

CREEP RESISTANCE IN Mg-Al-Ca CASTING ALLOYS

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Abstract

The automotive use of magnesium is currently restricted to low-temperature structural components. Its use in elevated-temperature structural components such as transmission and engine parts requires the development of cost-effective alloys that can meet the performance requirements of these components for elevated-temperature (150°C) strength and creep resistance. This study is on the development of a Mg-Al-Ca alloy system that has good creep-resistance at 150°C. The increased creep resistance of the alloy is due to the existence of an Al₂Ca intermetallic compound in the as-cast structure. Microstructural investigation of the alloy before and after creep loading shows the role of microstructure in creep resistance. The tensile yield strength and the ultimate tensile strength of the alloy at 150°C in the diecast state are equivalent to the more expensive rare-earth containing magnesium alloys. Corrosion resistance of the diecast alloys at 0.11- 0.23 mg/cm²/day, as measured through salt-spray corrosion test, falls in the range of high purity magnesium alloy AZ91D and the rare-earth containing AE42 alloy.

Introduction

The current use of magnesium in automotive applications is usually limited to non-critical parts such as valve covers, steering-column fixtures and instrument panels. However, the driving force for reduced emissions and fuel economy in passenger vehicles is now expanding automotive applications of magnesium to more critical components such as transmission and engine parts. Magnesium here faces a challenge in meeting the performance requirements of these components for elevated-temperature (150°C) strength and creep resistance as well as adequate corrosion resistance. There is a need, therefore, for the development of new creep-resistant magnesium casting alloys.

Creep Behavior of Automotive Magnesium Alloys

The hexagonal-close-packed magnesium creeps even at moderately low temperatures through a stress-recovery mechanism. Roberts (1) studied the creep resistance of pure magnesium in the 1950's and concluded that within a 90-300 °C range, the creep mechanisms at low temperatures is basal slip within the grains and sub-grain formation (transient creep) while at the higher temperatures diffusion-dependent mechanisms of grain boundary deformation and sliding (steady state creep)

become predominant. The same type of change was observed to occur as the stress level at a particular high temperature decreases.

Like pure magnesium, the commonly used Mg-Al alloys (Al 2-9wt%Al) also suffer from poor creep resistance. This alloy class which comprises the majority of the current magnesium die-casting alloys such as AZ91D (Mg-9%Al-1%Zn), AM60B (Mg-6%Al) and AM50B (Mg-5%Al) constitutes the bulk of the automotive applications. The microstructure of these alloys is characterized by the Mg-Mg₁₇Al₁₂ eutectic at the grain boundaries. The Mg₁₇Al₁₂ intermetallic is incoherent with the -magnesium matrix, exists at a wide composition range of 48-52wt% Al and has a low melting point (437°C). The compound is, therefore, prone to aging, has poor metallurgical stability as the temperature is increased (1) and may contribute to the poor creep resistance of the alloy at high temperatures.

Robert in the 50's suggested, for the Mg-Al alloys, that the discontinuous type of precipitation during aging effectively multiplies the grain-boundary area available for easy deformation in elevated temperature creep, and attributed the relatively poor elevated temperature creep resistance of these alloys to this factor. Miller (2) found that diecast AZ91 (Mg-9%Al-1%Zn) alloy creeps even at room temperature through a dislocation climb mechanism. Dargusch et al (3) have observed grain boundary sliding in these alloys and suggested that discontinuous precipitation of Mg₁₇Al₁₂ from a supersaturated matrix in diecast alloys aids grain-boundary migration and sliding and is instrumental in the creep deformation of Mg-Al. The use of these alloys, hence, cannot be expanded to transmission and engine components due to insufficient creep resistance at the operating temperatures of 150 °C.

The Mg-Al-Si alloys (AS41, AS21) which contain the thermally stable Mg₂Si phase in addition to the Mg₁₇Al₁₂ exhibit slightly improved creep resistance but are quite difficult to diecast; these alloys find limited use in automotive transmission applications. Addition of rare earths to magnesium and its alloys is known to improve the creep resistance. The ternary AE42 (Mg-4%Al-2% rare earths) diecasting alloy has only the thermally stable Al₂(RE) compound in its microstructure and no Mg₁₇Al₁₂ precipitates either as-cast or creep induced. The AE42 has improved creep resistance over the other alloys. However, this alloy has a cost disadvantage due the expensive rare-earth additions. There is a need, therefore, for the development of new magnesium casting alloys with acceptable creep-resistance and

cost. The new alloy developed in this study is based on the Mg-Al-Ca ternary system (4-6).

