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INTERMETALLIC COMPOUNDS AND CHOICE OF ALLOYING ELEMENTS FOR THE MANUFACTURE OF THIXOMOLDED CREEP-RESISTANT MAGNESIUM ALLOYS

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Abstract

This study aims at finding ways to improve the service properties of state-of-the-art creep-resistant Mg alloys for Thixomolding and minimise production problems. In doing so, micro-alloying with Si, Zn, Sr, Li, C, Ba and Bi, as well as the addition of rare earths is a viable solution.

Keywords: magnesium alloys, intermetallic compounds, creep-resistant

1. Introduction

Conventional magnesium alloys for pressure-die casting have properties limiting the use of such components in automotive engineering due to their increased susceptibility to corrosion and low creep resistance at elevated temperatures (Fig. 1). They are therefore unsuitable for the constant transfer

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of strong forces in engine components [1]. The temperature in use of the alloys AZ91D, AM60B, and AM50A is limited to a maximum 125 °C [2]. When this limit is exceeded, these alloys start to creep, i. e. they change their shape when subjected to heat even under low-stress conditions, which is usually harmless at ambient temperature.

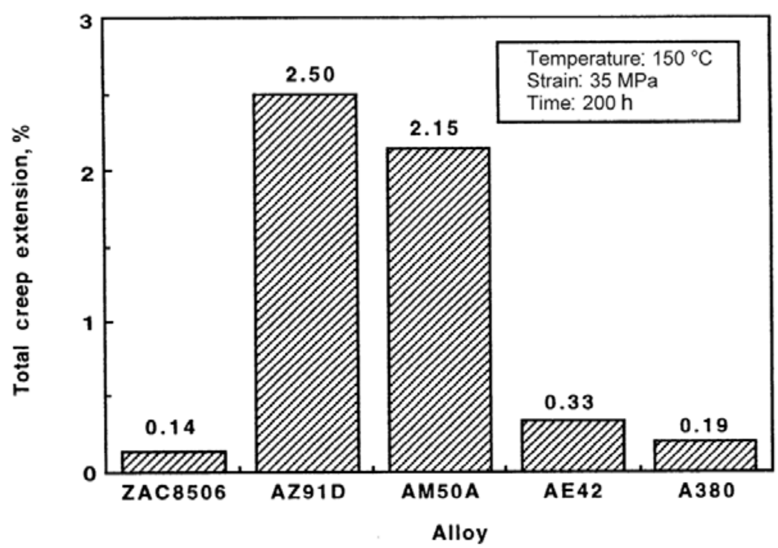

Fig. 1. Creep expansion values for some magnesium alloys [2]

It was shown that the quantity and character of the intermetallic compounds greatly influence the pouring characteristics and mechanical properties of the component. Intermetallic compounds affect the plasticity of the alloys in a semi-solid and solid state as well as their hot brittleness [3].

The structures of the Mg-Al alloys consist of a solid solution and the intermetallic compound $Mg_{17}Al_{12}$ at the grain boundaries. The compound $Mg_{17}Al_{12}$, as the phase solidifying last, fills interdendritic cavities and thus influences flowability, shrinkage, porosity, and the development of hot cracks (Table 1).

The strength and elasticity properties of the alloys depend on the character of the intermetallic phases (unbroken lattice, individual, globular inclusions or tapering and angular inclusions at the triangular junctions) and their quantity in the matrix. Intermetallic compounds are very effective as to improved properties at high temperature (e. g. creep resistance). It was found that inside a grain the creep resistance is lower than at the grain boundary [4]. At the grain boundaries discontinuous precipitations are formed that contribute to the creep-deformation process [4-6]. The continuous precipitations inhibit the dislocation movement, while the discontinuous precipitations create - boundary surfaces where dislocations can be developed and annihilated [4]. This can be achieved by a lower Al content and the addition of elements forming stable intermetallic phases in the area of the grain boundary [4]. The suitable elements, having only limited solubility in Mg (large differences in atom size), form secondary phases or stable compounds rather than dissolve in the solid solution [7, 8]. Table 2 shows the solubility of the most important alloying elements for magnesium. The remaining possible additions are Al, Zn, and rare earth elements [2, 4, 7, 8].

