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Effects of Tin on Artificial Ageing Response of a Binary Mg-Ca Alloy

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Abstract

In spite of having impressive eco-friendly properties, applications of Mg alloys are limited due to some complications. The majority of Mg alloys derives their mechanical properties from precipitation hardening. Alloying with tin (Sn) results in high creep resistance and strength due to precipitation of the Mg_2Sn phase. This work focuses on the effect of Sn containing magnesium-calcium (Ca) alloys on natural ageing response on microstructure and hardness and segregation behavior of the element. Alloys were cast in with different portions of Sn, homogenized at 410°C to reduce the effect of composition segregation at dendritic arms and natural ageing was done up to 21 days. Hardness values had no significant effect. Microstructure analysis, DSC, SEM and EDX results indicated presence of second phase particles (MgCaSn & Mg_2Sn). Particles increased with Sn percentage which also improved castability and grain growth of α-Mg matrix. Additionally, Sn being relatively cheap can help produce cost-effective Mg alloys with good mechanical properties.

Keywords: Magnesium Alloys, Natural Ageing, Second Phase Particles

1. Introduction

Magnesium and its alloys have appropriate properties, that is, density between 1.74 and 1.9 g/cm^3, tensile strength of around 160–365 MPa, and 45 GPa elasticity modulus [1]. Nevertheless, they have weak points such as low work hardening, weak corrosion resistance, being active, and high thermal expansion coefficients. The growing demand in different industries such as automobile or the increasing use of environmentally friendly light alloys in biomedical applications shows the importance of non-toxic magnesium alloys. In the past fifteen years magnesium alloys have been mainly of interest for automotive industries. The major target was and still is the reduction of weight without limiting the comfort and safety issues. This led to the introduction of a number of new alloys.
In recent years, the development of a new series of Mg-Sn alloys had been started. In these binary alloys the amount of Sn has been varied up 15 wt. % in the first. To achieve further knowledge about the influence of alloying elements these binary alloys have been modified using Al, Mn, Sr, Si, RE, and Ca. After preliminary investigations the decision was made to focus further research on ternary Mg-Sn-Ca alloys. The addition of Sn as well as the addition of Ca offers the possibility of both solid solution strengthening and precipitation hardening [2-6]. With regard to the binary phase diagrams Mg-Sn-Ca are also offering the potential to change the property profile with regard to different heat-treating regimes [7]. Moreover, the intermetallic compounds Mg_2Sn and Mg_2Ca are having high melting points of 770.5 ºC and 715 ºC, respectively. Therefore they are also promising candidates to improve the creep response of those alloys. Besides these binary compounds a ternary intermetallic phase CaMgSn may appear in these alloys and contributes to further improvement of the property profile [2]. Due to the fact that the properties of binary Mg-Sn alloys cannot meet the requirements for practical industrial applications, the optimization of alloy compositions through the additions of other alloying elements is inevitable. These alloying elements include Ca, Sr, RE (rare earths), Al, Zn and Sb. Among them, the additions of Ca, Sr or RE improves both the room temperature strength and high temperature creep resistance due to the formation of precipitates such as CaMgSn or CaMgSr. The phases CaMgSn and CaMgSr are high temperature stable [8]. They are very e ﬀective to improve the creep resistance of Mg-Sn alloys. Addition of alloying element such as Zn, Sr, and Sb etc. can improve properties. Like Zn increases precipitation, Sb refines dendritic microstructure & creep resistance, Sr improves corrosion resistance.
When analyzed, presence of MgCaSn, Mg_2Sn and Mg_2Ca particles were observed by DSC analysis [9]. Optical microscopy analysis showed dendritic structure when homogenized sample was observed and after ageing, particles could be observed. The particles were also seen by SEM BSE analysis and were verified by EDX analysis. Coarsening occurred when longer ageing time was applied and high hardness was denoted. Hardness values of the samples showed no specific pattern rather random fluctuations were observed but high hardness

values were observed for the structures having more particles and coarser ones. Increased percentage of Sn gave increased amount of particles but significant effect on hardness was not observed. A simple classical grain boundary segregation and solute drag model (the Cahn–Lu¨cke–Stu¨we model [10,11]) can be used to estimate the tendency for Ca & Sn to segregate to boundaries and the drag pressure they will produce. This model is based on the assumption that it is the misfit between the alloying elements (which are large) relative to the matrix Mg atoms that provides the driving force for boundary segregation.

