



MODIFICATION EFFECT OF LANTHANUM ON Mg₂Si IN HYPEREUTECTIC Mg-Si ALLOY

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ABSTRACT

Magnesium alloys are potential materials for automobile and aerospace industries due to its light weight, high strength-to-weight ratio, good cast ability, low elastic modulus, good machine ability and wear resistance. Among various Mg alloys, Mg-Si alloy have great potential for high temperature and wear resistance applications because of its hard Mg₂Si phase. However the mechanical properties of the hypereutectic Mg-Si alloys are not satisfactory because of coarse brittle dendritic Mg₂Si intermetallic and coarse lamellar eutectic Mg₂Si phases. In order to increase its mechanical properties various researches are undergoing. Among that addition of Lanthanum (La) is the one of the optimum way to modify the Mg₂Si phase. In the present study deal with the addition of La in Mg-6Si is to be investigated.

Different proportions of Lanthanum (La) 0, 0.3, 0.6 and 0.9wt % effect is proposed to investigate. In order to understand the microstructure of modified/unmodified Mg-6Si alloy with different La addition will be studied using optical microscope and SEM analysis. The formation of La containing precipitate and its modifying mechanisms and morphology changes in Mg-6Si alloys is also will be investigated through XRD, SEM and EDX analysis. The mechanical properties of improved microstructure of Mg-6Si alloy due to the La addition is analysed by subjecting to its tensile and hardness tests.

INTRODUCTION

Magnesium, which is considered the best alloy in the 21st century, is the lightest structural metal and has a high specific strength and stiffness. Magnesium alloys have become very attractive for a variety of technical applications, especially in the automotive and aircraft industries and the electronics sector. Using “Mg alloy” as the keyword and searching in the world famous “Web of Science Core Collection” database, it can be concluded that the total amount of literature containing magnesium alloys in the topic is as much as 39,422 reports between 2000 and 2018. The number of documents published annually ranged from 760 in 2000 to 3735 in 2018, representing a growth rate of 491%. This growth reflects the fact that magnesium alloys have become the most common metallic structural materials in the world. The Journal of Magnesium and Alloys (JMA) is an international journal for the publication of theoretical and experimental studies in magnesium science and engineering across the world. As a specialized resource for magnesium alloys, the journal has published 272 academic articles between 2013 and 2018 and has been cited 2853 times.

Magnesium (Mg) alloys are the lightest of the structure alloys and are receiving increasing attention because of their low density and adequate mechanical properties, including good machine ability, conductivity, and damping. However, their range of applications is more restricted than that of aluminium alloys due to their poorer corrosion behaviour. Common corrosion protection methods for Mg alloys include microstructure control, composition modification, and surface treatments and coatings. The corrosion behaviour of a Mg alloy depends on the environment, the alloy composition and production details. A better understanding of these factors will lead to better Mg alloys.

Many researches in the past few decades focused on Mg corrosion in aqueous solutions, especially in chloride containing solutions for automobile applications and in synthetic body fluids for biomedical applications. The influence of chemical composition, microstructure and surface condition and solution compositions was intensively investigated and is summarized in recent reviews. In contrast, there have been fewer investigations into the atmospheric corrosion of Mg alloys, even though atmospheric corrosion is important for most Mg components in practical service for auto-mobile, aerospace, military and telecommunication applications. This is partly because atmospheric corrosion of Mg alloys is less severe than aqueous corrosion and partly because there are greater experimental difficulties in understanding the electro-chemistry involved in atmospheric corrosion. New insights have indicated that atmospheric environmental factors have a much more complicated influence on the corrosion behaviour and their influence is difficult to predict based on the corrosion behaviour in aqueous solution. The important atmospheric parameters include: temperature, relative humidity, time of wetness, atmospheric composition, the presence of industrial pollutants and the presence of inorganic salts. The successful use of Mg components requires understanding the influence of these factors. Therefore, this critical review provides a framework on which to build the further development of Mg alloys that are particularly suited for atmospheric service. Magnesium based alloys and their use in medical implants have been the focus of significant recent research. Compared to conventional metallic implant materials such as titanium alloys, stainless steels and cobalt alloys, biomedical magnesium alloys have better degradability and absorbability.

1.1 Magnesium

Magnesium is the 9th most abundant element in the universe.

Magnesium is the 8th most abundant element in the earth's crust and the 3rd most abundant element dissolved in seawater after Cl and Na. Magnesium is the lightest structural element and has the lowest melting (923K) and the lowest boiling point (1363K) of all the alkaline earth metals. Magnesium is the 11th most abundant element by mass in the human body. Magnesium is important in bone formation and also helps in regulating blood pressure and production of cholesterol in human body. Magnesium production has been increased from 670,000 tons in 2007 to 910,000 tons in 2013 being in the third place after steel and aluminium in the world annual production of metals. This indicates that magnesium alloys are in high demanding, particularly, in automotive industry as this sector is working to improve the fuel efficiency through weight reduction. For industrial applications, pure Mg is too soft to use and it exhibit less strength, less corrosion resistance and less creep resistance. Pure polycrystalline magnesium is brittle and fractures easily along shear bands. Hence the pure Mg is alloyed with various elements to increase its physical as well as mechanical properties. Since the Mg is chemically active it can react with other alloying elements and can form intermetallic compounds. These compounds influence in enhancing the mechanical properties such as creep resistance, strength, ductility, etc., of Mg alloys by refining its microstructure.

