



# Development of New Combination of Grain Refiner-cum-Modifier for LM-21 Alloy



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#### **ABSTRACT**

The effect of combined grain refinement cum modification was studied on LM-21 alloy. For combined grain refinement and modification effect, the multifunctional Al-Ti-Sr, Al-B-Sr and Al-Ti-B-Sr master alloys were developed by melting individual grain refiners like Al-5Ti, Al-3B and Al-1Ti-3B with Al-Sr master alloys. The newly developed master alloys act as both grain refiner and modifier. The results also show simultaneous grain refinement of á-Al and modification effect of eutectic Si supported by improvement in mechanical properties.

**Keywords:** Aluminium-Silicon; Modification; Grain refinement; Master alloys.

### INTRODUCTION

Al-Si alloys are widely accepted as casting alloys for industries due to their excellent casting characteristics, good corrosion resistance, and good weldability. Application of binary Al-Si alloys varies from domestic food components to automotive and aircraft parts, some of which include cylinder heads and intake manifolds to achieve greater weight reduction [1-3]. In hypoeutectic Al-Si alloys, the major constituent is columnar  $\alpha$ -Al, with minor amount of randomly dispersed elongated plates or lamellae of silicon. However, the eutectic silicon in an untreated hypoeutectic alloys forms brittle coarse acicular or plate type with sharp edge shaped and these particles provides an effortless way for the commencement and propagation of fracture. This drastically lowers the tensile strength, elongation and tribological values of the alloy. To overcome this, modifiers in the form of Sb, Na, P and Sr are added [4-7]. Among these modifiers, Sr has the long lasting effect (up to 2 h of holding) and low oxidation solubility [2]. Hence, in the present work, the modifier in the form of Al-10Sr master alloy was used. The modifier transforms coral like Si particles into finer Si with better globular in shapes, thereby leading to improvement in mechanical properties [1,3,8-11].

The size and shape of  $\alpha$ -Al in Al-Si alloy directly contributes to the mechanical properties, and it is well known that finer á-Al will lead to improved mechanical properties as compared to larger grains. The finer equiaxed á-Al grains in the Al-Si alloy were obtained by adding varying ratios of Ti and B contained master alloys adding varying ratios of Ti and B contained master alloys is imultaneously in Al-Si melt, the above said master alloys are added in the form of chips to the melt in combined addition from the single rod instead of using chips of two different rods. The advantage of using single master alloy is to serve both purposes of grain refinement and modification, thus directly reducing the manufacturing cost and simplifying the foundry operations.

# **EXPERIMENTAL DETAILS**

Master alloys like Al-5Ti, Al-3B and Al-1Ti-3B were prepared indigenously by the reaction of molten Al with halide salts like K<sub>2</sub>TiF<sub>6</sub> and KBF<sub>4</sub> at a reaction temperature of 800°C with a reaction time of 60 min. in an induction furnace. The indigenously prepared binary Al-Ti, Al-B and ternary Al-Ti-B master alloys were melted individually with the Al-10Sr master alloy in a resistance furnace to form a new combination of ternary Al-Ti-Sr, Al-B-Sr and



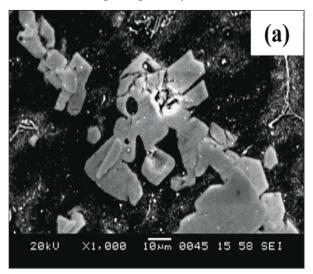


quaternary Al-Ti-B-Sr master alloys. These multifunctional master alloys were used for the grain refinement cum modification studies in LM-21 alloy. LM-21 allov was melted in an electrical resistance furnace under the cover flux and the melt was held at 720°C. After degassing with solid hexachloroethane, master alloy chips were added to the melt for grain refinement cum modification studies. The melt was stirred for 30 seconds with zircon coated iron rod after the addition of grain refiner cum modifier, without any further stirring. Parts of the melts were poured into a preheated cylindrical graphite mould at intervals of 0, 2, 5, 30, 60 and 120 and 120s min. The sample designated as '0' represents that part of the melt which was cast without the addition of master alloy and '120s' refers to the melt which was stirred for 10 seconds after 120 min. of holding. The grain refined cum modified samples were characterized by macroscopy and microscopy and the polished specimens were examined using SEM for microstructure studies and DAS measurement using image analyser. Table-1 shows the details of addition levels of grain refiner cum modifiers to LM-21 alloy.

