A Novel Technique for Hyper Eutectic Aluminium-Silicon Alloy Melt Treatment

R. K. Mahanti, Kishori Lal, A. N. Sinha
and C. S. Sivaramakrishnan

National Metallurgical Laboratory, Jamshedpur-831007, India

This paper deals with a novel technique of melt treatment of hyper eutectic aluminium-silicon alloys. Various potential degassers and modifying agents have been tried out through this technique and the results show that clean melt with good degree of degassing and modification is simultaneously produced without significant pollution problems. Comparative microstructural features and mechanical properties under different melt treatment agents are also discussed.

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I. Introduction

Aluminium-silicon hyper eutectic alloy containing small addition of copper, nickel and magnesium are widely used for automotive applications such as engine blocks, heads, bearings and pistons. These alloys possess excellent casting characteristics, light weight, acceptable thermal and mechanical properties. Their microstructures generally consist of a hard phase Silicon which contributes to wear resistance properties and a relatively soft matrix of Al-Si eutectic phase which enables embedding of any extraneous particles providing a smooth surface for a shaft to rotate inside.

A serious problem faced by the foundrymen in the production of Al-Si alloys is the difficulty in obtaining a completely homogeneous melt and exhibiting refined and modified microstructure free from porosities, segregation etc. During solidification primary silicon is the first phase to crystallise from the melt in the form of pro-eutectic silicon followed by the formation of eutectic. The primary silicon grows in the faceted manner developing a variety of complex polygon shapes depending upon the solidification rates to which the melt is subjected. Slow cooling conditions produce coarse primary silicon crystals which grow with {111} facets resulting in octagonal shape in perfect crystals. However, a variety of shapes of primary silicon from blocky to star have been reported⁽¹⁾. While the fraction of primary Si formed is a function of the alloy composition, the size, shape and distribution of primary silicon in the matrix depends largely upon the foundry parameters such as cooling rate and modifying/refining techniques. Thus at high cooling rates the structure shows the primary silicon particles surrounded by alpha aluminium dendrites⁽²⁾⁻⁽⁴⁾. However, a large difference in densities of aluminium and silicon creates problem of floatation of silicon to the top surface and consequent segregation making an uniform composi-

tion in hyper Al-Si alloys extremely difficult.

The present work deals with a novel technique of treating the hyper eutectic Al-Si melt and producing a sound casting with improved microstructural features. The technique uses a graphite diffuser through which a mixture of 10% chlorine and 90% nitrogen gas is introduced uniformly into the melt. Different modifying agents such as sulphur, strontium compounds and commercial flux were also introduced into the melt through the diffuser with a view to studying the performance efficiency of the diffuser. It was felt that introducing the vapour of these materials through the diffuser would be far superior to the conventional practice of plunging directly into the melt. The loss of material could be considerable in the latter practice besides introducing unwanted decomposition products of the fluxes into the material. Fine bubbles of the gases emerging out of the diffuser into the melt create conditions of intimate gas-metal interaction besides producing a smooth vibrational effect which would be favouring the refinement of primary silicon and eutectic structure without creating the kind of pollution problem encountered with chlorine degassing.

II. Experimental

20 kg heat of Al-18%Si alloy of Mahle composition (Table 1) was prepared in gas fired furnace in the conventional way. Flux consisting of chlorides and fluorides of

Table 1 Chemical composition of Mahle composition.

Si=17.0-19.0 Mass%
Cu=0.8-1.5 "
Mg=0.8-1.3 "
Ni=0.8-1.5 "
Fe=0.6 max "
Al=rest

sodium and potassium was used to cover the molten surface to prevent from oxidation. It was insured that the silicon has gone into solution completely by intermittent stirring of the molten metal using a graphite rod. The molten metal was then degassed and cast into 80 mm dia, 250 mm long cylindrical graphite ingot mould at about 720°C. These ingots were scrap cut and remelted for the present study of evaluating the efficiency of novel technique of melt treatment using a graphite diffuser. The diffuser is a graphite cylinder with dimension 30 mm outside dia., 25 mm inside dia. and 100 mm long. It is chemically treated to produce sufficient porosity of 25–30%. The treatment involved soaking the diffuser in a volatile organic liquid and burning off to dry. One end of the diffuser is closed and the other end connected to nitrogen gas cylinder through mild steel pipe and rubber tubing. In place of nitrogen, argon gas could also be used.