Properties of pure Mg

Atomic Number	-
Atomic Radius	-
Atomic Weight	-
Density at 20	-
Melting Point	-
Boiling Point	-

12

160 pm

24.30 g mol⁻¹1.74 g cm⁻³ 650

1090

Thermal Conductivity (25) - 156 W m⁻¹ K⁻¹ Specific Heat at 20 - 1025 J kg⁻¹K⁻¹ Volume Heat Capacity - 1783 J m⁻³ 10⁻³

Electrical Resistivity (20) - 4.45 Ω m x 10⁻⁸ E-Modulus - 45 GPa

Strength - 90 MPa Specific Strength - 52 m x 10⁶



Fig. 1.1 Magnesium Metal

Magnesium Alloy

Pure Mg is too soft to use for the most industrial applications. Hence, pure Mg is alloyed with various elements such as aluminium, zinc, silicon, rare earths, calcium, etc., to enhance its properties like creep resistance, ductility, strength, etc. Magnesium alloys have a hexagonal lattice structure, which affects the fundamental properties of these alloys. Magnesium is used as an alloying element in non-ferrous alloys, such as aluminium, zinc, and lead. A good number of alloying elements can be added to magnesium to obtain excellent properties including high specific strength, cast ability, damping capacity and formability. Mg alloy is also associated with a number of limitations compared to other metals, such as aluminium alloy. These limitations include low creep resistance, lower tensile properties (strength and ductility), poor workability due to its hexagonal structure, and low wear and corrosion resistance. Generally, surface treatment is an effective approach to solve the wear and corrosion issues. Also, rare earth elements addition is considered as an effective approach to increase the creep resistance and strength. Some examples of the commercially used RE in Mg alloys are gadolinium, neodymium and cerium. Silicon is the 8th most common element in the universe. Earth's crust consists of more than 90% of silicate materials and thus making silicon the 2nd most abundant element in the earth's crust after oxygen. It is a hard, brittle crystalline solid with a blue-grey metallic lustre and is a tetravalent metalloid and semiconductor. About 55% of the world consumption of metallurgical purity silicon goes for the production of Al-Si alloys. Addition of silicon to the aluminium significantly improved the hardness and wear resistance of the alloy. Silicates are used in Portland cement for mortar and stucco, and mixed with silica sand and gravel to make concrete for

walkways, foundations and roads. They are also used in white ware ceramics such as porcelain and in traditional quartz-based soda-lime glass and many other specialty glasses. Silicon compounds such as silicon carbide are used as abrasives and components of high-strength ceramics. Silicon is the basis of the widely used synthetic polymers called silicones.

Properties of Si

Atomic Number	-	14
Atomic Weight	-	28
Atomic Radius	-	117 pm
Density	-	2.32 g/cm ³
Melting Point	-	1410
Boiling Point	-	2355
Electronegativity	-	1.9