Table 1. Physical characteristics of the solid solution and the intermetallic phase [3]

Characteristic	δ solid solution	Intermetallic compound $Mg_{17}Al_{12}$
Linear expansion coefficient, 1/°C	$26 \cdot 10^{-6}$	$29.3 \cdot 10^{-6}$
Contraction at solidification, %	4.1-4.3	4.83
Specific volume, g/cm³	0.57	0.42

Table 2. Solubility of the most important alloying elements for magnesium [8-10]

	Al	Mn	Zn
Mg	12.7	2.2	8.4
Al	100	0.9	16
Mn	35	100	1.4
Zn	2.4	0.6	100

Paper [11] describes improved creep resistance in pressure-die cast Mg-Al alloys at elevated temperatures. The addition of rare earths (cerium) causes a major percentage of the phase $Al_{11}SE_3$ to be precipitated at the grain boundaries, which means that less aluminium is available to form the precipitation. For instance, the alloy AE_{42} contains 2 to 3 % cerium-pure mischmetal (RE) forming $Al_{11}RE_3$. If the rare earth fraction is increased to more than 1.4 %, the phase $Mg_{12}SE$ that increases the strength precipitates, too.

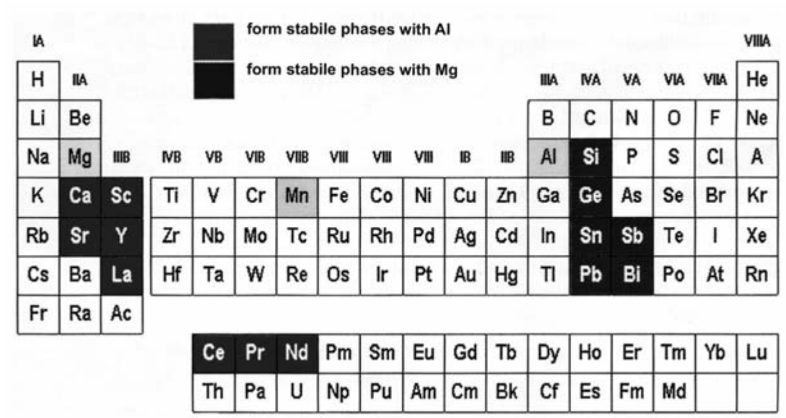

Fig. 2 presents the chemical elements in the periodic system that form stable intermetallic phases in Mg-Al alloys.

In all the cases the intermetallic phases disperse in the vicinity of the grain boundaries and affect creep by impeding sliding and dislocation movements at the grain boundaries. The shape and distribution of the intermetallic phases formed are of great importance with regard to the mechanical properties. Small, non-spherical precipitations are preferable, whereas coarse and block-shaped particles affect these properties negatively [4].

Problems caused by micro-shrinkage in the usual Mg-Al alloys, such as AZ91HP (HP: high purity) can be solved by micro-alloying with strontium, lithium, calcium (causes stickiness!), barium and bismuth, because these elements positively change the solidification morphology [4, 7, 12]. The example given by [4] is the positive effect on creep resistance of the alloy AE42 by adding 1 % strontium [4, 6, 13], increasing the stable intermetallic phases at the grain boundaries and disintegrating the over-saturated -Mg(Al) solid solution at the edge of the grain.

The addition of zirconium also has a grain-refining effect in magnesium alloy AZ91 [14]. The addition of up to 0.7 % antimony (Sb) increases the yield stress from 65 to 106 N/mm² at 200 °C [15]. The creep resistance also increased considerably, while the elongation at fracture was reduced to a large degree.

From this data, it follows that a combination of aluminium, zinc and manganese is favourable for a magnesium alloy [8] (Fig 3.). Al and Mn provide better alloying possibilities with other elements. The most unfavourable alloying partners in this case are Zn and Cd [8].