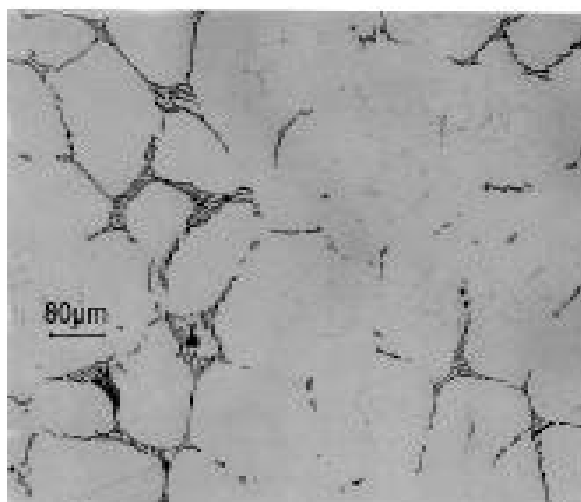
Experimental Method

Mg-Al-Ca alloys were prepared from the commercial Mg-6.0%Al alloy and a Mg-Ca master alloy (Timminco Metals) using a Lindberg electric resistance furnace. Small castings with various levels of Ca additions ranging from 0.2 - 2 % were prepared and aged in a Blue-M heat-treatment oven at 150°C for 100 hrs. The microstructures were then examined for coarsening or any high temperature change and compared to as-cast, unaged microstructures (Fig.1). No aging of the microstructure was observed in the alloys.

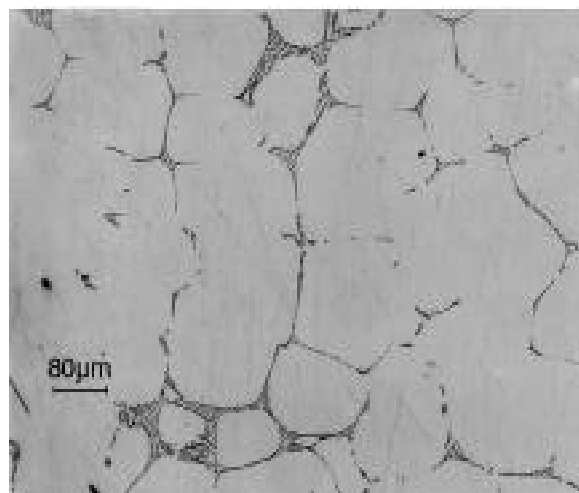
Three calcium levels were then selected for further development and diecasting. These were 0.6%, 0.8% and 1%Ca. A maximum level of 1% Ca was adopted to avoid hot cracking during casting. A 5% aluminum level was selected for the best compromise between strength and ductility. The alloys were tentatively designated AX506, AX508 and AX51 where X denotes calcium.

225-kg batches of the AX506, AX508 and AX51 alloys were prepared for diecasting test specimens. A 250-ton Frech hot-chamber diecasting machine of Intermag Technologies (formerly ITM Inc) was used to diecast mechanical (tensile, creep) and corrosion test specimens. Specimens of two commercial magnesium alloys, AZ91D and AE42, were also diecast to compare with the experimental AX alloys.

The casting temperature for all alloys except AX51 was set at 620°C; alloy AX51 was cast at 635°C. The die-surface temperature was maintained constant at ~280°C by a Thermocast die-heating unit. Diecasting of test specimens also indicated that the diecastability of the AX alloys was good. Some die-sticking problems occurred when the Ca level reached 1%. Die-sticking at this level was eliminated by the use of die lubricants and the proper casting temperature. Chemical analyses (ICP) of alloy samples taken from the melts and diecast parts are shown in Table I.



(a)



(b)

Fig 1. (a) As-solidified and (b) aged microstructures of a Mg-5Al-0.7Ca alloy.

