

# Chapter 1

## Introduction

### 1.1 Introduction

The high specific strength and dimensional stability of magnesium (Mg) alloys make them an excellent choice for developing lightweight products for the automotive. It is foreseen that the potential growth of Mg alloys' application is driven by their use in automotive powertrain parts that experience temperatures of 423 to 573 K [1]. The Mg alloys suitable for such an application should exhibit good creep resistance. The magnesium-aluminium alloys are suitable for applications in the interior parts of automobiles that do not involve elevated temperatures. Unfortunately, these alloys did not find applications in the powertrain components since their creep performance above 403 K is not satisfactory [1,2]. The intermetallic phase, namely  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> (M. P. 700 K), in Mg-Al alloys readily softens at above 403 K [1,2]. Hence, the enhancement of the creep performance of the Mg-Al alloy is possible by adding secondary elements which do not constitute the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase. Several studies have been conducted to manufacture Mg-Al alloys having superior creep resistance with the addition of Ca, Sr, and RE [3,4]. Yang et al. [5] concluded that the addition of Al above 1.0 (wt.%) in the Mg-2.85Nd-0.92Gd-0.41Zr-0.29Zn alloy deteriorated its creep property owing to the segregation of the Al<sub>2</sub>RE phase. Bai et al. [6] developed a new RE-based alloy, Mg-6.35Y-3.00Zn-0.73Al, that exhibited superior creep properties to the AE44 alloy. Yang et al. [7] reported that the Mg-8.0Al-1.0Nd-1.0Gd alloy in heat-treated conditions exhibited superior creep resistance compared to the as-cast alloy owing to the discontinuous precipitate of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase. Zhang et al. [8] showed that the addition of 1.0 (wt.%) RE in the Mg-9.0Al-0.3Ca-0.2Mn alloy significantly improved its creep resistance by suppressing the formation of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase and promoting the formation of thermally stable intermetallic Mg<sub>12</sub>RE and Al<sub>3</sub>RE phases. Thus, the RE-containing Mg alloys are promising for elevated temperature application; unfortunately, these alloys are not economical. On the contrary, Ca is comparatively more economical and less dense (i.e., 1.54 g/cm<sup>3</sup>) than the other elements. It also increases the oxidation resistance and improves the creep property of the Mg-Al alloys [9,10]. Chen et al. [11] investigated the creep behavior of the Mg-Al alloys with the addition of Zn, Sn, and Ca. They concluded that among the elements, Ca was more effective in improving its creep resistance. Li et al. [12] observed grain refinement in the Mg-Al alloy with the incorporation of Ca. The incorporation of Ca to Mg-Al encouraged the constitution of Mg<sub>2</sub>Ca (C14), Al<sub>2</sub>Ca

(C15), and  $(\text{Mg},\text{Al})_2\text{Ca}$  (C36) intermetallic phases that are thermally stable [13,14]. The work by Ninomiya et al. mentioned that only the  $\text{Al}_2\text{Ca}$  phase exists when the  $\text{Ca}/\text{Al}$  is less than 0.8, while for ratios greater than 0.8, both the  $\text{Al}_2\text{Ca}$  and  $\text{Mg}_2\text{Ca}$  phase exist simultaneously [15]. Suzuki et al. [16] reported that with the decrease in  $\text{Ca}/\text{Al}$  ratio, the dendritic eutectic structure in Mg-Al-Ca (AX) alloy contains more  $\beta\text{-Mg}_{17}\text{Al}_{12}$  phase. Zhang et al. [17] observed the presence of phase changes in the sequence of  $\text{Mg}_2\text{Ca}$ ,  $(\text{Mg},\text{Al})_2\text{Ca}$ , and  $\text{Al}_2\text{Ca}$  when the Ca to Al ratio reduced to 0.4 from 1.0. However, along with microstructure, the creep property of the AX alloys was highly influenced by the  $\text{Ca}/\text{Al}$  ratio. Nakaura et al. [18] observed that the minimum creep rate of the AX alloys decreased as the  $\text{Ca}/\text{Al}$  ratio increased to 0.3. The AXJ alloys with  $(\text{Ca}+\text{Sr})/\text{Al}$  ratios of 0.40 and 0.33 were better for creep over the alloy containing  $(\text{Ca}+\text{Sr})/\text{Al}$  ratio of 0.4 [19]. The enhanced creep resistance of the AJC511 (0.40) and AJC611 (0.33) alloys was accredited to the higher thermal stability of the  $\text{Al}_2\text{Ca}$  phase (M. P. 1352 K) present in these alloys than the  $\text{Mg}_2\text{Ca}$  (M. P. 988 K) phase present in the AJC411 (0.5) alloy. Itoh et al. examined the influence of Ca in Mg-Al-Mn (AM) alloy, and they observed the positive dependency of creep rate on Ca content [20]. Terada et al. [21] showed that the AX alloy with 1.72 (wt.%) Ca ( $\text{Ca}/\text{Al}=0.34$ ) was better for creep resistance than the alloys containing lower wt.% of Ca. Thus, a summary of the literature review on the creep behavior concludes that Mg-Al-Ca alloys containing  $\text{Ca}/\text{Al}$  of 0.4 exhibited the best creep resistance. Accordingly, the Mg-5.0Al-2.0Ca alloy satisfying  $\text{Ca}/\text{Al} = 0.4$  was considered for the present investigation.