### RESULTS AND DISCUSSION

# Characterisation of Multifunctional Master Alloys

Figure 1a shows the SEM microphotograph of Al-5Ti-3.3Sr master alloy, obtained by melting Al-5Ti with Al-3.3Sr master alloys in an electrical resistance furnace. Reaction of Al<sub>3</sub>Ti of Al-5Ti master alloy with Al<sub>4</sub>Sr particles of Al-3.3Sr master alloy leads to the formation of AlTiSr intermetallic particles. The master alloy also consists of large blocky type AlTiSr particles in an Al matrix. Figure 1b shows the EDS spectrum taken on the AlTiSr particle of ternary Al-5Ti-3.3Sr master alloy confirming Al, Ti and Sr peaks. Figure 2a shows the SEM image of Al-3B-2.1Sr master alloy, which clearly indicates the clustering of large SrB<sub>6</sub> particles in some regions. The Al-3B master alloy contains AlB<sub>2</sub> boride particles and when these particles are combined with Al<sub>4</sub>Sr particles



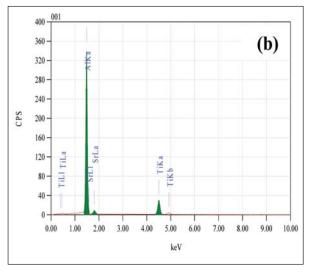


Fig. 1: (a) SEM image of Al-5Ti-3.3Sr master alloy showing Al<sub>3</sub>Ti, Al<sub>4</sub>Sr, and AlTiSr particles and (b) EDS spectrum of Al-5Ti-3.3Sr master alloy taken on the particle.

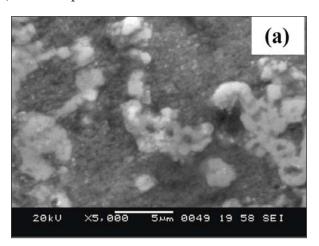
Table-1: Optimum Addition Levels of Ternary and Quaternary Master Alloys to LM-21 Alloy

All	oy Master alloy	Optimum addition level of master alloy, wt%	Ti%	В%	Sr%
LM	I-21 Al-5Ti-3.3Sr	0.45	0.0225	-	0.0150
	Al-3B-2.1Sr	0.70	-	0.0210	0.0150
	Al-1Ti-3B-2.3Sr	0.65	0.0065	0.0195	0.0150





that are present in the Al-2.1Sr master alloy, SrB, particles are formed. In addition, uniformly distributed smaller AlB, and Al Sr particles are also evident from Fig. 2a. Figure 2b shows the EDS spectrum of ternary Al-3B-2.1Sr master alloy taken on the bulk of the alloy, clearly indicating the presence of Al and Sr peaks. Due to the limitation, the boron peak was not observed during EDS analysis. Clustering of AlTiBSr particles in few regions is seen from SEM image (Fig. 3a) of Al-1Ti-3B-2.3Sr master alloy. Melting of Al-1Ti-3B master alloy with Al-2.3Sr master alloy leads to the reaction between mixed borides [(Al, Ti)B<sub>9</sub>] of grain refiner with Al<sub>4</sub>Sr particles of modifier, resulting in the formation of dense AlTiBSr particles. Figure 3b shows the EDS spectrum of quaternary Al-1Ti-3B-2.3Sr master alloy. This is taken on the particle of the alloy, clearly showing the presence of Al, Ti and Sr peaks.