Table I Chemical Compositions of the Die Cast Alloys

| ALLOY | Aluminum (wt%) | Calcium (wt%) | Manganese (wt%) | Zinc (wt%) | Iron (ppm) | Copper (ppm) | Nickel (ppm) | Rare Earth (wt%) |
|-------|----------------|---------------|-----------------|------------|------------|--------------|--------------|------------------|
| AX506 | 4.5 | 0.6 | 0.24 | 0.003 | 10 | 2 | 2 | - |
| AX508 | 4.5 | 0.8 | 0.25 | 0.003 | 10 | 2 | <2 | - |
| AX51 | 4.6 | 1.0 | 0.24 | 0.003 | 13 | 2 | <2 | - |
| AZ91D | 8.9 | - | 0.20 | 0.81 | 25 | 7 | 6 | - |
| AE42 | 4.1 | - | 0.29 | 0.01 | 38 | 20 | 10 | 2.2 |

Tensile and creep tests of the diecast specimens were conducted at Westmoreland Labs. Elevated-temperature (150°C with a soaking time of 30 minutes) tensile tests were carried out on round tensile specimens and flat tensile specimens (ASTM sub-size) were used for creep testing at 150°C and 35 MPa (tensile stress) for 200 hours. Creep testing was performed according to ASTM E139, and the total creep extension (% Creep) was measured from each elongation-time curve.

Salt-spray corrosion testing was conducted on diecast corrosion test plates (ASTM standard) of AX alloys and on AZ91D and AE42 magnesium alloys. For each alloy, six (6) plates were subjected to a 200-hour salt spray test in accordance with ASTM B117. An average corrosion rate was then obtained based on the weight loss during the test.

The microstructures of the diecast test specimens were examined under a Leco 300 optical microscope. Mg-Al-Ca alloy samples were also analyzed via scanning electron microscopy (SEM) using a JEOL 840 SEM coupled with energy dispersive spectroscopy (EDS) system to identify the intermetallic phases. X-ray diffraction (XRD) analyses were performed on the bulk specimens of AX alloys to confirm the secondary phases, using CuK radiation and silicon powder as an initial calibration reference.

Results and Discussion

Mechanical and Corrosion Properties

Elevated-temperature mechanical properties of the Mg-Al-Ca alloys were found to be very promising. These properties were evaluated at 150°C. Table II compares the results of creep tests carried out on the new AX alloys and the two commercial magnesium alloys. The total creep extension data, obtained on diecast specimens of the five alloys at 150°C and 35 MPa for 200 hours (Table II) demonstrate that the new AX alloys (Mg-5Al-0.6Ca, Mg-5Al-0.8Ca and Mg-%Al-1Ca) show one order of magnitude improvement in creep resistance over the conventional AZ91D alloys. The creep extension was 0.26-0.33% in the Ax alloys compared to a value of 2.5% in the AZ91D. As seen in the table, the creep performance of AX alloys is equal to or better than that of AE42 alloy which was 0.33%.

It was also observed that the new AX alloys also offer good high temperature (150°C) strength and ductility (Table III). The results show that the strength of the AX alloys increases with calcium content. AX508 and AX51 have 150°C ultimate tensile strength and yield strength values comparable to AE42 and AZ91D alloys. Elongation at 150°C is better than AZ91D and but less than AE42.

Salt spray corrosion test results on AX alloys in comparison with AZ91D and AE42 alloys shows that the corrosion resistance of the new Mg-Al-Ca alloys compares well with AZ91D and AE42 alloys (Table III).

These results show that the Mg-Al-Ca system offers a good base alloy for developing magnesium casting alloys with good creep and tensile properties at 150°C (International Patent Application WO 96/25529, 1996).

