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Comparative Study of Addition of Strontium in Aluminium (Aa6063)

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***Abstract*—Aluminium is used in huge variety of products including cans, foils, kitchen utensils, window frames, aeroplane parts etc. In this paper we are going to go through various areas in which aluminium scraps are being generated and by knowing so various application of aluminium in manufacturing and several other industrial fields were studied. Methods by which the aluminium strength is increased are studied. Iron composition has a major impact in the strength of aluminium which is a tramp element (as it is a major foreign impurity) and therefore reduction of iron content yields in improved mechanical properties. Alloying aluminium with certain metals like strontium, manganese, cobalt enhances the aluminium strength. Alloying metals and iron reduction methods were discussed. Finally the native aluminium and the alloyed aluminium with the reduction of iron content is compared and the results are discussed.**

***Index Terms*— Strontium, Aluminium**

I. INTRODUCTION

Aluminium when compared to other materials, has the highest potential for systematic recycling due to: i) their high economic value, ii) the large scrap volumes enabling economies of scale, as well as iii) their distinctive feature of excellent recyclability. Nevertheless, the contamination of the metal streams each time that re-circulates from residuals (alloying and foreign elements), especially those for which the removal from the melt is problematic and the makes processing more difficult.

For Aluminium (Al) more than 450 alloy designations/compositions have been registered by the Aluminium Association Inc. While iron (Fe) mainly occurs as foreign/impurity element (also known as tramp element), typical alloying elements for aluminium are: silicon (Si), copper (Cu), Zinc (Zn), magnesium (Mg) and manganese (Mn). Two major categories can be defined with respect to the concentration of the alloying elements: i) high purity wrought alloys (alloy content up to 10 wt. %) and ii) cast alloys with much higher, especially for Si, tolerance limits (alloy content up to 20 wt.%). Due to the mixture and/or accumulation of the alloying elements during the different life cycle stages, these elements can no longer be considered as valuable elements, but rather as contaminants.

Iron is one of the main impurity elements present in commercial aluminium alloys and due to its very low solid solubility in the aluminium matrix, is present predominantly in the form of second phase intermetallic particles. The phase diagram for Al–Fe indicates a maximum solubility of approximately 0.04wt. % at 655°C, decreasing to <0.001wt.% below »430°C. Under equilibrium conditions, iron in excess of the solid solubility will be present as the phase $Al3Fe$.

If equilibrium is not reached, iron may also be present in supersaturated solid solution or in the form of a number of non-equilibrium intermetallic phases.

Several previous studies have clearly demonstrated that the presence of ironcontaining intermetallic particles has a detrimental effect on corrosion resistance [2]–[5]. The primary aluminium (also called "potroom metal") typically contains about 0.1wt. % Fe, which is significantly above the solid solubility of Fe in Al at room temperature. Furthermore relatively few products are directly made from primary aluminium: a significant amount of recycled aluminium is used for making products, which increases the amount of Fe in aluminium alloys. Thus, the presence of iron is likely to be a significant factor in corrosion of aluminium alloys.

High purity aluminium is highly resistant to corrosion in neutral environments owing to the insulating nature of the alumina passive film. Iron rich phases are catalytic sites for cathodic reactions, and at the same time are sites for nucleation of pits [2]–[8]. Furthermore, iron is a noble element, and so it is possible that its presence in solid solution may affect anodic dissolution kinetics.

II. RECOVERY OF ALUMINIUM

Current treatment of bottom ashes Whatever reuse of the bottom ashes is applied, some treatments are required in order to prevent the negative environmental impacts that a direct reuse of the raw bottom ashes can cause due to their high content of heavy metals and polluting agents, as well as to increase their mechanical properties, in view of the recovery of inert materials. These include physical, chemical or thermal treatments such as:

- Size separation with screens or drums, aimed at selecting the most appropriate grain size from a geotechnical point of view and separating the fine and more contaminated fraction;
- Extraction of metals through magnetic and eddy current separators. Metals removal is usually carried out after the

size separation to increase its effectiveness;