2. Experimental procedure

The Mg-Ca-Sn alloys of changing percentage of Sn were casted in a metal mould. The metals were melted at 700˚C in an inert atmosphere using argon gas flow. Magnesium bars and granular shaped Sn and Ca were used as raw material. The moulds were preheated at 350 ˚C for 30 minutes. They were machined and homogenized at 410˚C for 9 hours straight for three consecutive days. Homogenization was done to get uniform distribution of solute and remove stress generated while machining. Water cooling was done after the heating process. 1% and 2% Sn containing alloys were denoted as sample A and B.

The samples were then naturally aged up to 21 days and the micro hardness values were observed for the samples using Vickers hardness testing machine. An FV-800 Vickers hardness tester is used for measuring the hardness by applying a load of 3kg for about 10 sec. Ageing causes second phase particle formation which may lead to hardening of the alloy depending on the particles that formed.

XRF, DSC tests were performed on homogenized sample and SEM, EDX analysis were done on the aged sample. DSC stands for differential scanning calorimetry and is used to monitor the amount of heat energy absorbed or released by the specimen when heated or cooled. In this technique, the difference in the heat amount to increase the temperature of a sample and reference is measured as a function of temperature. Heat flows through heat sink and holders and is proportional to the heat difference of heat sink and the holders. By calibrating the standard material, measurements for the unknown sample were achieved. XRF is performed to check the accuracy of the alloying elements percentage in the respective alloy.

SEM is done to get the view of particle distribution in an alloy. After ageing treatment of the alloy, second phase particle may have formed in the Magnesium matrix. A sample of 10mm diagonal and height was prepared. The sample was then grinded with emery paper and polished giving an un-etched final surface. A coating is applied on the surface of the polished specimen for better scanning of the surface. SEM micrographs were observed at different magnifications (500, 1000, 2000 and more) in back scattered mode and particles were observed in it distributed in a unique way. EDX stands for Energy dispersive X-ray spectroscopy which is used to analyze the elements present in a specific point of the structure or as an average of the whole. Each element has a unique atomic structure which gives different peaks on the electromagnetic emission spectrum. And from the peaks we get the elements and their percentage present in the surface of the sample.]. The same specimen for SEM were used for EDX analysis, nothing different preparation were required. The data gave the presence of elements that were included during the casting and also presence of oxygen was observed which indicates the presence of dirt in the specimen. Grain boundary segregation and drag pressure are also calculated using CLS model. The CLS model predicts that there are two drag pressure regimes as a function of boundary velocity. In the low velocity regime, drag increases as boundary velocity increases. In the high velocity regime drag pressure decreases with increasing boundary velocity. The maximum drag effect occurs at the transition between the regimes.[12]

3. Results and Discussion

Microstructure analysis

Homogenized sample: Sample A has dendritic structure which is both visible in un-etched and etched microstructures. The yellow parts are the magnesium dendrites and the black parts in between the dendrites are the different inter-metallic particles. It is also observed that on the microstructures in the middle part shows larger grains. It is because of non-uniform homogenization. Their microstructure consists of MgCaSn and Mg_2Ca intermetallic particles. [2]. Homogenized unetched sample B shows more secondary particles than sample A in the microstructure as observed in Fig. 1. In homogenized etched sample B (Fig. 2) the number of intermetallic particles seem to be higher than the one in sample A which is very much expected as they have more Sn percentage and thus the formation of MgCaSn, Mg_2Sn will be higher. It also has dendritic structure with both coarse and fine dendrites in different positions indicating non uniform homogenization. Interphase particles are Mg_2Sn and MgCaSn in this case as the ratio of Ca and Sn is higher than sample A.

Aged sample: The aged sample microstructures had the dendritic structures only with a finer grain structure. It is also observed that when aged for a shorter time, more dendritic structure were present than the longer timed structure which has more irregular shaped uniform grains.

After ageing, there are also particles observed inside the dendrites. During Ageing, Mg_2Sn particles forms by, the segregation of Sn inside the dendrites and lamellar MgCaSn particles are observed outside the Mg matrix. [2,9]. After ageing, as seen in sample A, sample B had lamellar MgCaSn structures were observed and granular Mg_2Sn particles were observed. Mg matrix was more uniform than regular dendritic structures.