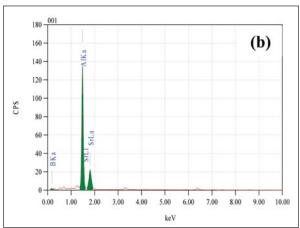
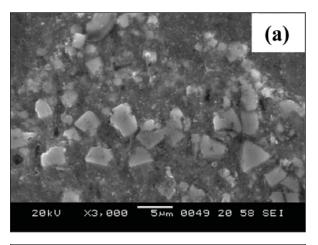


Fig. 2 : (a) SEM image of Al-3B-2.1Sr master alloy showing  ${\rm SrB}_6$  particles and (b) EDS spectrum of Al-3B-2.1Sr master alloy taken on the bulk of the alloy.



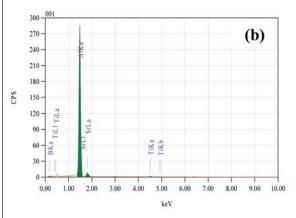


Fig. 3 : (a) SEM image of Al-1Ti-3B-2.3Sr master alloy showing  ${\rm SrB}_6$  and AlTiBSr particles and (b) EDS spectrum of Al-1Ti-3B-2.3Sr master alloy taken on the particle.

# **Grain Refinement-cum-Modification Studies DAS Analysis**

Figure 4 shows the results of DAS analysis of LM-21 alloy grain refined cum modified with optimum addition levels of various master alloys. It is clear from Fig. 4 that in the absence of grain refiner cum modifier alloy, LM-21 alloy has a DAS value of 88 mm. However, with the individual addition of 0.45 wt% of Al-5Ti-3.3Sr master alloy to LM-21 alloy leads to significant reduction in DAS value from 88 mm to 58 mm at 2 min. of holding and it remains same (~58 mm) even at longer holding periods (120 min.). The minimum DAS value of 58 mm is mainly due to the presence of AlTiSr particles present in the Al-5Ti-3.3Sr master alloy, which acts as heterogeneous nucleating sites during the solidification. Addition of 0.70 wt% of Al-3B-2.1Sr master alloy to LM-21 alloy shows a DAS of 36  $\mu m$  both at shorter (2 min.) and longer (120 min.) holding





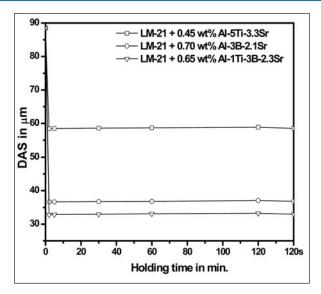


Fig. 4: DAS analysis of LM-21 alloy before and after the optimum addition levels of various master alloys.

time. This could be attributed to the fact that grain refining cum modifying particles (SrB<sub>6</sub>) act as nucleating centers ding the solidification. Further a minimum DAS value of 32 mm was obtained from 2-120 min. holding periods, when the LM-21 alloy melt was treated with 0.65 wt% of B-rich Al-1Ti-3B-2.1Sr master alloy. The overall DAS values suggests that AlTiBSr particles present in Al-1Ti-3B-2.1Sr master alloy are more efficient nucleating sites than AlTiSr particles present in Al-5Ti-3.3Sr master

alloy and  $SrB_6$  particles present in the Al-3B-2.1Sr master alloy.

### **Macroscopic Studies**

It is clear from Fig. 5 that in the absence of grain refiner, LM-21 alloy has coarse columnar α-Al dendritic structure (o min. samples). However, with the addition of 0.45 wt% of Al-5Ti-3.3Sr master alloy (Fig. 5a), LM-21 alloy has shown response towards grain refinement with complete structural transition from coarse columnar α-Al dendritic structure to fine equiaxed dendritic structure not only at shorter holding periods (2 min.) but also at longer holding periods (120 min.) as clearly evident from the macrophotographs. Such structural changes could be due to the presence of AlTiSr particles present in Al-5Ti-3.3Sr master alloy, which acted as heterogeneous nucleating sites for the solidification of  $\alpha$ -Al. However, stirring the melt for 10s after 120 min. of holding indicates the macrostructure similar to 120 min. sample. It is clear from Fig. 5b that the addition of 0.70 wt% of Al-3B-2.1Sr master alloy to LM-21 alloy results in complete transition of α-Al from coarse columnar structure to fine equiaxed structure at all holding periods of 2-120 min. The reason could be due to the presence of grain refining cum modifying SrB<sub>6</sub> intermetallic particles, which are formed