Fig. 1.2 Silicon Metal

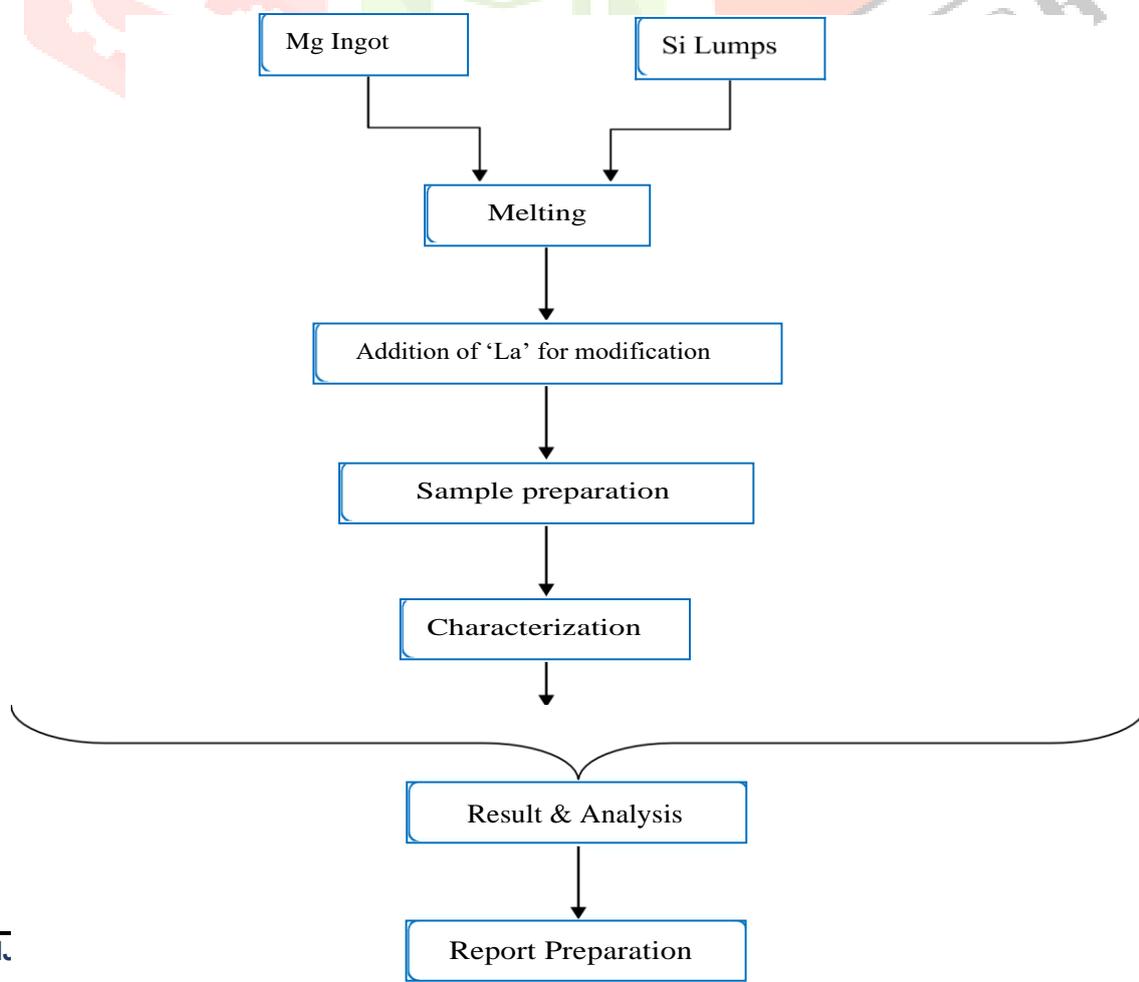
Lanthanum

Lanthanum is a chemical element with the symbol La and is one of the rare earth elements. The rare-earth elements (REEs) are 15 elements that range in Atomic number from 57 (lanthanum) to 71 (lutetium); they are commonly referred to as the “lanthanides.” Yttrium (atomic number 39) is also commonly regarded as an REE because it shares chemical and physical similarities and has affinities with the lanthanides. Although REEs are not rare in terms of average crustal abundance, the concentrated deposits of REEs are limited in number. Because of their unusual physical and chemical properties, the REEs have diverse defences, energy, industrial and military technology applications. The glass industry is the leading consumer of REE raw materials, which are used for glass polishing and as additives that provide colour and special optical properties to the glass. It is a soft, ductile, silvery-white metal that tarnishes slowly when exposed to air and is soft enough to be cut with a knife. It is the eponym of the lanthanide series, a group of 15 similar elements between lanthanum and lutetium in the periodic table, of which lanthanum is the first and the prototype. Lanthanum compounds have numerous applications as catalysts, additives in glass, carbon arc lamps for studio lights and projectors, ignition elements in lighters and torches, electron cathodes, scintillates, GTAW electrodes and other things. Lanthanum carbonate is used as a phosphate binder in cases of high levels of phosphate in the blood seen with kidney failure.

Properties of La	
Atomic Number	- 57
Atomic Weight	- 138.9
Atomic Radius	- 187 pm
Density	- 6.7 g/cm ³
Melting Point	- 920
Boiling Point	- 3469
Electronegativity	- 1.1



Fig. 1.3 Lanthanum Metal
METHODOLOGY



RESULTS AND DISCUSSION

In Mg-Si alloys, the solubility of Si in Mg is extremely low based on the Mg-Si binary phase diagram and also the most of the Si atoms react with the Mg atoms and form the Mg_2Si intermetallic compound. This chapter deals with the hypereutectic Mg-6Si with the modification effect of La addition. When the melt is solidified the Mg_2Si phase is formed in proportion to the following reaction:



