

Mechanical Properties and Corrosion Performance of AZ-Mg Alloy Modified with Ca and Sr

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ABSTRACT

Any new Mg-alloys for the power train application in the automotive industry should have better elevated temperature mechanical and corrosion properties than the traditional AZ91 magnesium alloy. The price of AZ-Mg alloy modified with Ca and Sr, which can have adequate properties suitable for its service conditions, is expected to be comparable to that of AZ91 alloy and cheaper than AE42 alloy. The formation of thermally stable intermetallics, which are necessary for the improvement of creep properties, makes it a promising candidate for high temperature applications. This work investigates the mechanical and corrosion properties of AZ-Mg alloy modified with (Ca, Sr) in comparison with those of AZ91; the work included bolt load retention (BLR) and ageing behaviour. The aim is to give a preliminary evaluation of the overall performance of this modified AZ alloy. It is found that this alloy has a superior BLR property compared to AZ91 alloy with a good corrosion resistance.

INTRODUCTION

Low cost magnesium alloys such as AZ91 cannot be used above 125 °C due to its low creep resistance. Commercially available creep resistant magnesium alloys such as AE42 are often too expensive to be used in automobiles. Besides, AE42 has poor castability even with HPDC, due to the fact that the melting temperature is higher compared to AZ91 and that higher pressure is necessary during HPDC. These and other factors such as corrosion resistance have continued to drive research activities in the development of cost effective alternatives for Mg alloys. The addition of calcium to Mg-Al based alloys decreases the grain size, and improves the mechanical strength and/or oxidation resistance at high temperatures [1-3], due to the formation of Mg₂Ca and Al₂Ca intermetallic phases. Previous investigations showed that in Mg-Al-Ca alloys, when Ca/Al mass ratio

was more than 0.8, both Mg₂Ca and Al₂Ca phases were formed. When this ratio was less than 0.8 only Al₂Ca phase was formed [3]. As most of the Mg alloys modified by Ca have Ca/Al mass ratio less than 0.8, the formation of Al-Ca intermetallic phases is most likely rather than Mg₂Ca. These precipitates such as Al₂Ca with a high melting point above 1000°C are generally present along the grain boundaries, and thus results in metallurgical stability of the grain boundaries and improvement of creep properties at elevated temperatures [4, 5].

Alloying with strontium also increases strength at high temperatures. A considerable grain refinement can be achieved even with the addition of small amount of Sr [6]. The Mg-Al-Sr based alloys (AJ alloy series) have shown superior tensile strength and creep performance at temperatures as high as 175 °C with stresses up to 70 MPa [7]. Sr almost has no solid solubility in Al and consequently high melting temperature phases such as Al₄Sr and Al₂Sr are formed, which contribute to increase in high temperature properties [7-9].

The ageing behaviour of AZ91 alloy without Ca or Sr modification has been reported by several authors [10-12]. The ageing strengthening is closely related to the precipitation of Mg₁₇Al₁₂ phases. This second phase has a weak strengthening due to its precipitation parallel to the basal plane. In contrast, the investigation on the ageing behaviour of AZ-Mg alloy modified with Ca and Sr receives less attention. The same situation can be observed for the investigations on their corrosion and bolt load retention (BLR) behaviours. Especially, up till now, only very few workers investigated the BLR behaviour in the field of researches on magnesium alloys, as indicated in a recent review [13]. Xu et al. used both the experimental and theoretical methods (finite elemental analysis) to investigate the BLR performance of AM50 and AE44 alloys [14].

Based on the above considerations, the present work gives a preliminary evaluation about the overall performance of AZ-Mg alloy modified with Ca and Sr, focusing on its ageing, bolt load retention (BLR) and corrosion behaviours. For comparison, AZ91 alloy without any composition modification is also investigated.

EXPERIMENTAL PROCEDURES

MATERIALS PREPARATION - The magnesium alloys AZ91 and AZ-Mg alloy modified with Ca and Sr were prepared by permanent mold casting. The samples were cast into a 20 mm diameter rod under the protection of 0.2% SF₆-argon mix cover gas. The nominal compositions are shown in Table 1.

Table 1 Nominal composition in (Wt. %).

Alloys	Al	Zn	Mn	Ca	Sr	Mg
AZ91	8.80	0.76	0.24	-	-	bal
AZ-Mg Modified with Ca,Sr	8.80	0.75	0.24	0.85	0.10	bal

MICROSTRUCTURAL EXAMINATION - The alloys were microscopically characterized using a Reichert-Jung MeF3 optical microscope. Scanning electron microscopy with energy dispersive X-ray analysis (EDX) was carried out on the samples using a ZEISS DSM-962 equipment operating at 15 kV. Specimens for optical observation and SEM investigations were chemically etched in a solution of 8 g picric acid, 5 ml acetic acid and 10 ml distilled H₂O in 100 ml ethanol for 10 seconds. X-ray diffractions (XRD) were carried out using a D5000 Siemens diffractometer operating at 40 kV and 40 mA with CuK_α radiation. Measurements were performed by step scanning 2θ from 20 to 120° with a step of 0.02°. A count time of 3 seconds per step was used. The amount of second phases was quantified using the method of Rietveld full pattern simulation.