Table II. Creep Resistance at 150°C, 35 MPa for 200 Hours

| Creep Extension (%) at 150°C, 35 MPa and 200 hrs (average of 3 tests) | ALLOYS | | | | |
|--|--------|-------|------|-------|------|
| | AX506 | AX508 | AX51 | AZ91D | AE42 |
| | 0.31 | 0.26 | 0.33 | 2.54 | 0.33 |

Table III. Tensile Properties at 150°C and the Salt Spray Corrosion Rates for the AX Alloys

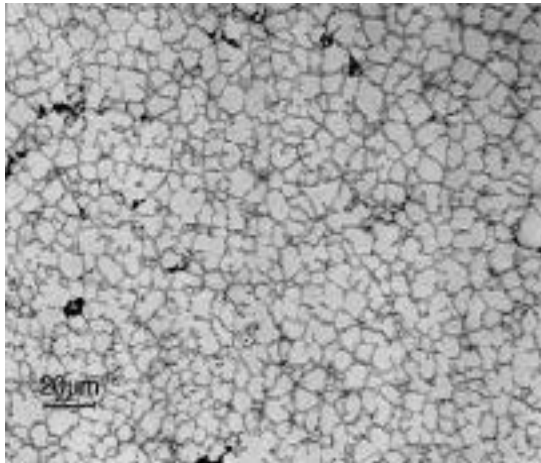
| PROPERTY * | ALLOYS | | | | |
|--|--------|-------|------|-------|------|
| | AX506 | AX508 | AX51 | AZ91D | AE42 |
| Yield Strength (MPa) | 95 | 102 | 112 | 110 | 107 |
| Ultimate Tensile Strength (MPa) | 156 | 161 | 165 | 159 | 160 |
| Elongation (%) | 8.4 | 7.4 | 8.4 | 6.7 | 36.0 |
| Corrosion Rate (mg/cm ² /day) | 0.11 | 0.16 | 0.23 | 0.21 | 0.11 |

* average of three samples

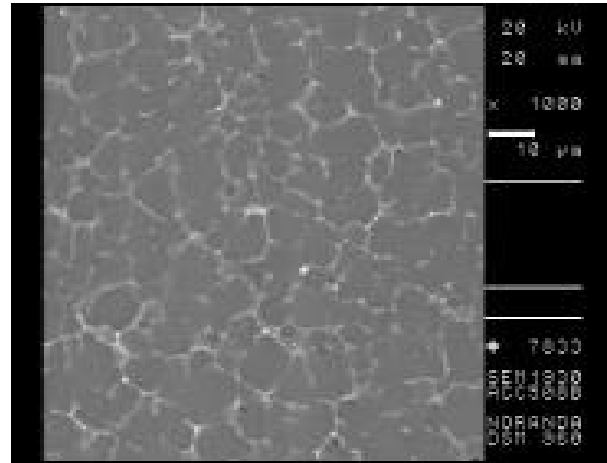
Microstructural Investigation

In order to elucidate the creep results, the microstructures of the new Mg-Al-Ca alloys were investigated. Figs. 2.a-c show the diecast microstructures of AX alloys. To identify the second phases present in the alloys, SEM/EDS analysis was performed. SEM image and the EDS spectrum obtained on the AX508 alloy sample in Figs. 2 c & f indicate that the second phase in the microstructure contains Al and Ca.

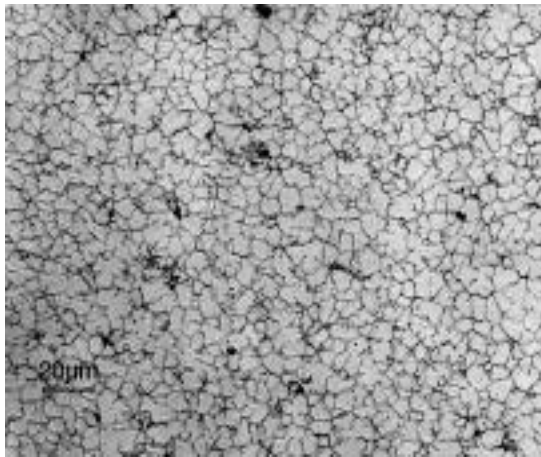
It was confirmed by the XRD analysis that this new phase is Al₂Ca. The formation of low melting point eutectic phase, Mg₁₇Al₁₂, which is generally present in aluminum-containing magnesium alloys is completely suppressed in the presence of calcium. The Mg₁₇Al₁₂ phase is not seen either in the as-cast structure or in the creep deformed microstructure of the alloys (fig. 2 d & f). The resultant new phase, Al₂Ca, is stable at high temperatures as it has a high melting point of 1079°C as shown in the Al-Ca phase diagram (Fig. 3).