XRD Analysis

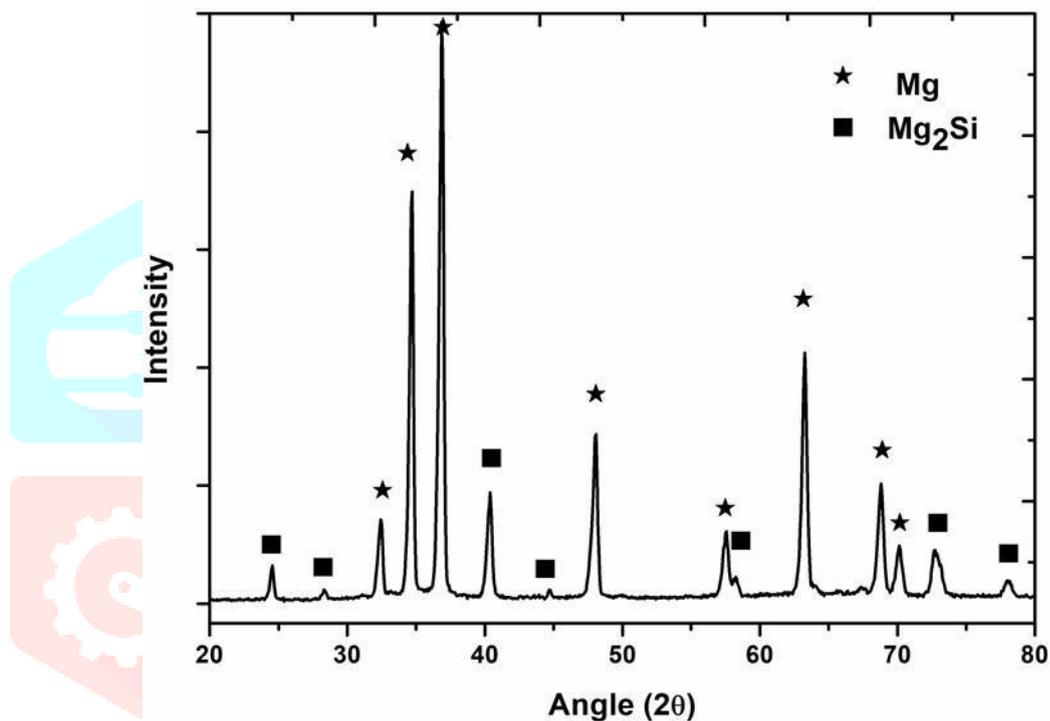


Fig. 6.1: XRD analysis of Mg-Si alloy

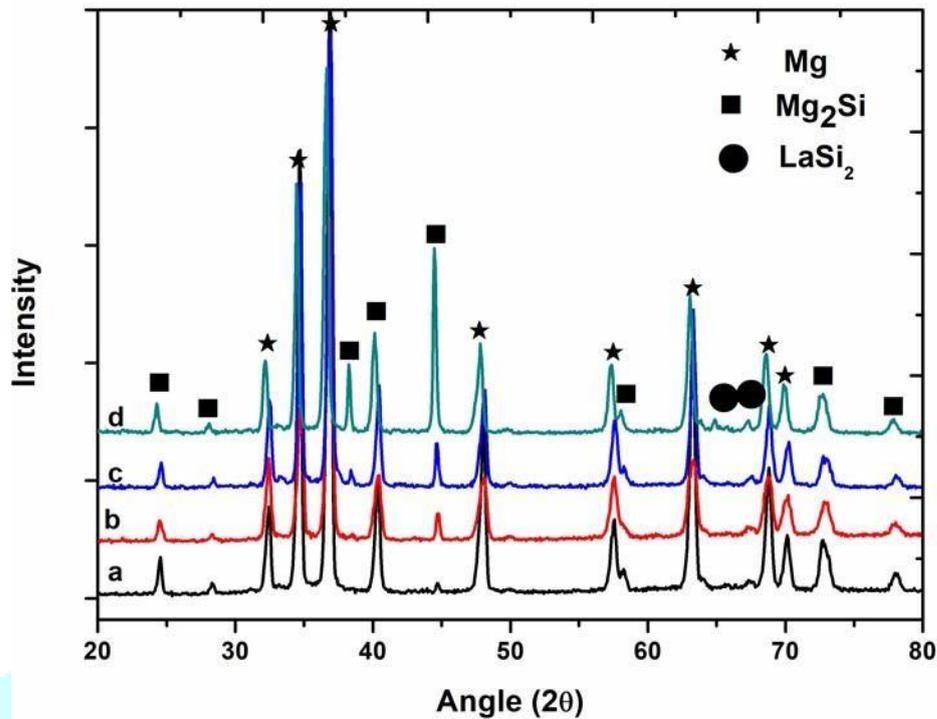
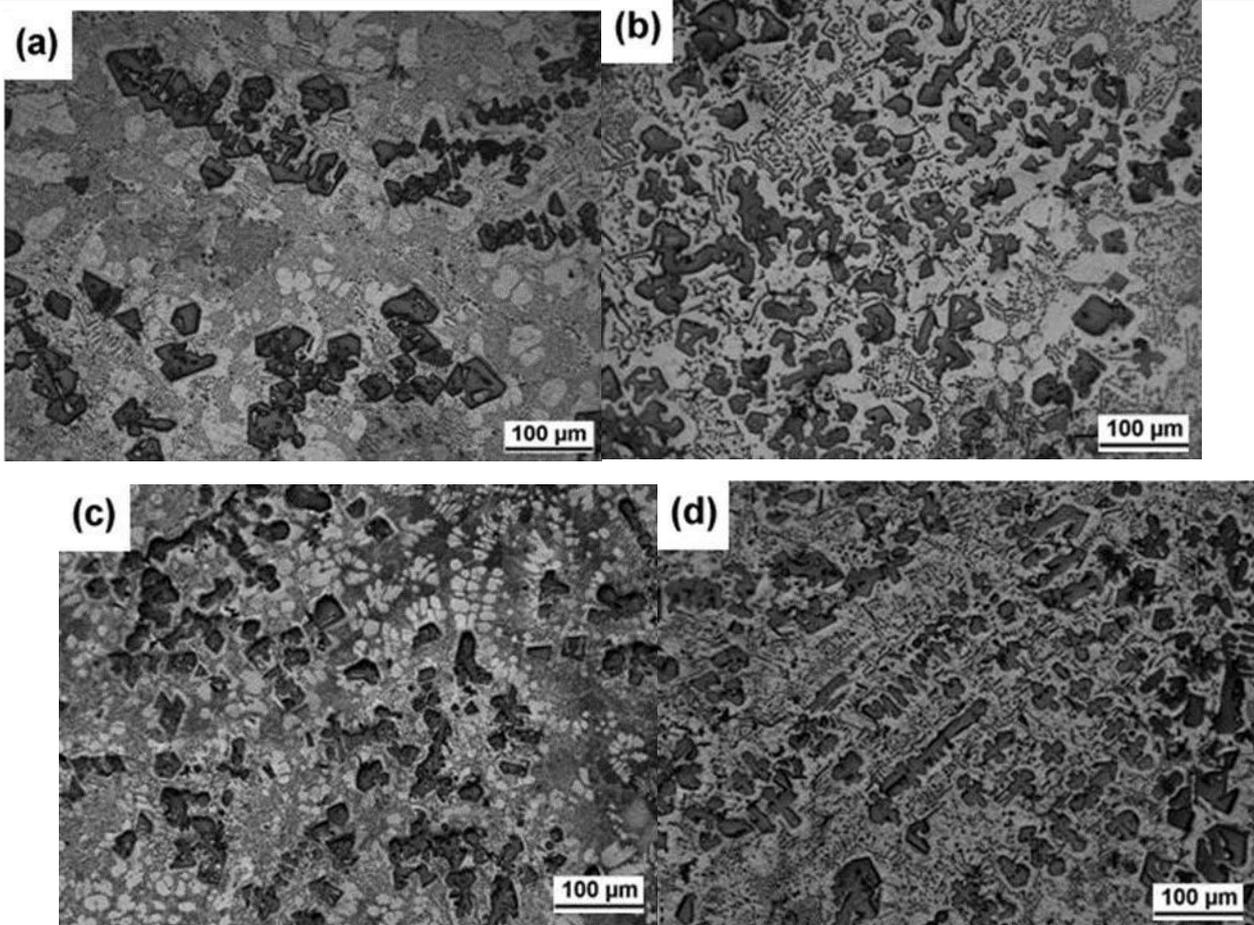


