MAGNESIUM ALLOYS have strong potential for weight reduction in a wide range of technical applications because of their low density compared to other structural metallic materials. Therefore, an extensive growth of magnesium alloys usage in the automobile sector is expected in the coming years to enhance the fuel efficiency through mass reduction. The drawback associated with the use of commercially cheaper Mg-Al based alloys, such as AZ91, AM60 and AM50 are their inferior creep properties above 100°C due to the presence of discontinuous Mg$_{17}$Al$_{12}$ phases at the grain boundaries. Although rare earth-based magnesium alloys show better mechanical properties, it is not economically viable to use these alloys in auto industries. Recently, many new Mg-Al based alloy systems have been developed for high temperature applications, which do not contain the Mg$_{17}$Al$_{12}$ phase. It has been proved that the addition of a high percentage of zinc (which depends upon the percentage of Al) to binary Mg-Al alloys also ensures the complete removal of the Mg$_{17}$Al$_{12}$ phase and hence exhibits superior high temperature properties.

ZA84 alloy is one such system, which has 8%Zn in it (Mg-8Zn-4Al-0.2Mn, all are in wt %) and shows superior creep resistance compared to AZ and AM series alloys. These alloys are mostly used in die casting industries. However, there are certain large and heavy components, made up of this alloy by sand castings that show lower mechanical properties because of their coarse microstructure. Moreover, further improvement in their high temperature behaviour through microstructural modification is also an essential task to make this alloy suitable for the replacement of high strength aluminium alloys used in automobile industry. Grain refinement is an effective way to improve the tensile behaviour of engineering alloys. In fact, grain refinement of Mg-Al based alloys is well documented in literature. However, there is no grain refiner commercially available in the market for Mg-Al alloys. It is also reported in the literature that the microstructure of AZ91 alloy is modified through the minor elemental additions such as Sb, Si, Sr, Ca, etc., which enhance its high temperature properties because of the
formation of new stable intermetallics. The same strategy can be used with the ZA84 alloy system to improve its high temperature properties further without sacrificing the other properties. The primary objective of the present research work, “Studies on grain refinement and alloying additions on the microstructure and mechanical properties of Mg-8Zn-4Al alloy” is twofold:

1. To investigate the role of individual and combined additions of Sb and Ca on the microstructure and mechanical properties of ZA84 alloy.

2. To synthesis a novel Mg-1wt%Al₄C₃ master alloy for grain refinement of ZA84 alloy and investigate its effects on mechanical properties.

The contents of the thesis have been organized in five chapters. Chapter 1 deals with the overall idea about the thesis. The applications of magnesium alloys in various industries and their importance are discussed in this chapter. The major problem of ZA84 alloy is identified as insufficient mechanical properties especially in respect of tensile strength and creep properties. Effective ways to improve the properties are also given. The grain refinement and alloying additions mechanism are discussed in brief.

Chapter 2 presents a comprehensive review of available literature. Based on a thorough study of the literature, the detailed methodology for achieving the objectives of the present work has been derived. A great deal of attention has been devoted to the various grain refinement methods, grain refining mechanisms and alloying additions effect on the tensile and creep properties of magnesium alloys.

Chapter 3 deals with the detailed experimental procedure followed for alloy preparation and characterization in the present research work. Magnesium alloys were prepared using the flux melting technique. To identify the phases present in the alloys, XRD studies were carried out using a PHILIPS PW1710 powder diffractometer with CuKα radiation. The microstructures were characterized using an optical microscope.
(OM), scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with energy dispersive spectroscopy and the solidification behaviour by differential thermal analyzer (DTA). Macrohardness and microhardness were measured on INDENTEC and CLEMEX instruments under standard test conditions. Room temperature and 150ºC tensile properties were evaluated using an INSTRON Universal Testing Machine at a crosshead speed of 2mm/min. Creep properties at 150ºC with an initial stress of 50 MPa were evaluated using a 3 ton ‘MAYES’ creep testing machine.

**Chapter 4** presents the results and discussion of individual and combined additions of Sb, Ca and Al4C3 on the microstructure and mechanical properties of ZA84 alloy.

An X-ray diffraction pattern of the as-cast ZA84 alloy confirmed that the alloy consisted of α-Mg matrix and Mg32(Al,Zn)49 phase. However, the microstructure of base ZA84 alloy consists of α-Mg matrix with two different morphologies of precipitates (continuous and isolated phases). The continuous τ-Mg32(Al,Zn)49 phase, which has the cubic crystal structure \(a=1.416\text{nm}\), and the other is isolated \(\phi\)-Mg5Zn2Al2 phase having a primitive orthorhombic structure \(a=0.8979\text{nm}, b=1.6988\text{nm}\) and \(c=1.9340\text{nm}\). These results are confirmed using SEM and TEM.