AGEING TREATMENT - The ageing treatments were carried out at 150°C and 210°C up to 1000 hours. Macrohardness tests were performed on the samples according to ASTM E92-82 standard. A 10 kg weight was used with a holding time of 15 seconds. The tests were performed in both the as-cast state and after ageing treatments.

TENSILE TEST – The tensile testes were performed according to ASTM standard B94-94. The room temperature yield stress, ultimate tensile stress (UTS) and elongation were measured.

BOLT LOAD RETENTION - The BLR test set up used in this work is similar to that of [15, 16], but here a high precision load cell is used instead of instrumented steel

bolt (Figure 1). Cylindrical samples with a size of 20 mm x 11 mm x 15 mm, as the outside diameter, inside diameter and height, respectively, were used for the bolt load retention analysis. The samples were fitted with a high strength M10 steel bolt and a load sensor. The furnace with silicone oil was heated to the test temperatures 100°C, 150°C and 175°C. The couple was then torqued to 8 kN load, which corresponds to 40 MPa. The bolted couple was usually torqued to about 5% above the preload and was held for 1 hour at ambient temperature, in order to minimize the effects of short term relaxation, which can be caused by factors such as the reduction of stress concentration in thread contact surfaces. Thereafter the preloaded specimen was immersed in the oil bath at the test temperatures. The data logger was programmed to record the data every 10 seconds for the first 20 minutes after inserting the bolted couple in the oil bath. The rate of data storage was manually adjusted afterwards to record the readings every 15 minutes. The initial recording mode is very important for monitoring the increase in load as a result of thermal expansion mismatch. The duration of the test was restricted to 72 hours; after testing the sample was cooled in air at room temperature.

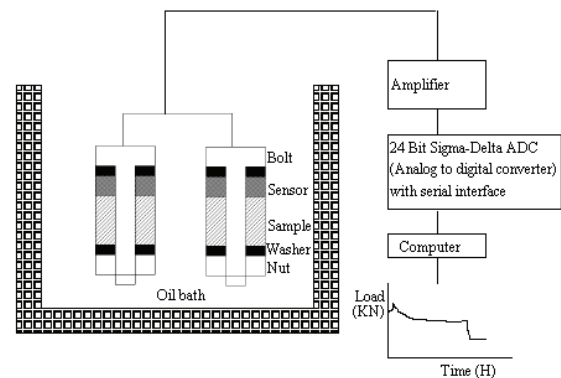


Figure 1. Schematic representation of the bolt load retention testing system.

CORROSION - Corrosion tests were performed on the samples in the as-cast condition and after ageing treatments using polarization technique (ASTM G5-82) and salt spray method (ASTM B117-85). Electrochemical polarizations were conducted in 5 % NaCl solution in distilled water at a pH value of 11.0. The pH was adjusted using NaOH. A three-electrode electrochemical cell was used in all experiments using a Ag/AgCl electrode as the reference electrode and platinum as the counter electrode. The specimens were used as working electrodes, which were in the form of slices of 20 mm diameter and 2 mm thickness and the exposed area of the specimen was 1 cm². After allowing the steady state corrosion potential to develop for 30 minutes, polarization scans were carried out at a rate of 0.2 mV/sec. Salt spray corrosion tests were performed in 5 % NaCl solution for 72 hours at a temperature of 35 °C. After the tests, specimens were immersed in chromic acid solution for 15 minutes to remove the oxide layer and then quickly washed with tap water and dried. The specimens were weighed before and after the tests. The

average corrosion rate in millimetres per year was then calculated based on the weight loss.

RESULTS

MICROSTRUCTURAL CHARACTERISATIONS – The Microstructure of AZ91 alloy consists of the grain boundary precipitates and very few widely distributed irregular shaped particles 1 to 6 μm in size. EDX point analysis shows the presence of Al and Mg in the grain boundary precipitates (Figure 2).

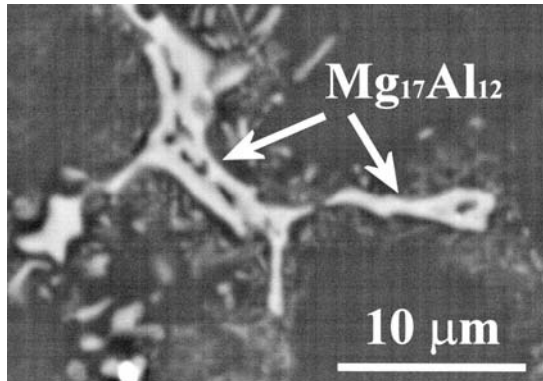


Figure 2. EDX point analysis of as-cast AZ91 alloy revealing Mg, Al enrichment at the grain boundary regions.