Fig. 6.2: XRD analysis of Mg-6Si alloy with different La additions (a) 0, (b) 0.3, (c) 0.6 and (d) 0.9

The typical XRD patterns of Mg-Si alloys and different Lanthanum addition are shown in Fig. 6.1 and 6.2 respectively. No Si peak appeared in the pattern which means all the added Si lumps reacted completely in the Mg melt forming Mg_2Si phase during the solidification. The XRD pattern of unmodified Mg-6Si alloy is shown in Fig. 6.1. The alloy composed of components Mg_2Si and α -Mg phases were revealed during the XRD analysis. The XRD patterns of the Mg- 6Si alloys modified with 0.3wt. %, 0.6wt. % and 0.9wt. % La is shown in Fig.

6.2. Based on the XRD patterns, the phase compositions of all the modified alloys with different contents of La are Mg and Mg_2Si phases. Even so it should be noted that the addition of La is not detected and this may be due to its low content and limitation of XRD analysis.



Optical micrographs of Mg-6Si alloy with different La additions (a) 0, (b) 0.3, (c) 0.6 and (d) 0.9 wt. %.

From Fig. 6.3 that the microstructure of the base Mg-6Si or unmodified alloy consist of coarse primary Mg₂Si phase, Chinese script type eutectic Mg₂Si and an α -Mg phase. It is noted that the α -Mg halos and the polyphase eutectic structure surrounds the primary Mg₂Si dendritic phase. Due to the solidification of the alloy under a relatively high cooling rate the microstructural feature is developed leading to the deviation from the equilibrium diagram. When the primary Mg₂Si phases develop the liquid phase encircling the Mg₂Si phase becomes enriched with Mg. Inevitably α -Mg halos are formed and that grow around the primary Mg₂Si phases.

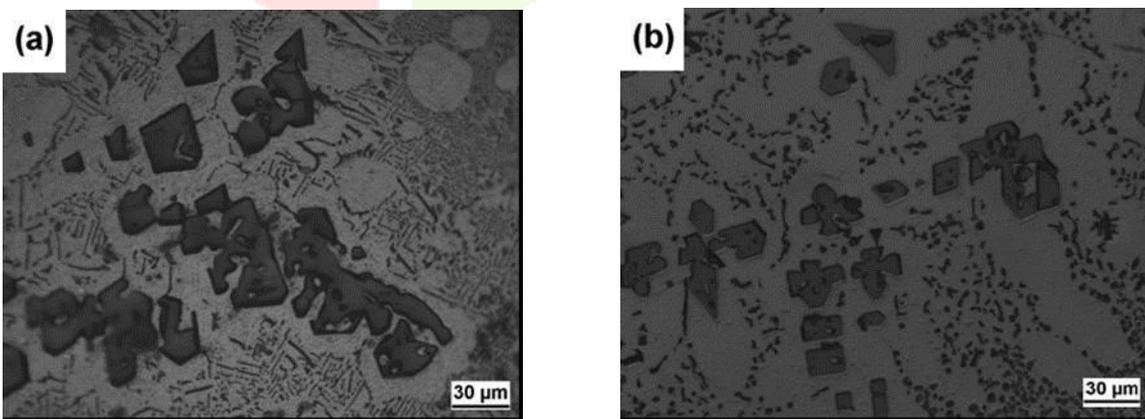


Fig. 6.4: Optical micrographs of high magnification of (a) Mg-6Si and (b) Mg-6Si-0.6La

SEM Analysis

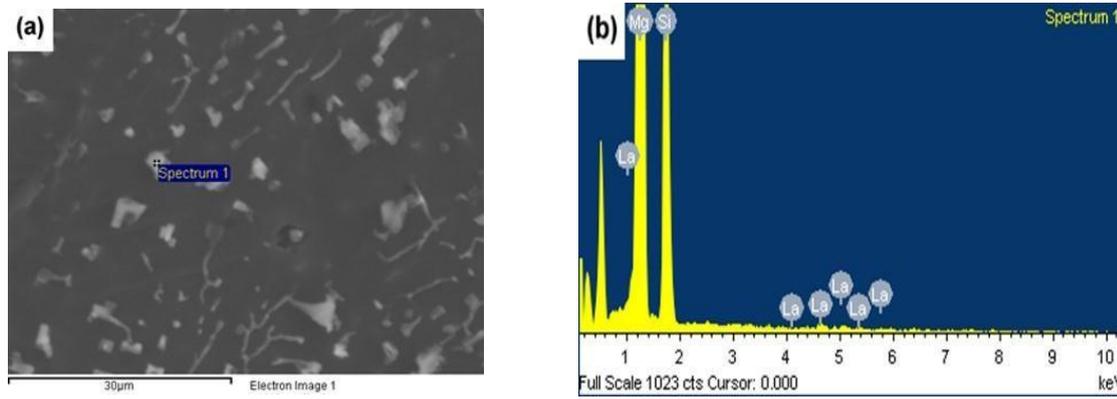


Fig. 6.5: SEM Micrographs and EDS for Mg-6Si-0.3La

Element	Weight%	Atomic%
Mg K	68.85	72.61
Si K	29.71	27.13
La L	1.43	0.26
Total		100.00