Additions of antimony (0.2, 0.5 and 1wt%) to base alloy introduce thermally stable Mg3Sb2 (823ºC) intermetallics at the grain boundaries and refine the ternary phase effectively. The morphology of Mg3Sb2 intermetallics has changed from fine phase to needle shape with increase in the Sb content. For all wt% of Sb addition, the strength (yield and ultimate tensile strengths) properties are found to increase both at ambient and elevated temperatures with slight reduction in the ductility as compared to that of ZA84 base alloy. However, the maximum strength properties are obtained with 0.2 wt% Sb addition. The improvement in strength properties owing to the Sb addition is attributed to the following: (1) refinement of the Mg32(Al,Zn)49 precipitates, (2) strengthening owing to the secondary Mg3Sb2 precipitates, and (3) strengthening by grain refinement. The 500
hr short-term creep test has revealed that the addition of Sb is also capable of improving the creep properties.

The addition of Ca (0.25, 0.5 and 1wt%) to ZA84 alloy has modified the precipitation behaviour with the formation of a new Mg-Zn-Al-Ca phase at 405°C in the grain boundaries. As a result, improved mechanical properties, especially creep properties, are obtained. The creep extension of ZA84 alloy is reduced from 0.6678 % to 0.4172 % with 0.5wt% Ca addition, which is lower than the base alloy. The improvement in creep resistance of Ca-added alloys is attributed to the following reasons: (1) Formation of new thermally stable quaternary precipitates along the grain boundaries (2) The diffusion of solute atoms of Al and Zn at elevated temperature is minimized as the amount of Al and Zn in solid solution of Mg matrix is to be lowered. The change in microstructure that accompanies Ca addition results in an alloy having a stable matrix with well-fortified grain boundary precipitates. The tensile properties decrease beyond 0.5wt% Ca addition because of an increasing number of brittle precipitates at the grain boundaries.

The combined addition of Sb and Ca to ZA84 alloy increases the stability of quaternary phase with Mg₃Sb₂ intermetallics and improves the tensile behaviour of ZA84 alloy. Besides giving better performance than the individual additions, the creep extension for 500 hr has been reduced by approximately 50%.

Al-5wt%SiC composites held at 750°C for 2 hrs after particle addition is found to be necessary to make the reaction between liquid Al and SiCₚ to form Al₄C₃ particles completely. The microstructure of composites consists of α-Al matrix, eutectic silicon and interfacial reaction products. The reacted Al₄C₃ particles have been separated out from the composites by salt (equimolar NaCl-KCl-5%NaF) flux addition and skimmed as fine particles. Those reclaimed Al₄C₃ particles (5-8 μm in size) are introduced into the magnesium melt to make Mg-1wt%Al₄C₃ master alloy.
The potency of Al₄C₃ as a nucleating substrate for primary Mg can be demonstrated by crystallographic matching between hcp magnesium matrix of lattice parameters \((a=3.208\text{Å}, c=5.200\text{Å} \text{ and } \gamma=120^\circ)\) the nucleating particle having hcp of \((a=3.338\text{Å}, c=24.996\text{Å} \text{ and } \gamma=120^\circ)\). Theoretically, the interfacial free energy at the nucleating interface is believed to be a key factor controlling heterogeneous nucleation efficiency. It is hence reasonable to suggest that Al₄C₃ itself is a potent nucleating substrate for primary Mg, and addition of Al₄C₃ into the melt is expected to increase the nucleation frequency, therefore leading to a refined microstructure. In addition, it is further explained that the hypothesis for grain refinement of Al₄C₃ compound with magnesium is considering a high melting point. The stable fine particles exist at normal melting temperature act as an effective nucleant for Mg grains. Among the hypotheses proposed to explain the mechanism of carbon inoculation refining method to Mg-Al based alloys, Al₄C₃ nuclei hypothesis is the most commonly accepted theory. Besides, the size of heterogeneous nuclei is a vital factor deciding nucleation potency. It is proposed that 5-8µm or less is optimum mean particle size for high performance heterogeneous nuclei using a model based on free growth control of grain initiation.

The microstructure of combined added Sb, Ca and Al₄C₃ in ZA84 alloy shows the three morphologies of precipitates, such as continuous bone-like coarse phase called \(\text{Mg}_{10}\text{Al}_6\text{Zn}_4\text{Ca}_2\) and the continuous without bone-like structure phase, called \(\text{Mg}_{32}(\text{Al},\text{Zn})_{49}\) and fine black \(\text{Mg}_3\text{Sb}_2\) phases at the grain boundaries. This alloy led to a greater improvement in the tensile properties (room as well as elevated at 150°C) and creep resistance than that of base alloy without drop in elongation.

**Chapter 5** presents a summary of the findings of this investigation, along with the contributions made to the knowledge and the avenues for further work.