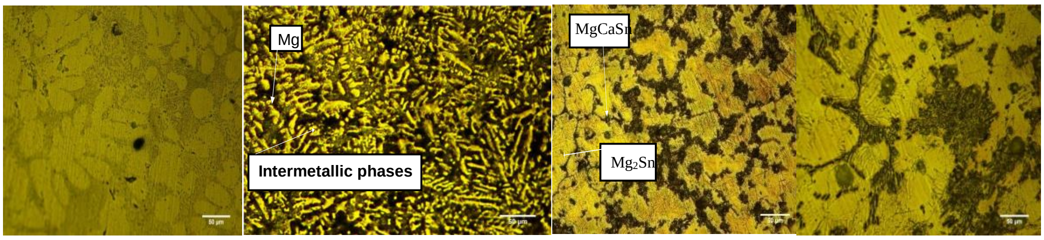

Fig. 1. Microstructure of homogenized unetched, etched and aged microstructures of sample A (from left to right)

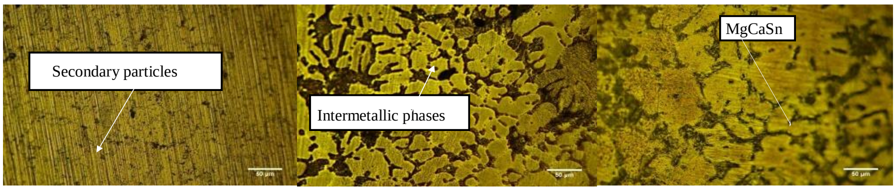

Fig. 2. Microstructure of homogenized unetched, etched and aged microstructure of sample B (from left to right)

In sample A, after DSC analysis (Fig. 3) one peak was observed in very low temperature at about 120˚C. No other significant peaks were observed. As our sample had only 1% of both the elements, the formation of Mg_2Sn didn't occur in homogenized structure and the MgCaSn particles are normally very stable to dissolute and due to low presence, their dissolution wasn't very much significantly seen.

The first peak observed at 120˚C was due to the dissolution of little amount of Mg_2Ca present in the microstructure which normally forms when Calcium Tin ratio is low and is very unstable in increased temperatures. In sample B after DSC analysis, 2 peaks were observed. As we already know our alloy has second phase particles Mg_2Sn and MgCaSn. These particles dissolute when heated and thus we get the endothermic peaks. In sample B after DSC analysis, 2 peaks were observed. As we already know our alloy has second phase particles Mg_2Sn and MgCaSn. These particles dissolute when heated and thus we get the endothermic peaks

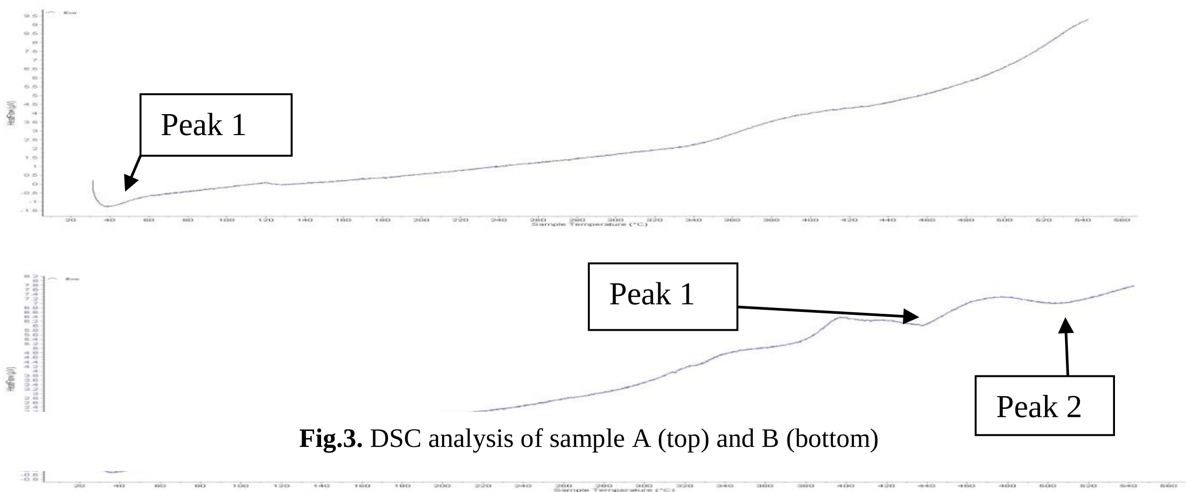

Fig.3. DSC analysis of sample A (top) and B (bottom)

Hardness testing after ageing

Hardness values showed no significant change or pattern during the ageing process. There were random values and fluctuations in a certain range.