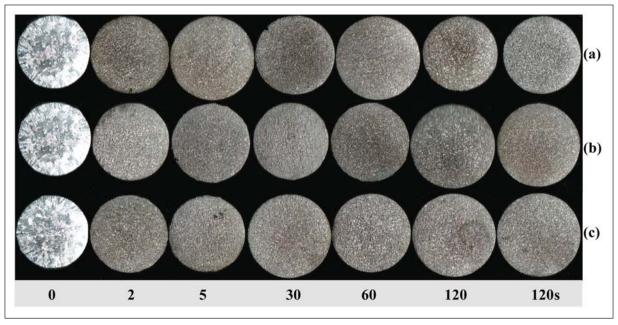


Fig. 5: Macrophotographs of LM-21 alloy before and after the addition levels of (a) 0.45 wt% of Al-5Ti-3.3Sr (b) 0.70 wt% of Al-3B-2.1Sr and (c) 0.65 wt% of Al-1Ti-3B-2.3Sr master alloys.





by the reaction of AlB $_2$  particles of Al-3B grain refiner with Al $_4$ Sr particles of Al-2.1Sr modifier. From Fig. 5c, it was observed that the individual addition of 0.65 wt% of Al-1Ti-3B-2.3Sr master alloy to LM-21 alloy significantly refines the elongated columnar  $\alpha$ -Al dendrites and converts them into fine equiaxed  $\alpha$ -Al dendrites at all holding periods. This clearly shows a finer and uniform distribution of grain refining constituents [mixed borides  $\{(Al,Ti)B_2\}$  along with Al $_3$ Ti] and grain refining cum modifying constituents (SrB $_6$  and AlTiBSr). The grain refining cum modifying constituents are mainly formed due to the reaction between mixed borides  $\{(Al,Ti)B_2\}$  of Al-1Ti-3B grain refiner with Al $_4$ Sr particles of Al-2.3Sr modifier. Thus the macroscopic observations (Fig. 5) are supported by DAS analysis of LM-21 alloy (Fig. 4).

#### **SEM Studies**

SEM analysis was carried out on LM-21 alloy both in the absence and presence of grain refiner cum modifiers to observe the microstructural changes. It is clear from Fig.

6a that, in the absence of grain refiner cum modifier, LM-21 alloy shows coarse columnar  $\alpha$ -Al dendritic structure with unmodified needle form eutectic Si. However, with the addition of 0.45% of Al-5Ti-3.3Sr master alloy to LM-21 alloy, the coarse columnar  $\alpha$ -Al structure gets converted to equiaxed α-Al structure as clearly seen from Fig. 6b. In addition, there is also a change in eutectic Si morphology. The Si present in the form of brittle needle form is converted into fine fibrous form. Such structural conversion could be due to the presence of AlTiSr particles present in the Al-5Ti-3.3Sr master alloy, which act as heterogeneous nucleating site during solidification of -Al resulting in equiaxed structure along with fine fibrous form of eutectic Si. However, with the individual addition of 0.70 wt% of Al-3B-2.1Sr master alloy to LM-21 alloy reveals good grain refinement of a-Al dendrites together with well modification of eutectic Si as clearly observed in Fig. 6c. The grain refining (AlB<sub>2</sub>) and grain refining cum modifying (SrB<sub>6</sub>) particles present in the Al-3B-2.1Sr