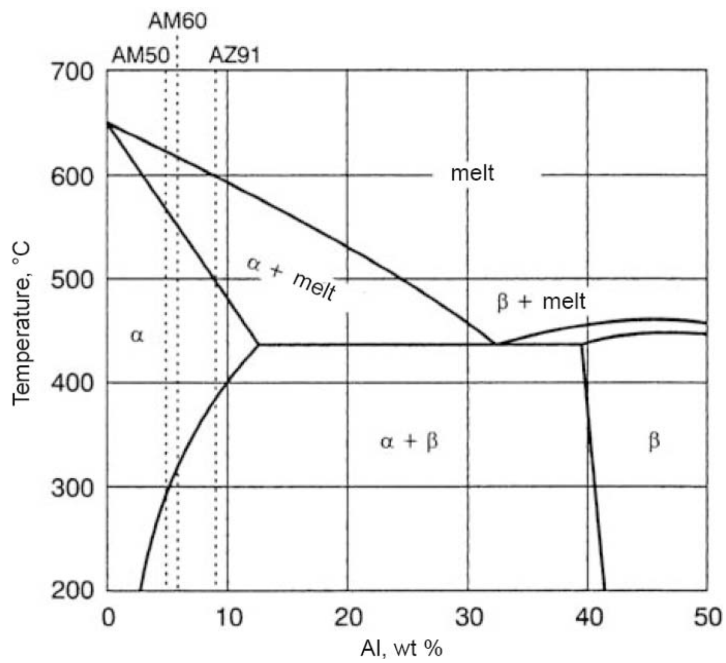

Fig. 3. Phase diagram magnesium-aluminium; effect of various alloying elements on the properties of Mg alloys [16]: Aluminium (3-11 %) - viscosity ↕ strength ↑ ductility ↕; Zinc (1-3 %) - viscosity ↕ ductility ↕; Manganese (0-2,5 %) - corrosion resistance ↑

The addition of Al and Ga leads to increased strength by solid solution hardening and precipitation hardening [17].

The reasons for the use of beryllium (0.001 to 0.002 % Be) in magnesium alloys are discussed in [18, 19], the main reasons being a lower percentage of oxides and dross during melting.

Adding lithium to magnesium significantly reduces the density (up to almost 1 g/cm^3) [20].

The addition of silicon increases the creep resistance; it also slightly compensates for the poorer castability due to the relatively low aluminium content (in AS21) [17].

Mn and Zn improve the resistance to corrosion [17].

The addition of Ca (0.05 to 0.15 % according to [19], or 0.1 to 0.2 % according to [21]), just as 0.5 to 0.7 % Zr have a grain-refining influence; the creep resistance is further increased, and the reactivity of the melt decreases. However, Ca to a great extent furthers the susceptibility to sticking in the die, which has considerable disadvantages during production.

Pettersen e. a. studied the effect of the most important alloying elements (Al and Si) on the creep resistance of Mg-Al alloys over 100 h at 150 °C and with a load of 50 MPa [4]. Fig. 4 shows the creep rate as a function of the Al content for a binary alloy Mg-Al, a Mg-Al-Mn alloy, and for Mg-Al 1 % Si-Mn. As to the Mg-Al alloy, the creep rate decreases as the aluminium content rises. The second group of alloys (AM alloys) shows a minimum rate of creep at about 2 % Al, and a maximum creep rate at about 5 % Al. The third group of alloys studied (AS alloys) containing 2 to 5 % Al shows the same tendency

