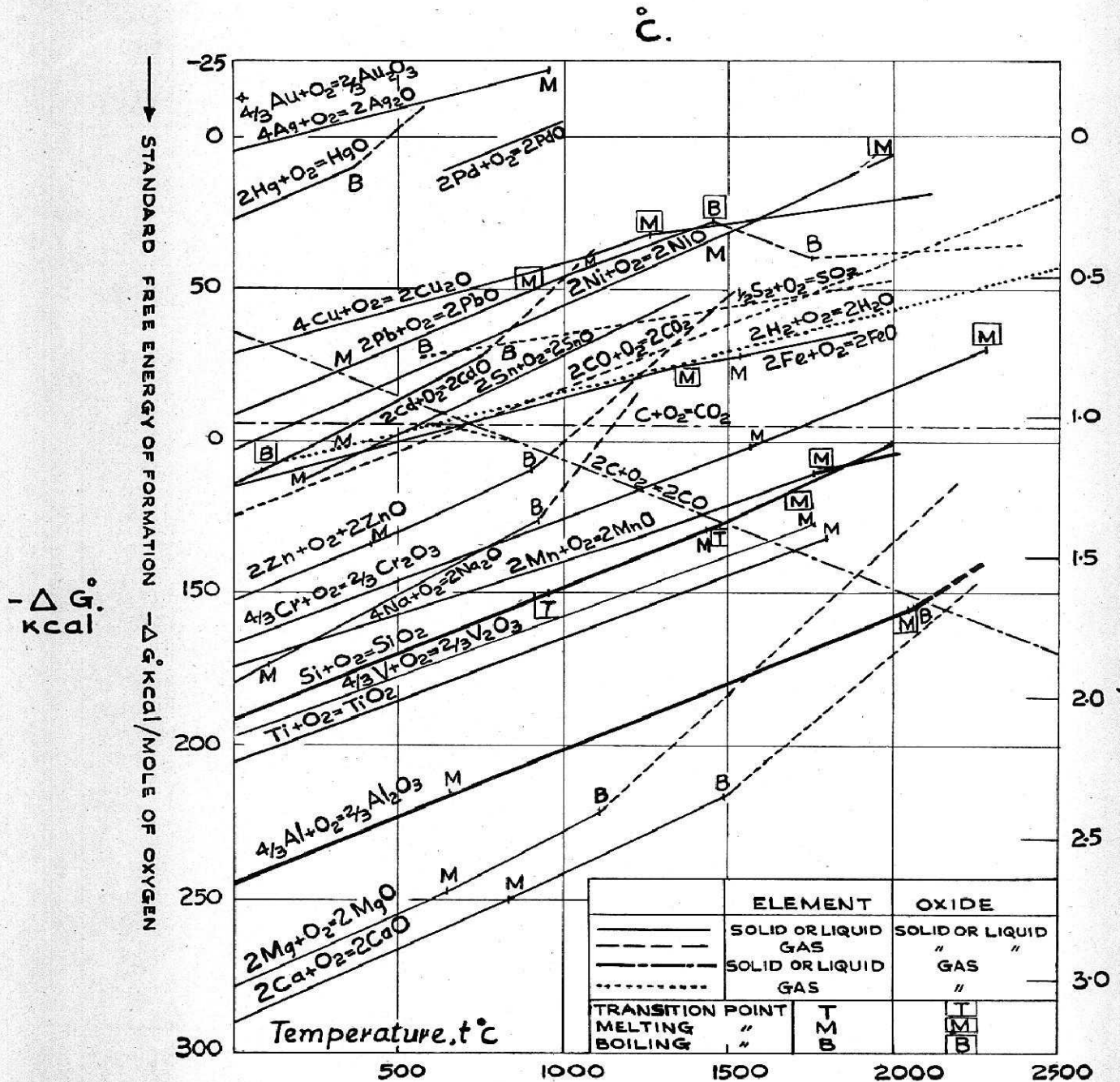


FIG. 1 — CHANGE IN THE STANDARD FREE ENERGY OF FORMATION OF THE OXIDES OF ALUMINIUM AND SILICON IN COMPARISON TO OTHER METALLIC OXIDES AT VARIOUS TEMPERATURES (ELLINGHAM⁷)