- Washing with water or chemical solvents to remove heavy metals and salts. Water is usually used for salt (Na and Cl) and sulphate removal, while acid or alkaline solutions (hydrochloric, nitric or sulphuric acid, aqua regia, etc.) or chelating agents (nitro triacetate – NTA, ethylene diamine tetra acetic acid – EDTA, diethylene triamine pentaacetic acid – DTPA) are required for heavy metals (Polettini et al., 2007);
- The ageing process, which promotes the transformation of bottom ash constituents into more thermodynamically stable forms. Bottom ashes are stockpiled for 3–12 months under atmospheric conditions. During this time, the precipitation of the carbonates, the degradation of the organic matter, as well as a change in pH occur, causing the mineralogical alteration of the bottom ashes, with an immobilization effect for Cu, Pb, Zn and chloride, while oxyanionforming elements such as Cr, Mo and Sb and also sulphate may become more mobile [1]
- The addition of Al(III) or Fe(III) salts and cements or other bonding agents which increase the sorption properties of the bottom ashes and reduce the metals mobility and hence their leaching. Positive effects are usually observed for Cu and oxyanion-forming metals such as Mo, Cr and Sb, while the use of Al(III) and Fe(III) salts can favour the mobilization of Ni, Zn and the major cations Ca, Mg and Na [2] • the vitrification or sintering to immobilize heavy metals into an amorphous glassy phase. However, due to the high energy consumption and the cost of energy, thermal processes are rarely applied in Europe.

For aluminium, eddy current separators show an average recovery efficiency of 30% of the aluminium fed into the furnace of the incineration plant, which corresponds to 1% of the bottom ash mass. However, some advanced technologies can reach higher recovery rates, up to 70%, as described by Muchova and Rem (2007) and Manders (2008). The recovery efficiency of ferrous metals is higher than that of non-ferrous: about 80% of the steel fed into the furnace, i.e. 6% of the bottom ash mass, can in fact be easily recovered. The relatively low recovery efficiency of aluminium compared to that of ferrous metals is also related to its peculiar behaviour during combustion. The thinner fractions of aluminium, such as foils or light packaging are in fact subject to a partial volatilization in the furnace, which leads to an appreciable mass loss, thus affecting the potential recovery from bottom ashes.

A. *Model Definition*

The amount of aluminium scraps which can be recovered from bottom ashes has been evaluated through a model specifically developed for this purpose. In the definition of the model we have taken into account the influence of different parameters related to the aluminium packaging production and to the whole waste management system. Aluminium packaging is in fact primarily recovered within the separate collection of waste, which affects the amount of aluminium contained in the unsorted residual waste (URW). In a framework where overall source separation levels are increasing, as requested for example by the EU Directive on waste (2008/98/EC), aluminium in the URWis expected to decrease accordingly. Things complicate when non packaging aluminium is also included in the evaluation, whose amount can only be estimated by analysing its content in the URW. The model is primarily based on the following four quantities:

- Amount of commercialized aluminium packaging;
- Gross MSW production;
- Overall separate collection rate;
- Capacity of waste-to-energy plants.

The model framework is explained as, the waste collected with the separate collection and the aluminium packaging available on the market have been evaluated; then, knowing the amount of aluminium packaging in the separate collection and the quantity of non-packaging aluminium in the URW, we have

TABLE I
PREDICTED VALUES FOR THE MODEL VARIABLES

ID	Variable Description	Number of Scenarios	Scenario	2000 (Tons Per Year)	2005 (Tons Per Year)	2010 (Tons Per Year)
A	Commercialized aluminium packaging	2	Moderate growth	118700	128500	135092
B	Gross MSW production	2	High growth	118700	145600	162358
C	Separate collection rate	1	Moderate growth	32.55	34.11	34.47
D	Aluminium packaging in the separate collection	1	High growth	32.55	36.66	38.61
E	Aluminium in RDF	1	-	27.5	39.93	45.3
F	Non-packaging aluminium in residual waste	1	-	0.43	0.39	0.37
G1	URW to incineration plants	1	-	0.6	0.6	0.6
H1	RDF to incineration plants	1	Base technology	0	30	30
H2	RDF to gasification plants	1	Advanced technology	70	70	70
I1	Aluminium recovery rate from incinerator bottom ashes	2	Base technology	40	40	40
I2	Aluminium recovery rate from gasification bottom ashes	2	Advanced technology	80	80	80

estimated the amount of aluminium in the residual waste. This aluminium is fed in part to incineration plants and in part to gasification plants, together with the URW. By considering also the aluminium content of the Refuse Derived Fuel (RDF), it is possible to evaluate the aluminium in the bottom ashes produced during the combustion of URW and RDF and therefore the amount of aluminium recoverable from the bottom ashes.