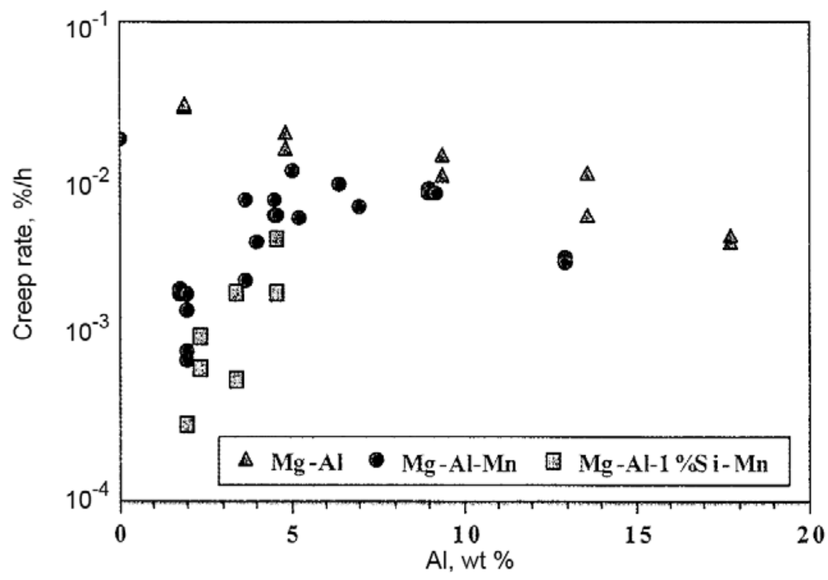

Fig. 4. Creep rate over 100 hours as a function of the aluminium content at a temperature of 150 °C and a load stress of 50 MPa [4]

as AM alloys, but with lower creep rates.

Fig. 5 shows the effect of the intermetallic compounds to the creep rate of magnesium alloys with an aluminium content of 2 %. In the binary Mg-Al alloy, the addition of 0.5 % Mn leads to a reduction of the creep rate by a factor of more than 10 [4]. The Mn is in the AlMn particles that are practically insoluble. A further addition of Si up to 1.2 % further reduces the creep rate (factor 6). This is put down to the increasing content of polyhedric, finely dispersed Mg2Si particles in the grain boundaries [4]. Another addition of Si

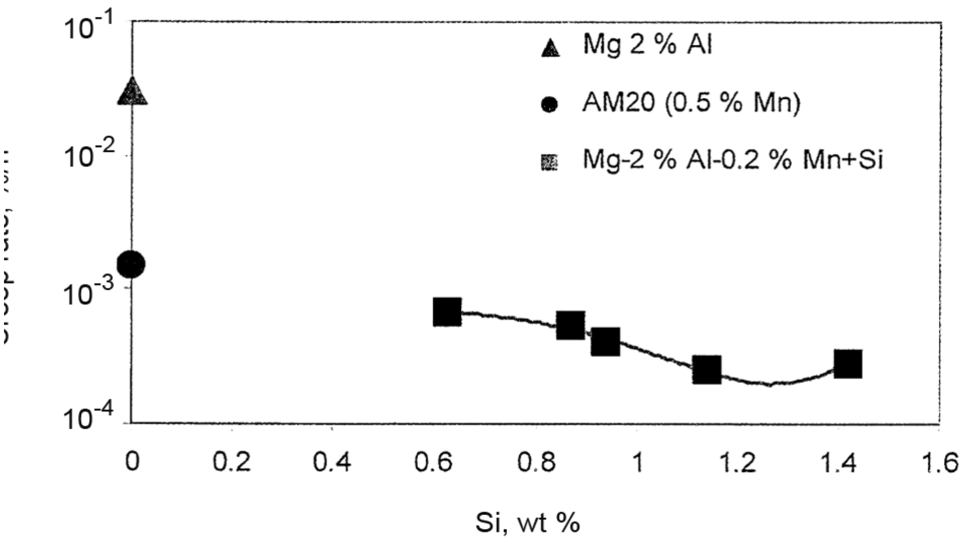

Fig. 5. Creep rate over 100 hours as a function of the silicon content for alloys containing 2 % Al [4]

(over 1.2 %) leads to the formation of coarse, block-shaped particles.