Melts of 500 g for each experiment were prepared using the above ingot in the electrical resistance furnace and one of the following was done:

- (i) Degassed using hexachloroethane pellets
- (ii) Degassed through NML developed graphite diffuser; the diffuser contained weighed quantity of hexachloroethane. Nitrogen from the cylinder was allowed to pass at the rate of 5 lit./min for 2 min through the diffuser carrying along with it the chlorine gas released from hexachloroethane into the melt.
- (iii) Treated with proprietary flux (36A from Greaves Foseco) containing phosphorus compounds in the diffuser and allowed to react with the molten metal.
- (iv) Treated with strontium compound like SrF_2 , SrCl_2 etc. in the diffuser along with hexachloroethane and nitrogen passed from the cylinder to drive the vapour of the compound through the diffuser into the melt.
- (v) Treated with sulphur and hexachloroethane in the diffuser and then nitrogen passed from the cylinder.

After the above treatment the melt was poured into 25 mm dia, 150 mm long graphite mould. The effects of the melt treatments were evaluated through metallographic studies by optical and scanning electron microscope, residual hydrogen analysis and mechanical properties.

III. Results

Table 2 gives the mechanical properties of cast Al-Si alloy of composition mentioned in Table 1. It also gives different agents used for refining/modifying through diffuser. Table 3 shows the residual hydrogen content of the samples giving an idea of the extent of degassing achieved under different agents. Hydrogen content was determined in a Fast Hydrogen Determinator Hymat 200 procured from Strohlein, Germany, through hot extraction technique. Table 4 gives the microstructural features like the reduction in size of primary silicon resulting after the treatment. These features are also shown through microphotographs in Figs. 1–3, of representative samples cut at 30 mm from the top of the ingots in all cases. Figure 1 shows optical microstructure of sample cast without any treatment. It can be seen that idiomorphic silicon, eutectic colonies and fine pseudo-primary aluminium dendrite are present as expected. The optical microstructures of the same alloy treated through the diffuser (a) 0.05%S (b) 0.05S+0.2%36A (c) 0.2% SrF_2 (d) 0.2% SrCl_2 (e) 0.4%36A through diffuser along with mixture of N_2 & Cl_2 (90:10) gases are given in Fig. 2. It

Fig. 1 Microstructure of hyper eutectic Al-Si alloy (Mahle) remelted and cast without any melt treatment. Idiomorphic silicon, eutectic colonies and fine pseudo primary aluminium dendrites are evident.
× 200 × 0.85

Table 2 Mechanical properties of hyper eutectic Al-Si alloy under different conditions of melt treatment.

Alloy desig.	Treatment through diffuser	UTS (MPa)	%El (25 mmGL)	%RA	Hardness (VPN)
M	Untreated	100	2	1	95
Cl-3	($\text{N}_2 + \text{Cl}_2$)	130	2	1	108
*Sr-1	0.2% SrF_2	120	2	1	96
Sr-2	0.2% SrF_2 & ($\text{N}_2 + \text{Cl}_2$)	125	2	1	98
Sr-11	0.2% SrCl_2 & ($\text{N}_2 + \text{Cl}_2$)	130	2	1	110
Sr-12	0.2% SrCl_2 + 0.2%36A & ($\text{N}_2 + \text{Cl}_2$)	140	2	1	110
S-1	0.05%S & ($\text{N}_2 + \text{Cl}_2$)	130	2	1	107
S-5	0.02%S & ($\text{N}_2 + \text{Cl}_2$)	110	2	1	103
*P-1	0.4%36A	110	2	1	106
P-2	0.4%36A & ($\text{N}_2 + \text{Cl}_2$)	160	2	1	115

*Conventionally treated.

Table 3 Hydrogen content of hyper eutectic Al-Si alloy after different conditions of melt treatment.

Alloy design.	Treatment through diffuser	H ₂ content (cm ³ /100 g)	% removal of H ₂
M	Untreated	2.5655	—
Cl-3	(N ₂ + Cl ₂)	0.5569	78.0
*Sr-1	0.2%SrF ₂	1.3697	46.0
Sr-2	0.2%SrF ₂ & (N ₂ + Cl ₂)	0.7019	73.0
Sr-11	0.2%SrCl ₂ & (N ₂ + Cl ₂)	0.7702	70.0
Sr-12	0.2%SrCl ₂ + 0.2%36A & (N ₂ + Cl ₂)	0.5863	77.0
S-1	0.05%S & (N ₂ + Cl ₂)	1.1500	41.0
S-5	0.02%S & (N ₂ + Cl ₂)	0.6563	74.0
*P-1	0.4%36A	2.0482	20.0
P-2	0.4%36A & (N ₂ + Cl ₂)	0.4827	81.0

*Conventionally treated.

may be noted that eutectic is more modified in (d). The variations in microstructures as a result of different

agents given in Table 4 are evident. Tensile fractured samples surfaces were also seen under SEM (Jeol 330) to characterise the mode of fracture with a view to understand if any ductility is introduced through these treatments. The details of SEM of samples are (a) without any treatment (b) treated with N₂ & Cl₂ mixture through diffuser. Some ductility in (b) could be noticed in Fig. 3.