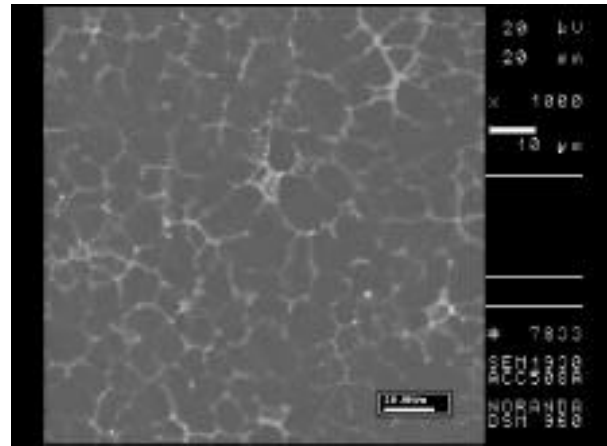
(a)



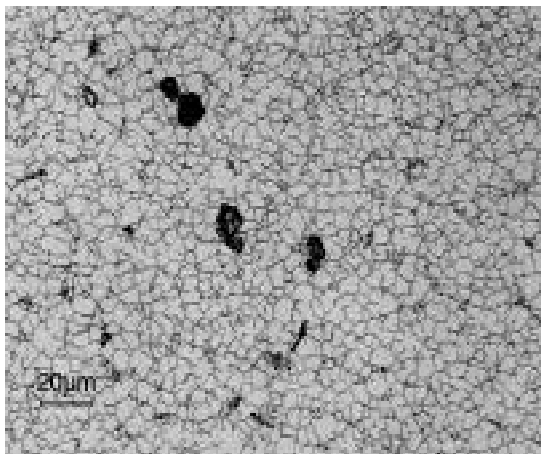
(d)



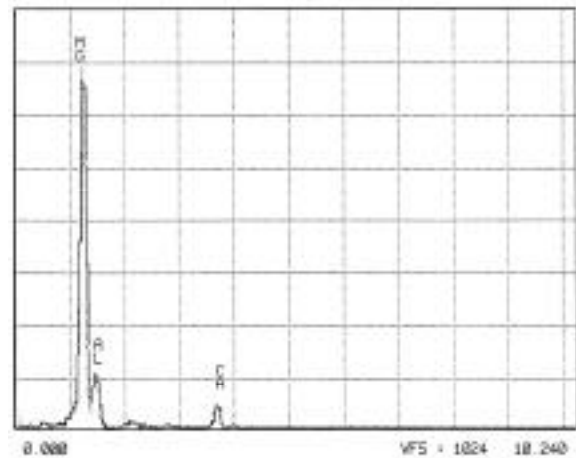
(b)



(e)



(c)



(f)

Fig 2. Diecast microstructures (a) AX506 (b) AX508 and (c) AX51 alloys. SEM micrographs of diecast AX508 (d) before and (e) after creep testing and (f) EDX analysis of showing the Al-Ca intermetallic (Mg signal is from the -Mg matrix).