III. NEED OF IRON REDUCTION

A. Effects

In the aluminium conductor materials, iron is added to improve strength without substantial conductivity loss. Specifications normally permit considerably more Fe to be present in permanent mould and pressure die-cast alloys compared to sand-cast alloys because the cooling rate is higher in these cast conditions, thus, the size of the constituents is finer. Particularly, in the commercial process of pressure die casting, the Fe content is above 0.8wt%, and the precipitated eutectic Al-Si-Fe composition prevents the molten alloys from sticking (called ‘‘soldering’’ to the die that causes a deterioration in the mould) and hence improves the surface quality of the component. In these cases, Fe is an alloying element. Fe-rich intermetallic phases have much more complex morphologies, with fragile and brittle appearance. The presence of Fe is generally reported to have a detrimental effect on the ductility, strength, and fatigue properties of aluminum alloys. Increasing of Fe content reduces the elongation (ductility) and tensile strength.

IV. ADDITION OF STRONTIUM

Sr was also applied to transform the platelet Fe-rich phases to aAlFeSi. Addition of Sr promoted the formation of a-AlFeSi and improved the extrusion characteristics significantly tensile strength and conducting property were improved by approximately 0.1wt% Sr addition into aluminium alloys

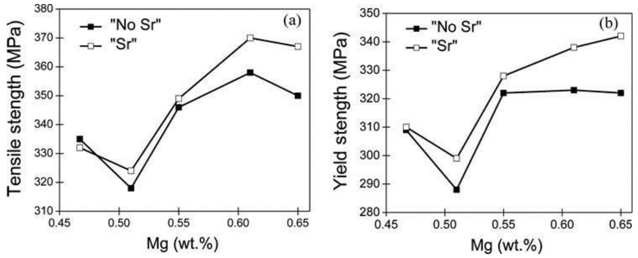

Fig. 1. Wt. % vs. Tensile strength, Wt. vs. Yield Strength

V. RESULTS OF ALLOYING ALUMINIUM

The use of aluminium-magnesium alloys for the production of castings received a strong boost in 1920 when Pacz discovered that by adding small amounts of sodium or its salts to the molten alloy, the structure of these alloys were significantly modified. The modification treatment causes the disappearance of the primary magnesium crystals, with the formation of an extremely fine eutectic globular magnesium instead of a needle-like structure. An improvement in the mechanical properties is associated with this structural modification, particularly in the case of aluminium—magnesium eutectic alloy, which acquires a high degree of plasticity. A review of the literature [2]-[4] shows that a great deal of effort has been made to replace sodium by strontium for modification of aluminium magnesium alloys. One important feature of strontium is that it has a low oxidation sensitivity and its use leads to the elimination of two major problems associated with sodium modification, namely, fume generation and control of the amount or addition. These have led towards a growing importance of strontium as a strong modifier. However, there are some limitations of using this metal to affect modification, in that it must be added according to specific criteria to obtain satisfactory results. The general theme of the present investigation was to explore further the effects of strontium on the structure and properties of aluminium alloys in more detail. The result shows the structure of the same alloy but modified with strontium, which consists of aluminium and fine globular-like eutectic magnesium instead of primary crystal and the acicular divorced eutectic type. Due to this structural refinement (modification), the tensile properties of the alloy show marked improvement, as can be seen. However, the higher strength and ductility of the chill cast specimens result from the finer structure which is associated with rapid cooling and modification. The appearance of the fracture surfaces after tensile testing also shows these differences in the structures. The following conclusions can be made from the results of the present investigation. Strontium in the form of an Al-14% Sr master alloy can be used for the modification of LM-6 type alloy. The change in micro-structure due to strontium modification produces an improvement in the tensile properties of the alloy cast in metal moulds.

Strontium is a well-known trace-element addition in the aluminium industry and is widely used as a modifier for the Al–Mg alloy system in order to change the shape of the eutectic magnesium from acicular to fibrous, resulting in better mechanical properties and machinability. A few studies on the effect of strontium on the oxidation behaviour of aluminium alloys have been studied.

The Al–Mg alloys used in this study were prepared from high-purity starting materials, whose chemical analyses are given in Table-2 and 3. A 90% Al–10% Sr master alloy was used to achieve the intended amount of strontium in the alloy.

Melting was carried out in an induction furnace, and the melt was cast into a cylindrical graphite mold. The metal rod obtained after solidification was machined into cylindrical samples of 28 mm in diameter and 15 mm in height.