Thermodynamic Considerations of the Chemical Reaction

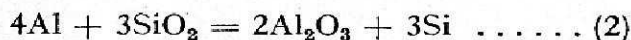
In any chemical reaction, the standard free energy change at temperature T can be

calculated from the simplified equation given below according to Kubaschewski and Evans⁵:

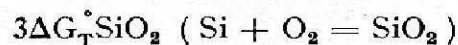
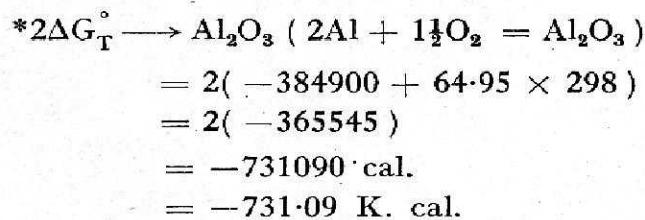
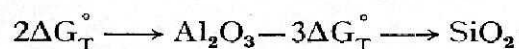
$$\Delta G_T^\circ = A + BT \log T + CT \dots (1)$$

where ΔG_T° = standard free energy change expressed in calories for the reaction involving one gram molecule of oxygen at temperature T, and A, B and C are constants of the reaction.

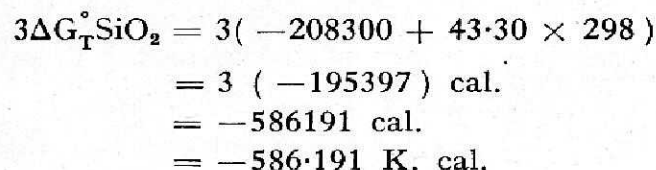
From this equation, the net free energy change for the reaction



can be calculated from the difference of the change in standard free energies of the reactants and resultants. Aluminium and silicon being pure metals, their values of ΔG_T° are zero. The standard free energy change of the reaction, therefore, resolves itself to the difference in ΔG_T° values of alumina and silica for any temperature T (absolute). At temperature 25°C., i.e. 298°A., net free energy change of the reaction (2), therefore, becomes equal to



Substituting the values of A, B and C given by Kubaschewski and Evans in equation (1) and T being equal to 298° absolute,



Therefore, net free energy change for the reaction (2) at 25°C. or 298°A.

$$\begin{aligned} &= -731.090 - (-586.191) \\ &= -144.9 \text{ K. cal.} \end{aligned}$$

$$\text{Since } \Delta G_T^\circ = -RT \log_e K \dots\dots\dots (3)$$

where ΔG_T° = standard free energy change

*Substituting the values of A, B and C given by Kubaschewski and Evans in equation (1) and T = 298° absolute.

at temperature T, expressed in calories, for the reaction involving one gram molecule of oxygen, R = gas constant (1.986 cal./mol./degree), T = absolute temperature (t°C. + 273°), K = equilibrium constant at temperature T of the reaction.

From equation (3)

$$\begin{aligned} \log_e K &= -\frac{\Delta G_T^\circ}{RT} \\ &= -\frac{\Delta G_T^\circ}{1.986T} \end{aligned}$$

$$\text{or } \log_{10} K = -\Delta G_T^\circ / 4.575T \dots\dots (4)$$

Substituting the values of ΔG_T° and T (298°A.) in equation (4)

$$\begin{aligned} \log_{10} K &= \frac{144.9 \times 10^3}{4.575 \times 298} \\ &= 105.6 \\ K &= 3.9 \times 10^{105} \end{aligned}$$

Similarly, the values of ΔG_T° and K at 727° and 1527°C. were calculated and the results are summarized in Table 1 and Fig. 2.

Although data on the thermodynamical aspect of a chemical reaction do not give either its kinetics or the speed of the reaction, yet from the values of ΔG_T° and K furnished in Table 1 (*vide* FIG. 2), the following inferences may be drawn:

1. The magnitude of the driving force of the reaction represented by its change in standard free energy values is far higher, viz. 144.9 K. cal., than the necessary minimum of -10 K. cal. required for any chemical reaction to proceed spontaneously to a

TABLE 1—STANDARD FREE ENERGY CHANGE OF THE REACTION AND ITS EQUILIBRIUM CONSTANT AT VARIOUS TEMPERATURES

Sl. No.	TEMPERATURE, °C.	NET ΔG_T°	K
1	25	-144.9 K. cal.	3.9×10^{105}
2	727	-144.6 K. cal.	3.02×10^{99}
3	1527	-144.5 K. cal.	3.02×10^{17}