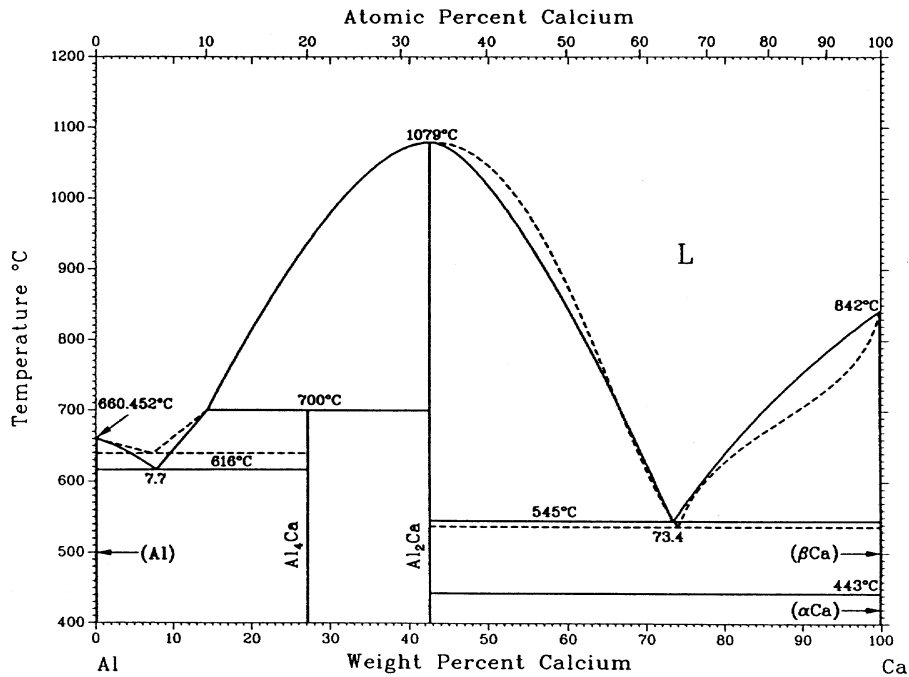


Fig 3. Al-Ca Binary Phase Diagram (7).

Table IV Characteristics of Second Phases in Magnesium Diecasting Alloys

| ALLOY | SECOND PHASES | | | CREEP RESISTANCE |
|--|------------------------------|--|---------------|------------------|
| | PHASE | TYPE | MELTING POINT | |
| Mg-Al (AM20, AM50, AM60) and Mg-Al-Zn (AZ91) | $Mg_{17}Al_{12}$ | Composition range: 42-58% Al Incoherent with α -Mg | 437°C | Low |
| Mg-Al-Si | $Mg_{17}Al_{12}$ | See above | | Borderline |
| | Mg_2Si | Line compound (Laves phase) | 1085°C | |
| Mg-Al-RE (AE42) | Al_2RE (e.g. Al_2Ce) | Line compound (Laves phase) | 1480°C | Good |
| Mg-Al-Ca | Al_2Ca | Line compound (Laves phase) | 1079°C | Good |

The microstructure of the AX alloys resembles the creep resistant AE42 alloy where the second phase is an $Al_2(RE)$ intermetallic with similar characteristics to the Al_2Ca . Both phases are Laves type line compounds with high melting point. Table IV summarizes the characteristics of second phases in various magnesium diecasting alloy systems.

Al_2Ca is generally present along the grain boundary in the diecast microstructure. It is likely that the thermally-stable

phase at grain boundaries impedes grain boundary sliding and diffusion-related dislocation climb at high temperatures, and can partly explain the improved creep resistance in the new AX alloys. The other point to note for Mg-Al-Ca alloys is the absence of the $Mg_{17}Al_{12}$ intermetallic and any aging and creep-induced precipitation in the alloy structure which contribute to improved creep resistance in these alloys. Future work in this study will be dedicated to an in-depth understanding of the creep behavior of Mg-Al-Ca alloys.

Conclusions

1. The creep resistance (total creep extension at 150°C, 35 MPa for 200 hours) of the new Mg-Al-Ca diecast alloys (AX series) at three levels of calcium shows approximately one order of magnitude improvement over that of AZ91D or AM50. The tensile properties of the AX alloys at 150°C, as well as the salt spray corrosion resistance, are comparable to those of AZ91D and AE42 magnesium alloys.
2. Mg-Al-Ca alloys offer the same level of creep resistance as that of AE alloys at much lower costs, as the new alloy system does not contain the expensive rare earth elements. The low cost of the Mg-Al-Ca alloys will certainly make them a strong candidate material for automotive transmission applications.
3. Microstructural study of the Mg-Al-Ca alloys confirms a new strengthening phase, Al₂Ca, suppressing the formation of the low melting point eutectic phase, Mg₁₇Al₁₂, at the grain boundaries in the microstructure of the diecast parts. The Al₂Ca phase has a high melting point (1079°C), and thus, results in metallurgical stability of the grain boundaries at elevated temperatures. This is likely to be the cause of the good creep resistance and tensile strength of the alloy at 150°C.

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