Sample surfaces were ground using 400 and 600 grit abrasive SiC grinding paper and rinsed with alcohol to remove both the contamination built up on the surface during machining and obtain a consistent surface prior to the oxidation test. Test

TABLE II
CHEMICAL COMPOSITION OF ALUMINIUM

Elements	Si	Fe	Cu	Mg	Mn	Ti	Zn	Cr	Al
Wt. (%)	0.006	0.007	0.0013	0.0021	0.0001	0.0001	0.0002	0.001	99.99

TABLE III
CHEMICAL COMPOSITION OF MAGNESIUM

Elements	Al	Zn	Mn	Fe	Ni	Cu	Si	Pb	Mg
Wt. (%)	0.003	0.004	0.0023	0.0022	0.0003	0.0002	0.002	0.001	99.98

samples were contained in high-purity alumina crucibles that were fabricated in house using ceramic slip casting.

Oxidation experiments were carried out in a vertical mullite tube furnace equipped with a thermo gravimetric balance shown schematically in Fig. 2. Samples in the alumina crucibles were placed in the hot zone of the furnace and suspended from a Ni–Cr wire that was connected to a CAHN D-100 microbalance. The furnace chamber was evacuated to approximately 300 mTorr and back-filled with argon several times. A continuous flow of argon was then introduced from the bottom of the furnace, which was then heated to the test temperature (750 C), at which point dry air was introduced into the system and the data acquisition was started. The oxidation tests were performed for a period of 48 h in order to have a better understanding of the kinetic behaviour of the samples. The weight-change-data acquisition through the microbalance was gathered using the Thermo Can data acquisition software.

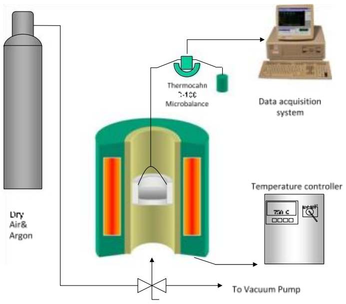

Fig. 2. Experimental setup for the thermo gravimetric analysis

The chemical composition of the alloys was quantified using a vacuum-emission spectrometer (Spectrovac 1000). The oxide surface morphologies and polished cross.

Fig. 2 Experimental setup for the thermogravimetric analysis sections were analysed by scanning-electron microscopy (Hitachi S-4700). The reaction products were also identified by low-angle XRD (Rigaku Rotaflex) and EDS techniques.

VI. RESULTS

A. Thermogravimetry

The thermo gravimetrically determined weight-change curves for Al–0.5% Mg, Al–1% Mg and Al–5% Mg alloys at 750 C under dry air are shown in Fig. 3. It can be clearly seen that the lowest weight gain was obtained with Al–0.5% Mg alloy and the highest weight gain obtained with Al–5% Mg alloy. All three alloys had an initial protective oxidation stage followed by breakaway and linear oxidation, and finally the parabolic oxidation stage where the weight gain slows down and shows an asymptotic behaviour.

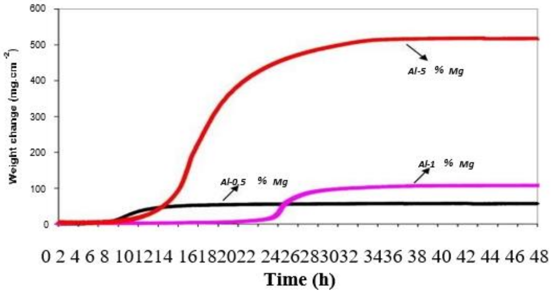

Fig. 3. Weight change with time for the different Al–Mg alloys

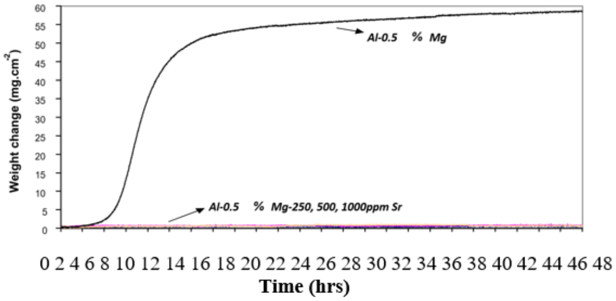

Fig. 4. Effect of different strontium additions on the oxidation of the Al–0.5% Mg alloy