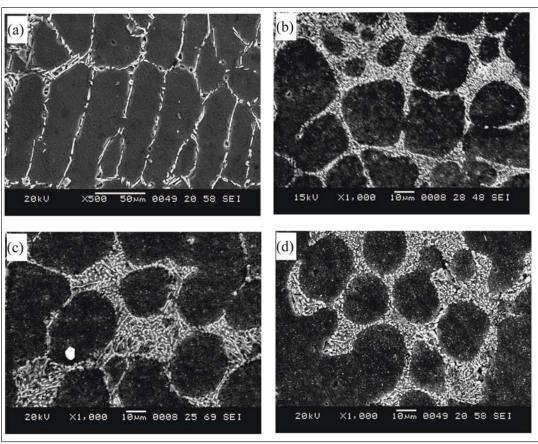


Fig. 6: SEM images of LM-21 alloy (a) without master alloy and with the addition levels of (b) 0.45 wt% of Al-5Ti-3.3Sr (c) 0.70 wt% of Al-3B-2.1Sr and (d) 0.65 wt% of Al-1Ti-3B-2.3Sr master alloys.





Table-2: Evaluation of Mechanical Properties of LM-21 Alloy Before and After Addition of Al-1Ti-3B-2.3Sr Master Alloy

Alloy	Master alloy used	Optimum addition level of master alloy, wt%	2% Proof Stress	UTS (MPa)	S%E
LM-21	-	-	115.27	187.27	06.32
LM-21	Al-1Ti-3B-2.3Sr	0.65	126.91	222.81	08.95

master alloy acts as substrates for the heterogeneous nucleation of  $\alpha$ -Al dendrites during solidification. Results also suggest that the addition of 0.65 wt% of Al-1Ti-3B-2.3Sr master alloy to LM-21 alloy (Fig. 6d) is required to achieve complete transition from coarse columnar  $\alpha$ -Al dendritic structure to fine equiaxed  $\alpha$ -Al dendritic structure together with good modification of eutectic Si. Sufficient numbers of AlTiBSr particles present in the melt are responsible for the combined effects of grain refinement and modification in LM-21 alloy. Thus the overall results of SEM (Fig. 6) are supported by the results of macroscopy (Fig. 5) and DAS analysis (Fig. 4).

### **Evaluation of Mechanical Properties Studies**

The tensile properties of LM-21 alloy depend both on the shape and size of the  $\alpha$ -Al grains and eutectic silicon morphology. As a result, improvements in the mechanical properties have been observed in LM-21 alloy by the addition of grain refiner cum modifier. For each composition, the result of each tensile test reading is the average of three test readings. Table 2 shows the mechanical properties of LM-21 alloy without and with the addition of Al-1Ti-3B-2.3Sr master alloy. It is clear from the table 2 that the improvement in mechanical properties was observed, which is mainly attributed due to the fact that nucleating Al $_3$ Ti, TiB $_2$ , (Al, Ti)B $_2$ , Al $_4$ Sr, SrB $_6$  and AlTiBSr particles present in the melt of Al-1Ti-3B-2.3Sr master alloy are responsible for combined grain refinement cum modification effect.

# **CONCLUSIONS**

Multifunctional ternary (Al-5Ti-3.3Sr and Al-3B-2.1Sr) and quaternary (Al-1Ti-3B-2.3Sr) master alloys have been developed in the laboratory by melting individual conventional grain refiners with modifier.

- Addition of 0.45 wt% of Al-5Ti-3.3Sr, 0.70 wt% of Al-3B-2.1Sr and 0.65 wt% of Al-1Ti-3B-2.3Sr master alloys to LM-21 alloy shows the simultaneous effects of grain refinement of á-Al dendrites and modification of eutectic Si up to 120 min. of holding time.
- Quaternary B-rich with Ti and Sr containing master alloy is more efficient grain refiner cum modifier on LM-21 alloy when compared to other ternary (Al-5Ti-3.3Sr and Al-3B-2.1Sr) master alloys. This is due to the presence of more efficient nucleating particles {(Al,Ti)B<sub>2</sub>, Al<sub>3</sub>Ti and commonly formed SrB<sub>6</sub> and AlTiBSr particles of the two master alloys in the combined addition}.
- Significant improvement in the mechanical properties was observed by the addition of newly developed Al-1Ti-3B-2.3Sr master alloy to LM-21 alloy compared to its absence.

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