In addition, the incorporation of Mn significantly improved the creep performance of Mg alloys [22-25]. Homma et al. [22] concluded that the minimum creep rate of AX22 alloy is decreased by one-tenth due to the addition of 0.3 (wt.%) Mn. Samimi et al. [23] assessed creep resistance of 0.3, 0.5, and 0.8 (wt.%) Mn added Mg-5.0Al-1.5Ca alloy. They identified that the creep property of the alloy increased up to 0.5 (wt.%) Mn, while further Mn incorporation deteriorated the creep property. Zhu et al. [24] confirmed that the creep performance of Mg-Al-RE alloy does not change significantly beyond 0.3 (wt.%) Mn. Lamm et al. [25] observed that 0.3 (wt.%) Mn addition stabilized the Ca clusters in Mg-Al-Ca-Mn (AXM) alloys, enhancing their creep resistance. Celikin et al. [26] reported improved creep performance of Mg-1.5 (wt.%) Mn alloy compared to pure Mg, resulting from the dynamic precipitation of  $\alpha\text{-Mn}$  during creep. Thus, Mg-5.0Al-2.0Ca alloy with 0.3Mn addition (wt.%), i.e., Mg-5.0Al-2.0Ca-0.3Mn (AXM520) alloy, is expected to exhibit good creep resistance.

However, the application of AXM520 alloy might be restricted to 473 K. Ferkel and Mordike [27] reported that the dispersion of 3.0 vol.% SiC nanoparticles improved the creep response of pure Mg. The improved creep property of AS41 with 2.0 and 5.0 (wt.%) Al<sub>2</sub>O<sub>3</sub> nanoparticles was reported by Kumar and Chaudhuri [28]. Katsarou et al. too reported a positive effect of 1.0 (wt.%) AlN addition on the creep response of Electron21 alloy [29]. Ganguly and Mondal [30] reported the dual advantage of alloying and SiC nanoparticles dispersion on the creep behavior of AZ91 alloy. Yang et al. [31,32] showed that better dispersion and increased amount of AlN and/or Al nanoparticles additions provided better creep response in Electron21 alloy. In a similar work, Zhou et al. [33] showed that the addition of 1.0 (wt.%) SiC nanoparticles addition decreased the creep rate of AS91 alloy by one order. Ganguly et al. [34] showed that the impression creep response of AZ91+0.6Sb was improved after the addition of 2.0SiC (wt.%). Thus, the dispersion of ceramic nanoparticles will bring plausible alteration in the microstructure and improve the creep resistance of the AXM520 alloy further, which might make it suitable for application beyond 473 K. Accordingly, the microstructural modification and creep behavior of Mg-5.0Al-2.0Ca-0.3Mn (AXM520) alloy with SiC nanoparticles (SiC<sub>np</sub>) dispersion have been investigated.

The Mg-Al-Ca-Mn (AXM) alloy exhibits unsatisfactory ambient temperature strength, restricting its widespread application. Further, the tensile properties of the as-cast AXM-based alloys deteriorated, and the nature of failure became more brittle as the value of Ca/Al in the alloy increased [35]. The Ca-rich secondary phase acted as a crack initiation point leading to fracture. However, adding nanoparticles to pure Mg and Mg-based alloys significantly improved their tensile and compressive properties [36], which is beneficial. Therefore, an attempt has been made to improve the ambient temperature strength along with the ductility of the squeeze-cast AXM520 alloy with the addition of SiC<sub>np</sub>. Thus, the ambient temperature tensile and compressive properties of the squeeze-cast AXM520 alloy and its nanocomposites are also investigated.