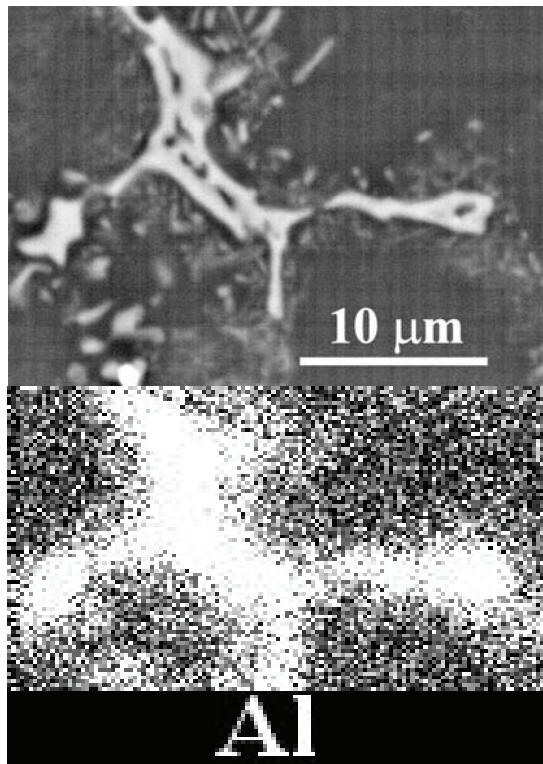


Figure 3. EDX map confirming the presence of Al in the grain boundary of as-cast AZ91 alloy.

EDX map, as shown in Figure 3, also indicates that grain boundary region is heavily enriched with Al. EDX point scans revealed that these precipitates contain between

37-39 at.% of Al, suggesting that β -phase ($\text{Mg}_{17}\text{Al}_{12}$) is present.

This result is in agreement with that obtained by XRD. In addition, the intermetallic compound Al_8Mn_5 with an irregular morphology can be observed. There are also regions around the grain boundary phases, which appear much brighter than the grain interior. This was due to the segregations of Al and Zn at these regions (0.7-0.9 at.% Zn was revealed by EDX point scans). Two types of grain boundary precipitates, and small particles ranging from 1-6 μm in size exist in the AZ-Mg alloy modified with Ca and Sr (Figure 4).

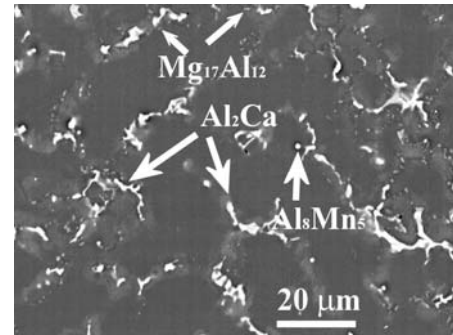


Figure 4. Point analysis showing gray grain boundary precipitate in the as-cast AZ-Mg modified with Ca, Sr.

The bright grain boundary precipitates contain higher amounts of Ca. Quantitative analysis of EDX point scans shows that this precipitate contains 2-3 at.% Ca and 30-33 at.% Al. The grey precipitates containing Al and Mg were identified as β phase ($\text{Mg}_{17}\text{Al}_{12}$) precipitates. Small amounts of Sr and Zn are also present in these precipitates. EDX mapping clearly indicates that the grain boundary area is enriched with Al and Ca (Figure 5).

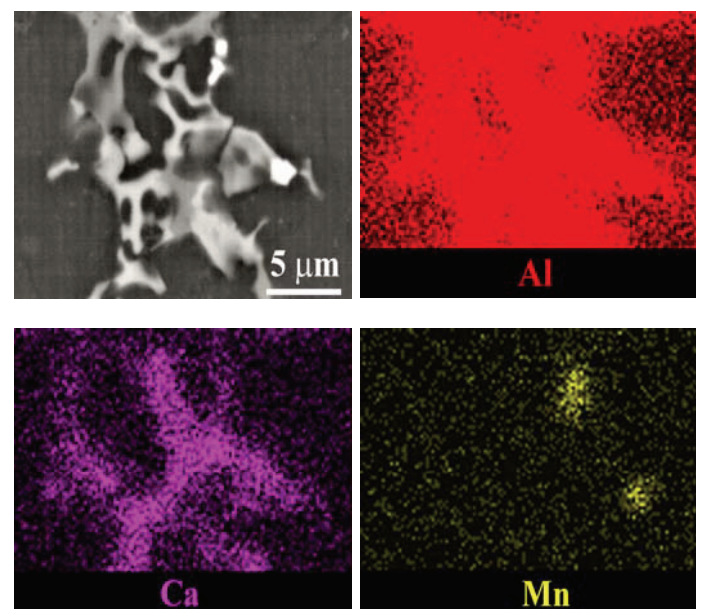


Figure 5. EDX map for the as-cast AZ-Mg modified with Ca, Sr.