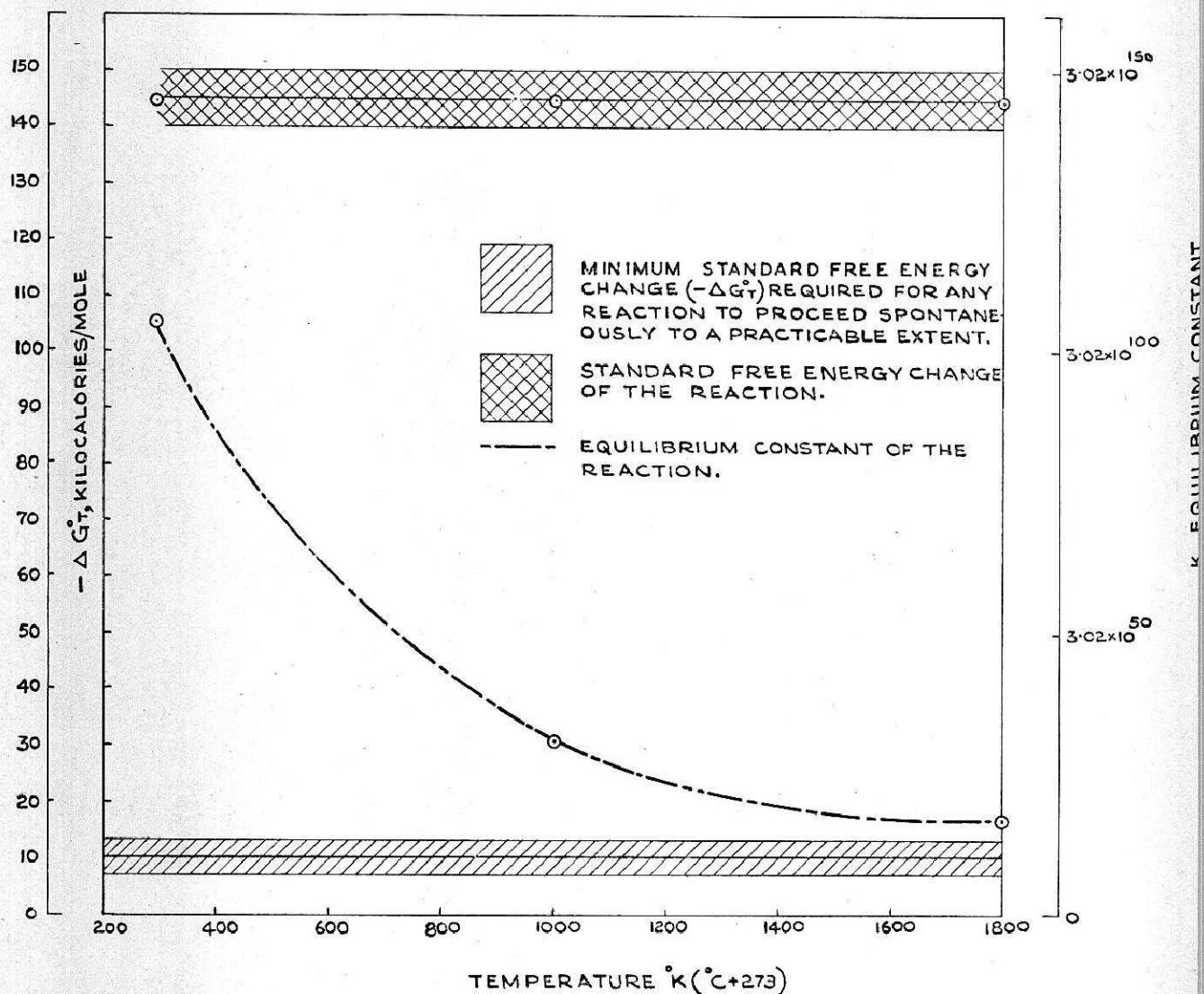


FIG. 2 — STANDARD FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT OF THE REACTION AT VARIOUS TEMPERATURES

practicable extent. As the magnitude of the driving force of the reaction also remains practically the same over a wide temperature range, the reaction has a high reaction potential throughout and the reduction of silica by aluminium is definitely practicable.