Table 6. 1: EDS analyses of Mg-6Si-0.3La alloy

It can be seen from Fig.6.3 (b) that the morphology and the size of the primary phase are changed by the addition of La. When the La content is 0.3 wt.%, compared with Fig. 6.3(a), the morphology of the primary Mg₂Si is changed almost completely from a dendritic shape to a polygonal block shape considering that the size is also significantly reduced to below 40µm, indicating that the anisotropic growth of the primary Mg₂Si phase during solidification is suppressed effectively by La addition. When 0.6wt. % La is added into the melt, the size of the primary Mg₂Si is further reduced to 25 µm or less and its morphology still keeps the polygonal block shape as shown in Fig.6.3(c).When the La content is further increased to 0.9 wt. %, most of the primary Mg₂Si exhibits a tendency to grow into a coarse dendritic phase, as shown in Fig. 6.3

(d) and its size increases which is equivalent to the unmodified alloy. Based on this result it can be concluded that La has an evident modification effect on the primary Mg₂Si in the Mg-6Si alloys and the optimal modification effect is obtained when 0.6 wt. % La is added.

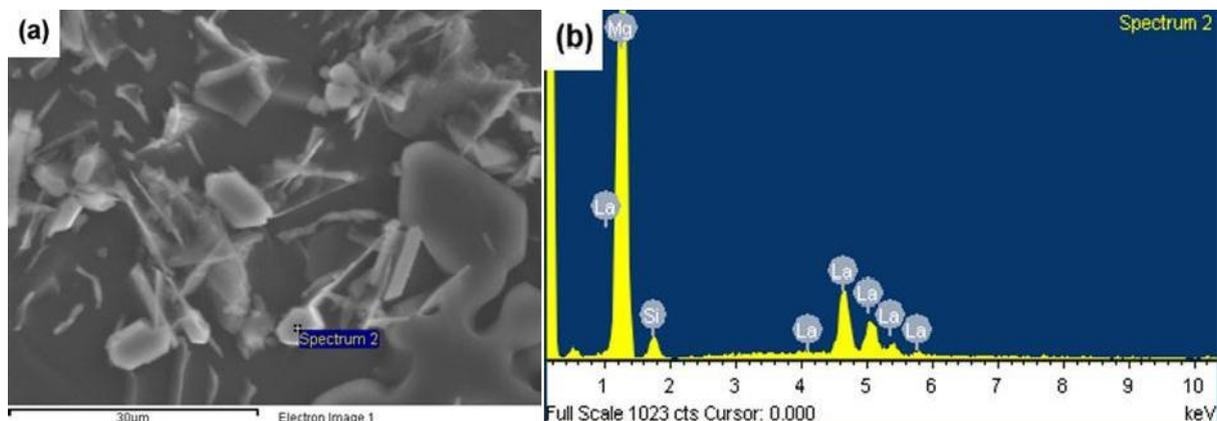


Fig. 6.6: SEM Micrographs and EDS for Mg-6Si-0.6La

Table 6.2: EDS analyses of Mg-6Si-0.6La alloy

Element	Weight%	Atomic%
Mg K	63.68	87.44
Si K	4.04	4.80
La L	32.28	7.76
Total	100.00	

SEM microstructures of the Mg-6Si alloys modified with 0.3wt. % La addition is shown in Fig. 6.4 (a). The tendency to change the size and morphology of the primary Mg_2Si with the increasing of La content can be seen more obviously in Fig. 6.4 (a). Meanwhile, some white needle-shaped and block shaped phases are also observed in the solidified structure of the alloy with 0.3wt. %, 0.6 wt. % and 0.9 wt. % La and in addition to distributing in the matrix, most of them are present mainly in the primary Mg_2Si phases are always attached throughout the primary Mg_2Si phases. It is also seen in Fig. 4.6 (a) that with the increasing La content in the alloy the amount and the size of these phases increase minutely. The sizes of the block shaped compounds are about 16 μ .

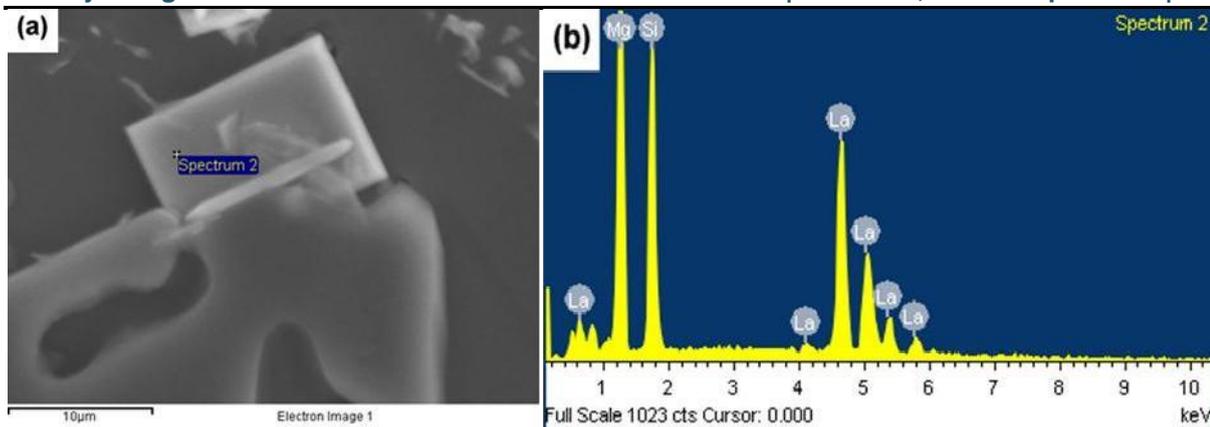


Fig. 6.7: High Magnification SEM-EDS point analysis and area analysis of Mg-6Si-0.6La