SEM and EDX analysis

The SEM BSE micrograph (Fig. 4) of sample A were observed. Both the Mg_2Sn and MgCaSn particles were observed in the sample. From SEM micrographs, the predetermined particles can be verified. The lamellar MgCaSn and the granular Mg_2Sn were observed in the micrographs. The percentage of their composition when EDX analysis was done spotting a specific particle confirmed their presence (Table 1). Sample B showed same particles. The amount of particles in sample B is higher than the ones in sample A.

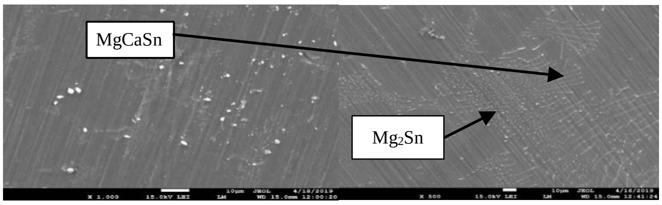

Fig. 4. SEM analysis showing particles of sample A and B (top and bottom)

Table 1. EDX analysis percentage of elements

Sample name	Atom% of Mg	Atom% of Ca	Atom % of Sn
180-72A single particle	97.62	1.18	1.20
180-72A overall distribution	98.63	0.82	0.55
170-24 B Single particle	96.17	1.73	2.11
170-24B overall distribution	98.79	0.55	0.66

Solute drag model

The measured level of segregation on the grain boundaries can be used to provide a more accurate prediction of the solute drag effect with the CLS model [11]. The value of ΔG_{seg} is shown in Fig. 5. The level of segregation measured from ΔG value. For sample A, Sn segregates more than Ca. However in sample B it is opposite.

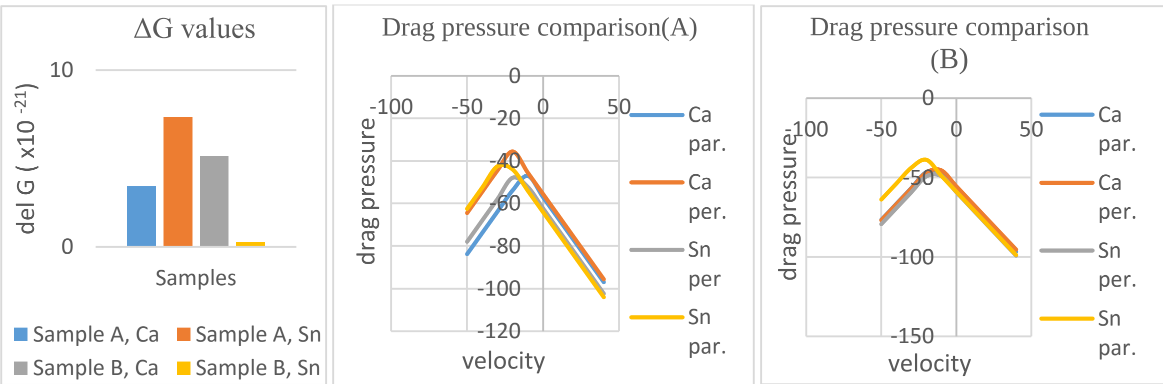

Fig. 5. ΔG values of elements, drag pressure values with respect to velocity for Ca and Sn in the alloy of sample A and B (left to right)

Using these values of ΔG_{seg}, the CLS model has been used to predict the variation in drag pressure for the solutes at 673 K as a function of boundary velocity, and this is shown in Fig. 5. These plots show the transition between the low and high velocity regime, with the peak drag pressure corresponding to the transition point. For both elements parallel and perpendicular dislocation movement drag pressures are plotted. For sample A in low regime Ca parallel has lowest and Sn parallel has highest and transition point of boundary velocity is lower for Ca perpendicular and higher for Ca parallel.

For sample B in low regime Sn parallel has lowest and Sn perpendicular has highest and transition point of boundary velocity is lower for Sn parallel and others value are close enough.

4. Conclusions

The alloy after casting was homogenized and aged. The structure after homogenization and ageing with 1% and 2% Sn addition were studied. Microstructure of the homogenized sample had dendritic grains with intermetallic particles such as MgCaSn, Mg_2Ca, Mg_2Sn that were present between the dendritic structures (grain boundary). MgCaSn particles are lamellar and the other two are granular. Mg_2Ca particles are not stable in heat so after homogenization and ageing, no Mg_2Ca particles remained. The other two can sustain increased temperature and Mg_2Sn even forms during ageing. Overall hardness data evaluation showed no specific pattern of hardness change with time but particle size and quantity effect could be observed with increased Sn percentage when analyzed. Using higher amount of Sn and performing artificial ageing might enhance the properties to te desired values.

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