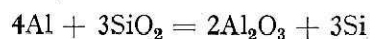
2. The equilibrium constant of the reaction has also high values thereby indicating that the reaction will proceed substantially to the right over a wide range of temperature.

3. The decrease in the values of the equilibrium constant with increase of temperature

further indicates that the reduction of silica by aluminium will be retarded at relatively high temperatures.

Experimental Data and Results

The reaction takes place according to the chemical equation



which means that 90 g. of SiO_2 will require 54 g. of aluminium for the purposes of reduction yielding 42 g. of Si associated with

the formation of 102 g. of Al_2O_3 . At 100 per cent efficiency of reduction, the presence of an excess of aluminium over that required for the reaction will result in a definite amount of silicon in the final alloy. It may be mentioned that under commercial conditions the efficiency of reduction cannot attain this theoretical figure. The charge consisted of commercially pure aluminium or aluminium scrap free from objectionable impurities, quartz and cryolite. At the temperature of reaction, the quartz remains solid. Since in solid particles fine meshes offer greater surface area for reduction, the quartz was ground to about -200 mesh. It was done by calcining it at 1100°C . and followed by crushing in jaw and roll crushers and finally pot-milled in water medium. The charge was melted in a gas-fired Morgan furnace. The exposed surface of the charge was kept covered to prevent oxidation and the molten charge was occasionally stirred to facilitate reduction. The alloy was finally cast in cast iron moulds.

From the experimental observations it was noticed that the reduction of silica by aluminium depended upon various factors, chief of which were particle size of quartz, amount of cryolite in the charge, temperature of the reactants and the holding time.

As regards particle size, it was found that coarse particles, if used, resulted in the sintering of the charge with poor yield of silicon while finer ones of the order of -200 mesh gave a higher yield of silicon with absence of sintering.

A certain amount of cryolite was found necessary to make the reaction proceed in the forward direction, and below which the percentage of silicon in the alloy appreciably decreased. However, the rate of increase in the percentage of silicon was marked up to only a certain amount of cryolite in the charge, beyond which the yield of silicon was not so much marked in relation to the increase in the quantity of cryolite added.

As regards the temperature for reduction, it was observed that an optimum temperature

range existed, below which the reaction rate was very sluggish with corresponding low yields of silicon and also that of the final alloy. Besides, below the optimum temperature the entire charge got sintered. Above this optimum temperature range, the slag became highly viscous and yield of the alloy correspondingly decreased even though the percentage of silicon was not as much affected, possibly due to oxidation and volatilization of aluminium.

Holding time was likewise found to be critical with respect to the percentage of silicon in the final alloy inasmuch as below and above the critical holding time limit, the percentage yield of silicon progressively decreased in both ways. Lower limit is set by the time needed for the reaction to be completed while excessive holding time favoured oxidation.

Figs. 3-7 show the micro-structure of the alloys obtained, from which it may be observed that the alloys had relatively fine-grained structure in the as-cast condition and reasonably free from non-metallic inclusions, particularly of silica particles.

Study of Mechanical Properties

A comprehensive comparative study of the mechanical properties of the alloys produced

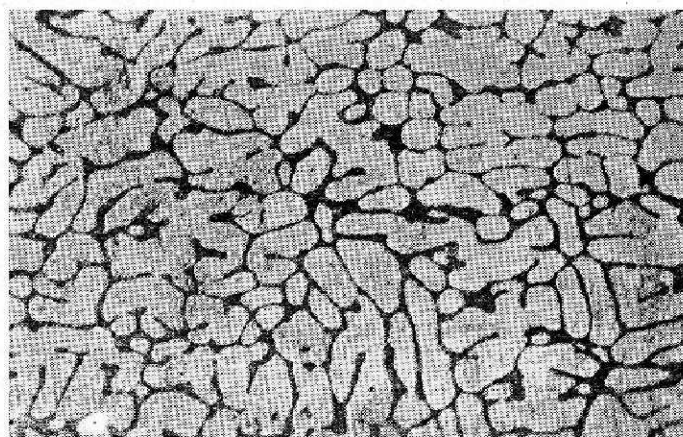


FIG. 3 — 5 PER CENT Al-Si ALLOY CAST IN SAND MOULD SHOWING DENDRITES OF PRIMARY Al AND EUTECTIC OF Al-Si IN THE GRAIN BOUNDARIES [Unetched $\times 100$]