Fig. 6.7 (a) and (b) show the EDS line scan and point analysis of the white phases and fig. 6.7(c) and (d) shows the EDS line scan and area analysis of the white phases. The EDS line analysis suggests that the white phases consist of Si and La elements, which can be validated as La-Si intermetallic compounds. Ten EDS point analyses specify that the atomic ratio of La to Si is close to 1:2 i.e., the phase is a LaSi_2 compound. Because of the active characteristics and the low solid solubility of La in the Mg alloy, the La element added into the Mg-6Si alloys may react with Mg or Si to form an Mg-La or La-Si compound distinctly. Based on the other results the possibility of the compound formation between elements generally depends on the value of the electronegativity difference. The larger the electronegativity difference, the higher the binding force between elements and the easier the formation possibility. The electronegativity of Mg, Si, and La is 1.2, 1.8 and 1.1 respectively. The electronegativity difference between Si and La (0.7) is larger than that between Mg and La (0.1). Correspondingly, La is more vulnerable to react with Si to form LaSi_2 during the solidification of the alloy. Generally, it is well known that with a minute inclusion of RE elements can result in the microstructural refinement. Since rare earth metal is a surface active element. It can easily segregate at the solid-liquid interface or be absorbed into the growth front and thus change both the solid-liquid interfacial energy and the surface energy of the crystal which effectively poisons the growth steps leading to the isotropic growth of crystals. In addition to that the rare earth elements can react with the alloy elements to form intermetallic compounds which act as the nucleating medium and increase the nucleation rate additionally modifying the microstructure of the material. In the present study, despite the melting point of the formed LaSi_2 being 1520°C and the stability being very high, there is a huge difference between Mg_2Si and LaSi_2 in the lattice parameter and lattice type. Furthermore, according to Fig. 6.6 (a) and 6.7 (a), a large number of coarse dendritic Mg_2Si phases appear with the formation of more LaSi_2 compounds. Hence, it is concluded that the possibility of the LaSi_2 compound being the nucleus is very low. Consequently, it is expected that the La atoms may be adsorbed onto the growth front of the Mg_2Si phase and change its surface energy by lattice distortion due to the larger radius size of the La atom compared with those of Mg and Si atoms. It results in the suppression of the directional growth and growth steps of the Mg_2Si phase due to the poison effect. When the content of La addition is 0.3wt.%, the number of La atoms is comparatively low and insufficient in the alloy and the amount of La atoms provided for the adsorption is less. Thus, the size and the morphology of the primary Mg_2Si are only modified limitedly. As the La content is increased to 0.6 wt. %, more La atoms are adsorbed to effectively inhibit the formation of the coarse primary Mg_2Si phase and fully modify the size and morphology of the primary Mg_2Si phase. In addition to being denied and forced into the front of the solid-liquid interface some of the La atoms are adsorbed onto the growth front of the growing primary Mg_2Si phase during solidification. Hence, the enriched La atoms enclose the growing primary Mg_2Si phase and change its surface energy which makes it difficult for the external Si and Mg atoms to continue to diffuse into the internal Mg_2Si phase and further stop the growth of the primary Mg_2Si phase. Although, it is worth noting that a small quantity of the LaSi_2 compounds is also found and that may be due to the local segregation of La atoms resulting in the formation of LaSi_2 . It is observed that more La atoms are adsorbed onto the growth front of the primary Mg_2Si phase when the La content is further increased to 0.9% which provides sufficient La for the formation of LaSi_2 . Consequently, some La atoms are inclined to react with the diffused Si atoms to form a large LaSi_2 intermetallic. Appropriately, this does not effectively halting the diffusion of Mg and Si atoms into the growing front of the primary Mg_2Si

phase and additionally aids the formation of a coarse primary Mg₂Si phase resulting in the invalidation of La modification.