When studying the effect of other alloying elements on the creep resistance of thixomolded [22] Mg-Al-Ca-X alloys (X = Si, Zn, Mm, Ba, Sr) found [23] that the addition of Al (from 4 to 8 %) did not have a major effect (Fig. 6). As the percentage of Si and Zn increases, the creep resistance decreases (Fig. 7). Addition of mischmetal (Mm) has no effect whatsoever on the creep resistance (Fig. 8 a), but it improves the elongation at fracture at elevated temperatures (Fig. 8 b). Minor addition (0.03 %) of barium or strontium has an important effect on the creep resistance at higher stresses and temperatures (Fig. 9). These results correspond to data obtained from other authors [24].

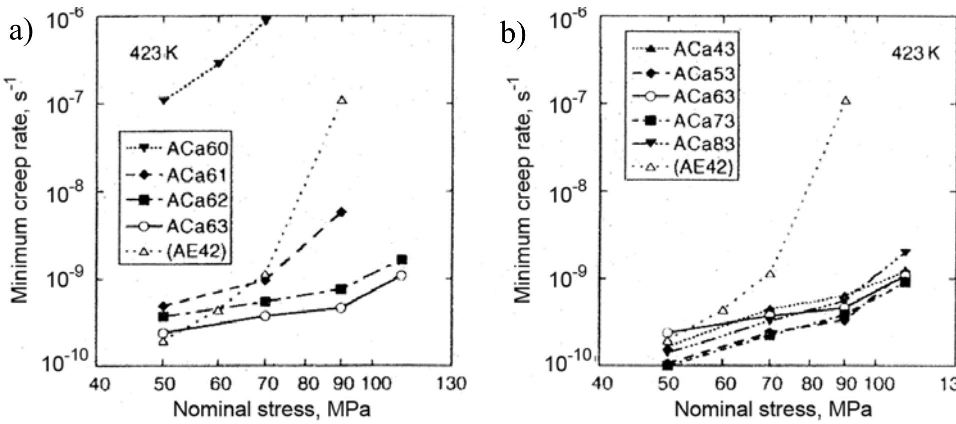

Fig. 6. Effect of the aluminium content on the creep resistance of thixomolded magnesium alloys [23]

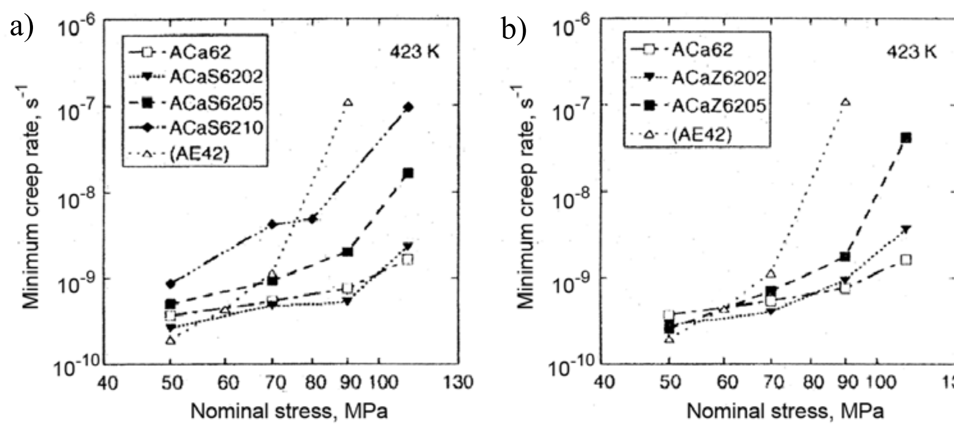

Fig. 7. Effect of silicon (a) and zinc (b) on the creep resistance of thixomolded magnesium alloys [23]

The same authors in another publication [25] report on the effect of Ca on the creep resistance of thixomolded magnesium alloys. They found that the creep resistance rises with an increasing Ca content (Fig. 10 a). With a load of 50 MPa the Mg-Al alloy with 3.25 % Ca had the same creep resistance as AE42. As the load increases (>70 MPa), the creep resistance exceeds AE42. After 100 h the creep deformation of a Mg-Al-Ca alloy remains under 0.2 % (Fig. 10 b).