The high corrosion rates of Mg alloys limit their potential for widespread applications. The presence of the secondary phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> influenced the galvanic corrosion of the Mg-Al-based alloys and deteriorated their corrosion resistance [37,38]. The Mg alloys reinforced with microparticles exhibited more detrimental corrosion properties than the parent unreinforced alloy [39-41]. On the contrary, recent studies suggested that adding nanoparticles might significantly protect the Mg-based alloys from corrosion [42-45]. The presence of Ca and Mn

is expected to improve the corrosion behavior of the Mg-Al-based alloys [46,47]. However, the influence of the SiC<sub>np</sub> addition on the corrosion response of the AXM520 alloy is unclear. Thus, the ambient temperature corrosion behavior of the newly developed squeeze-cast AXM520 alloy and its nanocomposites is also investigated.

Several studies were conducted on the creep characteristics of dispersion-strengthened pure Mg and Mg alloys [48]. The summary of the literature review concludes that the dispersion of nanoparticles in Mg alloys imparts significant enhancement in creep properties. Further, age-hardening improves the strength of Mg alloys [49]. Unfortunately, to the best of the authors' knowledge, the creep behavior of age-hardened and dispersion-strengthened Mg alloys has not been explored yet. Therefore, the microstructural alteration and creep characteristics of the squeeze-cast age-hardened AXM520 alloy with SiC nanoparticles additions are also investigated. A correlation of the creep responses of age-hardened AXM520 alloy and its nanocomposites with their initial and creep-deformed microstructures has also been established. For the first time, deformation mechanism maps for Mg-Al-Ca alloys and their nanocomposites are constructed.

Thus, the present thesis aims to explore the microstructural alteration, creep characteristics, and corrosion behavior of the squeeze-cast AXM520 alloy with SiC nanoparticles additions. The microstructural alteration and creep characteristics of the squeeze-cast age-hardened AXM520 alloy with SiC nanoparticles additions are also explored. A correlation of the creep responses of age-hardened AXM520 alloy and its nanocomposites with their initial and creep-deformed microstructures has also been established.

## 1.2 Objective of the present thesis

The objectives of the present thesis are to investigate the microstructure, creep characteristics, and corrosion behavior of the squeeze-cast AXM520 alloy with SiC nanoparticles additions. Further, the microstructural alteration and creep characteristics of the squeeze-cast age-hardened AXM520 alloy with SiC nanoparticles additions are also explored. The salient objectives of the present thesis are as follows.

1. The fabrication of the AXM520 alloy and its nanocomposites (NCs) with SiC nanoparticles additions by squeeze-casting.

2. A detailed microstructural characterization of the fabricated AXM520 alloy and its nanocomposites.
3. The evaluation of the ambient temperature tensile and compressive properties of the AXM520 alloy and its nanocomposites.
4. The evaluation of the creep behavior of the squeeze-cast AXM520 alloy and its nanocomposites.
5. The evaluation of the corrosion behavior of the AXM520 and its nanocomposites.
6. To explore the microstructural alteration and creep characteristics of the squeeze-cast age-hardened AXM520 alloy and its nanocomposites.

### 1.3 Organization of the thesis

The present thesis consists of nine chapters, and the content of each chapter is as follows.

- **Chapter 1** consists of a brief introduction to the present investigation, discusses the objective of the present thesis, and provides the organization of the thesis.
- **Chapter 2** discusses the detailed literature review relevant to the present work and summarises the motivation for the current research.
- **Chapter 3** describes the details of the materials and experimental procedure followed.
- **Chapter 4** provides the detailed microstructural characterization of the squeeze-cast AXM520 alloy and its nanocomposites.
- **Chapter 5** investigated the tensile and compressive behavior of the AXM520 alloy and its nanocomposites. Additionally, the strengthening mechanisms involved in the nanocomposites are addressed.
- **Chapter 6** evaluates the creep response of the squeeze-cast AXM520 alloy and its nanocomposites.
- **Chapter 7** explored the corrosion response of the squeeze-cast AXM520 alloy and its nanocomposites.
- **Chapter 8** discusses the microstructure and creep response of the squeeze-cast aged-hardened AXM520 alloy and its nanocomposites.
- **Chapter 9** summarizes the major conclusions drawn from the present investigation and discusses the scope for future work.

The references cited in the entire thesis are enlisted in the reference section.