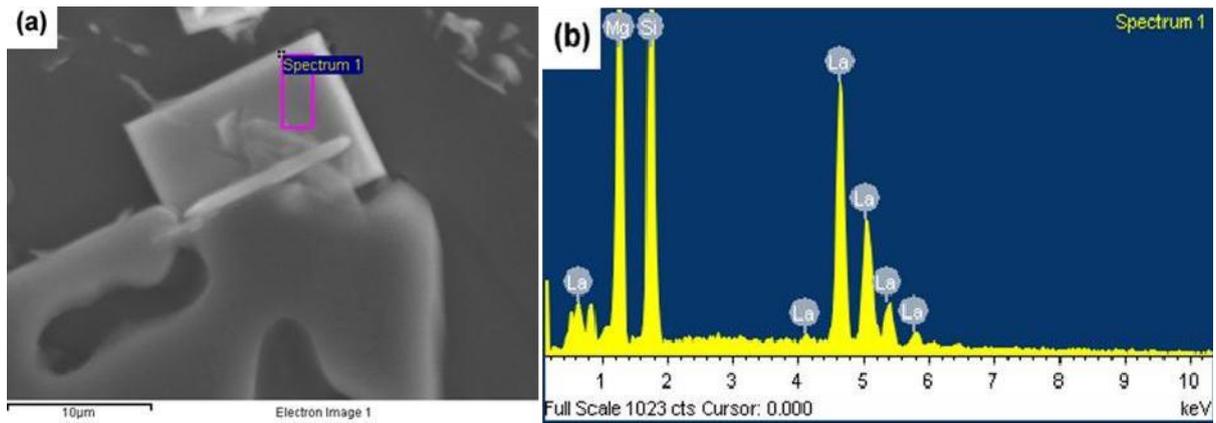


Fig. 6.8: High Magnification area analysis SEM Micrographs and EDS for Mg-6Si 0.6La

Element	Weight%	Atomic%
Mg K	29.85	53.26
Si K	20.16	31.13
La L	49.99	15.61
Total	100.00	

Element	Weight %	Atomic%
Mg K	27.17%	49.35%
Si K	21.92%	34.47%
La L	50.91%	16.18%
Total	100.00	

Table 6.3: EDS Analyses of Mg-6Si-0.6La alloy

Generally, it is well known that with a minute inclusion of RE elements can result in the microstructural refinement. Since rare earth metal is a surface active element. It can easily segregate at the solid-liquid interface or be absorbed into the growth front and thus change both the solid-liquid interfacial energy and the surface energy of the crystal which effectively poisons the growth steps leading to the isotropic growth of crystals. In addition to that the rare earth elements can react with the alloy elements to form intermetallic compounds which act as the nucleating medium and increase the nucleation rate additionally modifying the microstructure of the material. In the present study, despite the melting point of the formed LaSi₂ being 1520°C and the stability being very high, there is a huge difference between Mg₂Si and LaSi₂ in the lattice parameter and lattice type. Furthermore, according to Fig. 6.6 (a) and 6.7 (a), a large number of coarse dendritic Mg₂Si phases appear with the formation of more LaSi₂ compounds. Hence, it is concluded that the possibility of the LaSi₂ compound being the nucleus is very low. Consequently, it is expected that the La atoms may be adsorbed onto the growth front of the Mg₂Si phase and change its surface

energy by lattice distortion due to the larger radius size of the La atom compared with those of Mg and Si atoms. It results in the suppression of the directional growth and growth steps of the Mg₂Si phase due to the poison effect.

When the content of La addition is 0.3wt.%, the number of La atoms is comparatively low and insufficient in the alloy and the amount of La atoms provided for the adsorption is less. Thus, the size and the morphology of the primary Mg₂Si are only modified limitedly. As the La content is increased to 0.6 wt. %, more La atoms are adsorbed to effectively inhibit the formation of the coarse primary Mg₂Si phase and fully modify the size and morphology of the primary Mg₂Si phase. In addition to being denied and forced into the front of the solid-liquid interface some of the La atoms are adsorbed onto the growth front of the growing primary Mg₂Si phase during solidification. Hence, the enriched La atoms enclose the growing primary Mg₂Si phase and change its surface energy which makes it difficult for the external Si and Mg atoms to continue to diffuse into the internal Mg₂Si phase and further stop the growth of the primary Mg₂Si phase. Although, it is worth noting that a small quantity of the LaSi₂ compounds is also found and that may be due to the local segregation of La atoms resulting in the formation of LaSi₂. It is observed that more La atoms are adsorbed onto the growth front of the primary Mg₂Si phase when the La content is further increased to 0.9% which provides sufficient La for the formation of LaSi₂. Consequently, some La atoms are inclined to react with the diffused Si atoms to form a large LaSi₂ intermetallic. Appropriately, this does not effectively halting the diffusion of Mg and Si atoms into the growing front of the primary Mg₂Si phase and additionally aids the formation of a coarse primary Mg₂Si phase resulting in the invalidation of La modification.

CONCLUSION

The present project investigated the hypereutectic Mg-6Si and its modification effect due to the addition of Lanthanum (La). In the present study the microstructural refinement of Mg-Si alloy is done through the different proportion of La addition. The modification of microstructure and the changes in the morphology have been investigated through optical microscope, scanning electron microscope and X-ray diffractometer. It is proved that the addition on La to the Mg-Si alloy can significantly modify the microstructure and improve the mechanical properties. Thus the results concluded are given below:

- The Lanthanum (La) addition in the primary Mg₂Si phase in the Mg-6Si has significantly modified and refined the microstructure of the alloy.
- When the addition of La was 0.6wt. % the morphological change of the primary Mg₂Si phase occurred and changed from a coarse dendritic shape to a small polyhedral shape and the size of the primary Mg₂Si is decreased to 25μm or less.
- Although the La addition reaches 0.9wt. % the primary Mg₂Si becomes coarse again. Hence it is found to be the optimal modification of primary Mg₂Si phase while the addition of La is 0.6wt. %.
- The increasing in the La content to the alloy leading to the formation of white-needle shaped and block-shaped phases and their amount and size increased with the addition of La furthermore.
- The EDS experiments recognized them as LaSi₂ compounds.
 - The hardness value increases with the increase in the addition of La content in Mg-6Si alloys.
 - The UTS, YS and elongation values significantly increase upto 0.6% La addition that is 121 MPa, 78 MPa and 3.7% respectively

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