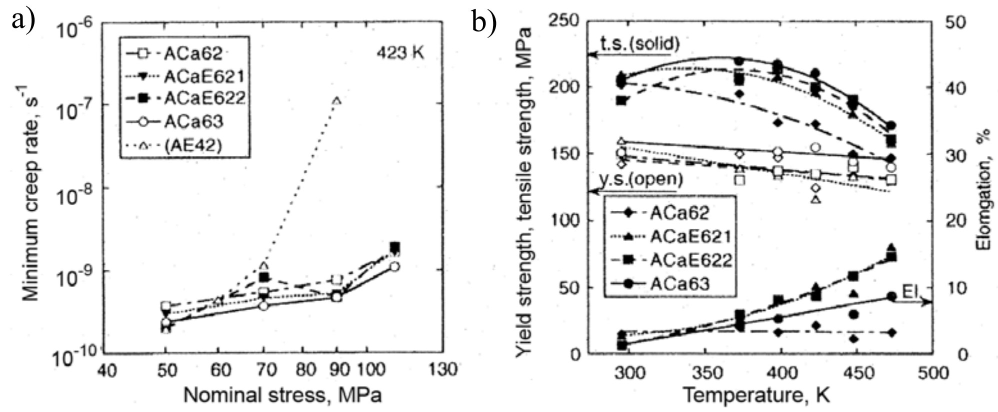

Fig. 8. Effect of mischmetal (Mm) on the creep resistance (a) and the mechanical properties (b) of the thixomolded Mg alloys at increased temperatures [23]

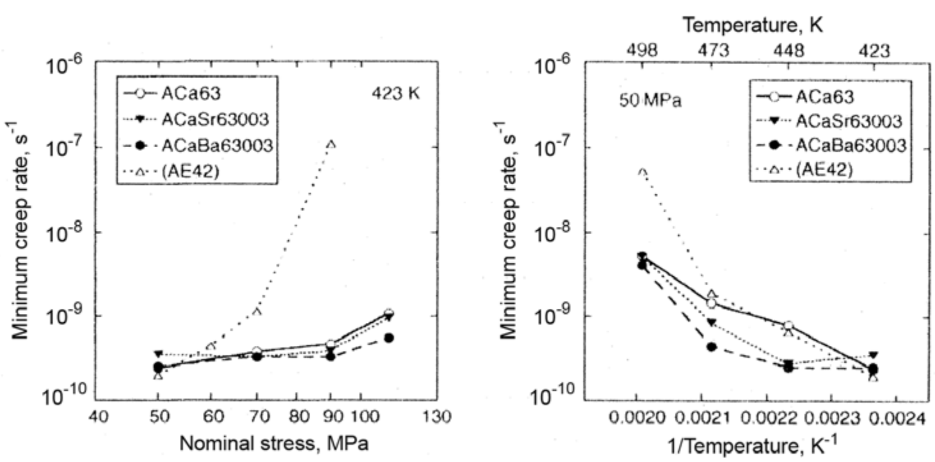

Fig. 9. Effect of barium and strontium on the creep resistance (a, b) of thixomolded magnesium alloys [23]

Ca and Al have a distinct tendency to grain-boundary segregation, which is why the concentration of these elements in the matrix is kept at a very low level. Several authors report on the eutectic phases in the Mg-Al-Ca system.

Fig. 11 shows a "magnesium corner" of the Mg-Al-Ca diagram [26]. In the quasi-binary section α-Al_2Ca the eutectic point was determined at approx. 15 % Al and 11 % Ca. In the triangle α-Mg-Al_2Ca-Ca a eutectic point was determined with 8 to 10 % Al, 16 to 20 % Ca, and the remaining Mg.