FIG. 4 — 11 PER CENT Al-Si ALLOY OBTAINED BY ALUMINOTHERMIC REDUCTION AND CAST IN PERMANENT MOULD. DENDRITES OF PRIMARY ALUMINIUM IN A MATRIX OF Al-Si EUTECTIC

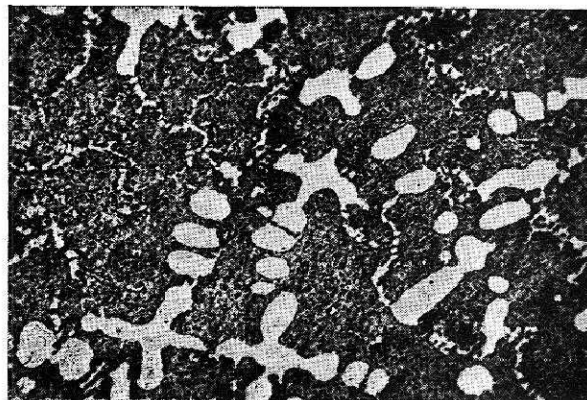


FIG. 6 — 12 PER CENT Al-Si ALLOY OBTAINED BY REDUCTION METHOD AND MODIFIED. CAST IN PERMANENT MOULD. PRIMARY CRYSTALS OF ALUMINIUM (WHITE) IN A MATRIX OF MODIFIED Al-Si EUTECTIC [Unetched $\times 100$]

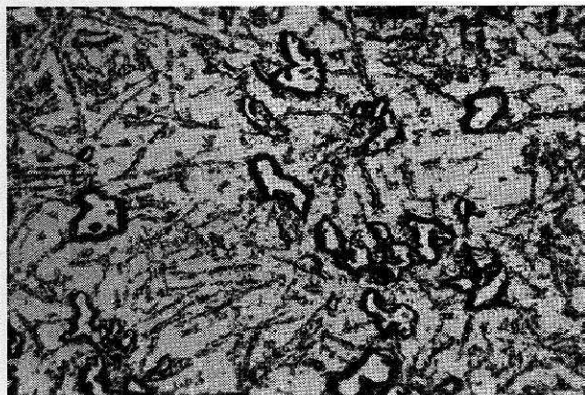


FIG. 5 — 12 PER CENT Al-Si ALLOY, OBTAINED BY REDUCTION METHOD AND CAST IN SAND MOULD. PRIMARY CRYSTALS OF Si IN BACKGROUND OF Al-Si EUTECTIC [Unetched $\times 100$]

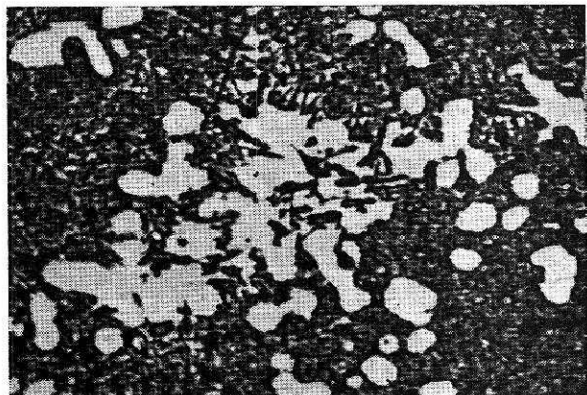


FIG. 7 — SAME AS FIG. 5 BUT CAST IN SAND MOULD SHOWING COARSE EUTECTIC MATRIX [Unetched $\times 100$]

by the technique reported here was made with the alloy made by the conventional method of alloying pure silicon with aluminium in both the ranges of silicon, viz. 4.5-6 per cent and 10-13 per cent Si, in accordance with B.S. Specifications 1490/LM.18M and 1490/6.M respectively. Both chill and sand cast test-pieces were cast and machined according to the D.T.D. Specifications. It has been noticed that regardless of the method of preparation of the alloy, either identical or slightly superior physical proper-

ties were obtained in the alloys prepared by the thermal reduction. It may be due to the effect of finer structure of these alloys, which is believed to be due to the mode of making it.

In conclusion, the authors like to point out that in a country wholly dependent on importation of silicon, the process offers an alternative method of preparing these important class of alloys, the economics of which during normal times may not apparently appeal for its commercial exploitation.

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