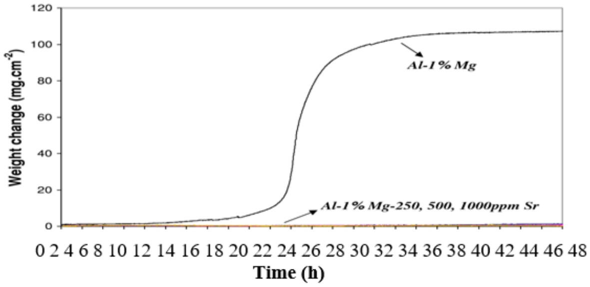

Fig. 5. Effect of different strontium additions on the oxidation of the Al–1% Mg alloy

In the case of the Al–0.5% Mg alloy, the breakaway oxidation always occurred sooner than for the Al–1% Mg alloy. That could be explained by the fact that a more continuous and thicker oxide layer formed on the latter due to the higher Mg content of the alloy, providing higher mechanical strength and a stronger barrier for breakaway oxidation.

TABLE IV
COMPARISON OF TOTAL WEIGHT GAINS (MGCM^{-2}) AFTER 48 H OXIDATION FOR 0, 250, 500 AND 1000 PPM SR ADDITIONS

	Weight gain in mgcm^{-2}		
	0.5% Mg	1% Mg	5% Mg
No Sr	48	107	518
250 ppm Sr	0.7	1.25	165
500 ppm Sr	0.7	0.76	150
1000 ppm Sr	0.7	0.6	102

Analysis of the oxidation curves of the Al–0.5% Mg and Al–1% Mg alloys with and without three different strontium contents (250, 500 and 1000 ppm) revealed that the addition of strontium into Al–0.5% Mg and Al–1% Mg alloys lowered the weight gains by more than 95% and totally changed the oxidation kinetics. The three oxidation stages (breakaway, linear and parabolic) that were observed with Al–0.5% Mg and Al–1% Mg alloys, were not exhibited when strontium was added. The oxidation behaviour of these alloys is summarized in Fig. 4 and 5.

Unlike the Al–0.5% Mg and Al–1% Mg alloys, when three different strontium contents were added to the Al–5% Mg alloy, the breakaway, linear and parabolic oxidation kinetics were still observed with Al–5% Mg alloys containing 250 and 500 ppm strontium. The Al–5% Mg-1000 ppm strontium alloy showed a more protective behaviour, as seen in Fig. 6. The comparison of approximate total weight gains (mg/cm^{-2}) after 48 h oxidation for three different strontium additions is summarized in Table-4.

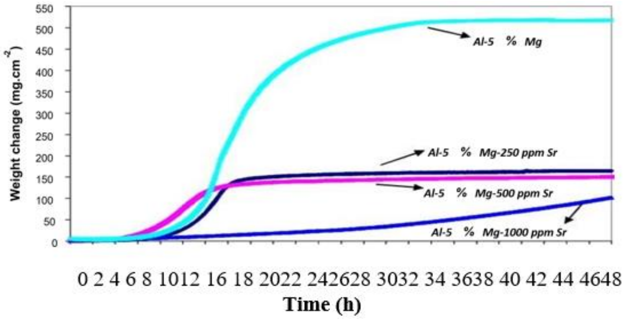

Fig. 6. Effect of different strontium additions on the oxidation of the Al–5% Mg alloy

VII. RESULTS AND DISCUSSION

A. *Effect of Strontium*

Small amounts of strontium can transform the morphology of the eutectic silicon phase present in Al–Si casting alloys from coarse plate-like to fine fibrous networks. In order to understand this, the strontium distribution was studied in atomic resolution by atom probe tomography and in nanometre resolution by transmission electron microscopy. The combined investigations indicate that Sr co-segregates with Al and Si within the eutectic Si phase. Two types of segregations were found:

(i) nanometre-thin rod-like co-segregations of type I are responsible for the formation of multiple twins in a Si crystal and enable its growth in different crystallographic directions

(ii) type II segregations come as more extended structures, restrict growth of a Si crystal and control its branching. We show how Sr enables both kinds of mechanisms previously postulated in the literature, namely "impurity-induced twinning" (via type I) and growth restriction of eutectic Si phase (via type II). A typical eutectic microstructure of both unmodified and Sr-modified (200 ppm) Al–10 wt.% Si–0.1 wt.% Fe alloy is shown in Fig. 7 for two different magnifications. The unmodified alloy in Fig. 1 a and b reveals primary Aldendrites (bright in Fig 7 (a)) and a eutectic Si phase that appears as needles just in two dimensions but as coarse.