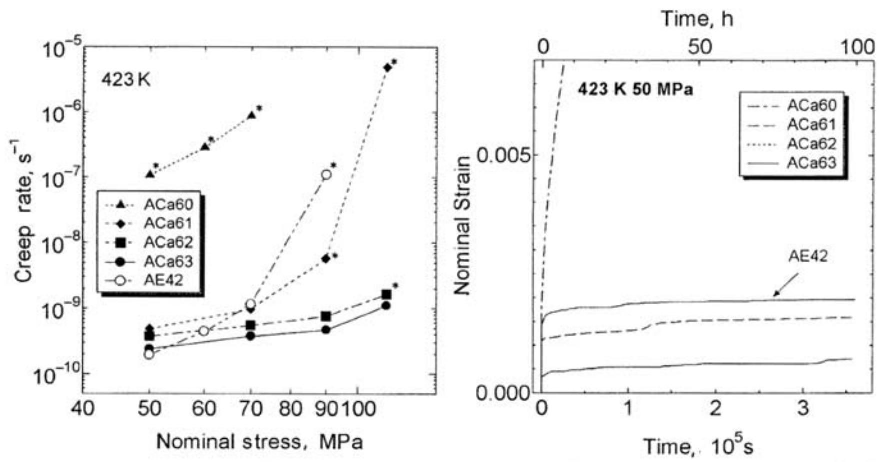

Fig. 10. Typical creep curves of thixomolded magnesium-aluminium-calcium alloys and AE42 at a temperature of 423K and 50 MPa [25]

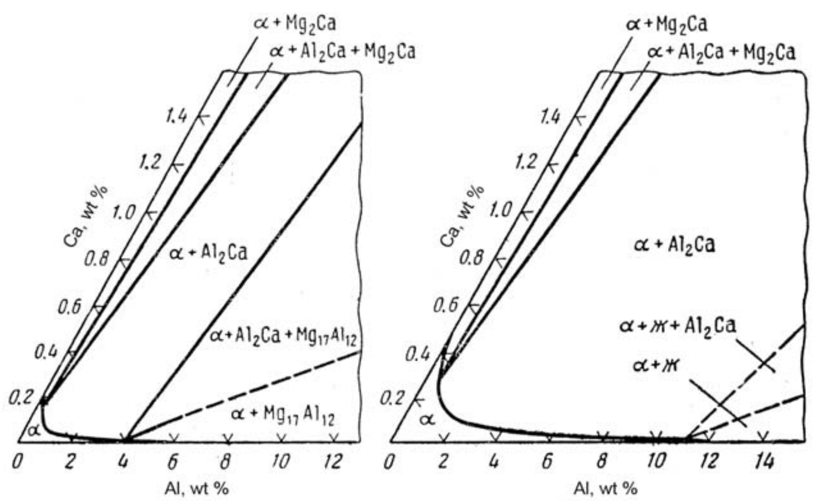

Fig. 11. "Magnesium corner" of the magnesium-aluminium-calcium phase diagram; isothermal section at a temperature of 290 °C (a) and 450 °C (b) [26]

The ternary solid solution area rapidly decreases with temperature. Ca significantly reduces the solubility of Al in solid Mg, particularly in the section α-Al_2Ca. The Al_2Ca compound shows a cubic lattice with a lattice constant a = 8.038 Å and a narrow area of homogeneity [26]. The solid solution area of magnesium borders on the phases $\alpha + Al_2Ca + Mg_2Ca$ and $\alpha + Al_2Ca + Mg_{17}Al_{12}$.

Following [27-29], the chemical affinity between Al and Ca is so high that Al_2Ca and α-Mg eutectic phases form at the grain boundaries with a small addition of Ca. An EDX analysis revealed [25] that the precipitated eutectic compound are not Al_2Ca, but Mg_2Ca and $Mg_{17}Al_{12}$.

5. Summary

State-of-the-art creep-resistant Mg alloys for thixomolding are developed to achieve improved service properties and reduce the manufacturing problems of castings. The analysis carried out shows that these objectives can be reached successfully by suitable micro-alloying with Si, Zn, Sr, Li, C, Ba and Bi, as well as rare earths (cerium).

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