IV. Discussion

Normally phosphorus or phosphorus bearing compound are used for the refinement of primary silicon as it is believed that phosphorus in the form of AlP forms the nucleants for the silicon crystals. Refining agents like Ga, Ge, Se, Be, Te, Li, Cd, Zn, Mn, V, Cb, Bi, Mo, Hf and S either individually or in combination have also been used⁽⁵⁾⁽⁶⁾. These elements along with Na would give both silicon refinement and eutectic modification but due to

Fig. 2. Optical microstructures of hyper eutectic Al-Si alloy (Mahle) treated with N₂+Cl₂ gas mixture along with (a) 0.05%S, (b) 0.05%S+0.2%36A, (c) 0.2%SrF₂, (d) 0.2%SrCl₂ and (e) 0.4%36A. Significant refinement of silicon in (d) and (e) may be noted.

× 200 × 0.85

Table 4 Effect of different melt treatments on the size of primary silicon in hyper eutectic Al-Si alloy.

Sl. No.	Treatment through diffuser	Si size, $d/\mu\text{m}$	Standard deviation, $\sigma^\pm/\mu\text{m}$	*Coeff. of variation, $V/\%$	% Refinement	Remarks
1.	Untreated	63	27	43	—	Fig. 1
2.	0.05%S & ($\text{N}_2 + \text{Cl}_2$)	25	17	68	60	Fig. 2(a)
3.	0.05%S + 0.2%36A & ($\text{N}_2 + \text{Cl}_2$)	13	4	33	79	Fig. 2(b)
4.	0.2% SrF_2 & ($\text{N}_2 + \text{Cl}_2$)	25	13	52	60	Fig. 2(c)
5.	0.2% SrCl_2 & ($\text{N}_2 + \text{Cl}_2$)	22	13	59	65	Fig. 2(d)
6.	0.4%36A & ($\text{N}_2 + \text{Cl}_2$)	21	12	56	67	Fig. 2(e)

* $V = (\sigma/d) \times 100\%$

Fig. 3. SEM photograph of fractured surface of hyper eutectic Al-Si alloy (Mahle) produced (a) without melt treatment (b) melt treated with $\text{N}_2 + \text{Cl}_2$ gas mixture through diffuser. Notice some ductility in (b) showing a good fraction of dimples.

vapourisation of Na, effect of eutectic modification is not always achieved to a desired level. Literature also cites the use of Ce in the form of Misch metal for the modification of hyper eutectic Al-Si alloys but the results have not always been favourable⁽⁷⁾.

There is in recent times a great spurt in strontium treatment of Al-Si alloy and this work, therefore, has given particular emphasis on this.

From the microstructures of the cast samples under various treatments reported in Figs. 1-3, it is evident that the treatment of the melt with strontium bearing com-

pounds, proprietary modifier (36A) and S in conjunction with N_2 & Cl_2 through the diffuser always produce the structural refinement to varying degree. The silicon size has been reduced from $100\mu\text{m}$ to $20\text{--}25\mu\text{m}$ approximately. The porosity and silicon counts in the eutectic phase are also considerably reduced. Additional advantage of the present treatment is the effective degassing achieved without causing any serious pollution problem about which the authors have dealt with in earlier papers⁽⁸⁾⁻⁽¹⁰⁾.

It is also well known that hydrogen removal is obtained by the interaction of fine bubbles of chlorine, inert gases like nitrogen, argon etc. or a combination thereof purged through the diffuser. Basically hydrogen is diffused into the bubbles or adsorbed on the surface of the bubbles. The efficiency of hydrogen removal (E) depends on the area of contact of the melt with the bubble, the flow rate of the degassing media etc. as given in the following equation⁽¹¹⁾:

$$E = C_s / C_e$$

$$= \left(\frac{KA}{Q} + 1 \right)^{-1}$$

where C_s and C_e are final and initial hydrogen concentration, K is a constant which depends upon the system, A is the area of contact of bubbles with the melt and Q is the flow rate of the purging gas.

It is clear that finer the bubble and greater the rate of flow the better will be the gas removal from the melt. In the present system the diffuser produces fine bubbles because of its microporous cavities through which the gas purges and as a result good reduction in the level of hydrogen is achieved.

V. Conclusions

A systematic study on the microstructure of hypereutectic Al-Si piston alloy under various agents introduced through a microporous graphite diffuser has shown that simultaneous refinement of microstructure and high degree of degassing without causing significant pollution problem is achieved. The diffuser produces smooth bubbling ensuring effective degassing and marked reduction in silicon size. About 70% reduction in hydrogen content and silicon size to the level of nearly $25\mu\text{m}$ have been obtained. Unlike the conventional process of degassing/modifying through pellet/chlorine treat-

ment, in the present case the dross generated, metal loss through entrapment in the dross etc., are also insignificant and the melt cleanliness is very high.

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