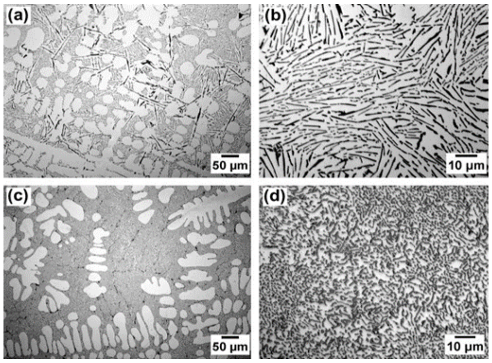

Fig. 7. Optical micrographs of Al–10 wt. % Si–0.1 wt. % Fe alloy showing a eutectic microstructure: (a and b) unmodified alloy, (c and d) alloy modified by 200 ppm Sr.

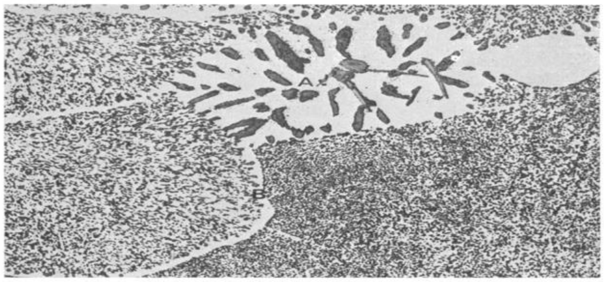

Fig. 8. Commercial purity AI - Si over modified with a combined addition of sodium and strontium

Combined APT and TEM investigations of the eutectic Si phase in Sr-modified (200 ppm) Al–10 wt. % Si–0.1 wt. %Fe alloy demonstrated that type II Sr–Al–Si co segregations inhibit and restrict growth of the eutectic Si phase and thus induce a morphological change to a highly branched arrangement of eutectic Si phase. The addition of progressively increasing amounts of strontium has two effects. The undercooling required for the flake-fibre transition is decreased for all silicon contents within the range examined, though more slowly at the eutectic composition. In hyper-eutectic alloys this is accompanied by a complete suppression of primary silicon precipitation. In the presence of 0.02 % Sr no primary silicon appears in any alloy up to 17% Si. (Higher silicon contents were not investigated.) It is notable that strontium modification has no effect on the incidence of primary ct dendrites. The dendrite-eutectic transition boundary remains un-changed, and dendrites are present in all hypo-eutectic alloys, whether the eutectic is modified or unmodified.

The Area A contains coarse over modified particles. Addition of a large excess of strontium (3%) did not produce over modification bands, although impurity cells are still formed. Instead, the excess strontium precipitates repeatedly at the growth inter-face as a compound approximating to SrAl3Si3.

B. *Effect of Magnesium*

The effect of magnesium addition to aluminium-silicon eutectic alloy was investigated also. The initial addition of 0.4% magnesium to this alloy increased the strength at the expense of the ductility, but beyond this amount the tensile properties decreased for both rates of cooling. The high-magnesium-content modified specimens showed more porosity than the unmodified specimens, although the tensile properties were higher due to the structural modification.

The percentage of magnesium in the alloy is increased beyond 0.4%, the strength and ductility decrease for both low- and high-rate of cooling. This may be because of the presence of a magnesium-bearing phase in the structure, which has little beneficial effect on the proper-ties of the as-cast alloy. Even after modification, the alloys containing 0.7% and 1.0% Mg show little improvement in tensile properties, indicating that such alloys respond poorly to the modification.

VIII. CONCLUSION

The following conclusions can be made from the re-suits of the present investigation.

1) Strontium in the form of an A1-14% Si-10% Sr master alloy can be used for the modification of LM-6 type alloy. The change in micro-structure due to strontium modification produces an improvement in the tensile properties of the alloy cast in sand or metal moulds.
2) The fractured surfaces show that the unmodified alloys have a brittle fracture, which follows the eutectic silicon needles and is further supplemented by contributions from the iron-rich phase, whereas the modified alloys have a ductile fracture which follows largely through the plastic aluminium matrix.
3) Additions of strontium expand the coupled region and suppress the formation of primary Si, but do not affect the crystallisation of primary dendrites. Addition of 0.02 % Sr causes complete modification of the eutectic at all freezing rates down to about 10 lam/sec.
4) The suppression of primary silicon is attributed to a higher growth velocity of the modified eutectic at any temperature at which it can form.
5) For LM-6 type alloy containing up to 0.4% magnesium (in the as-cast condition), the strength increases at the expense of ductility, whilst beyond that percentage the strength and the ductility decrease for both low-and high-rate cooling. These alloys also respond very poorly to the modification.

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