Magnesium Die Casting Alloy Design

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Abstract

The properties of an alloy are closely linked to composition and processing parameters. Magnesium applications demand different critical properties, such as creep resistance for automotive drive train components, ductility and energy absorption in safety parts, and high yield strength in structural parts. Consequently, alloy design must be targeted to achieve specific microstructural features for the various application areas. In the alloy development process, thermodynamics is an important tool in identifying promising candidate compositions. However, the phase morphology and material grain size cannot be predicted from thermodynamics. The experimental work of casting test samples and evaluating them in the laboratory is thus an inevitable part of building new knowledge about the relationships between composition, microstructure and properties. This paper presents some fundamental considerations for designing magnesium alloy compositions, as well as results from investigations of selected die cast alloy samples.

Background

Due to its light weight and favourable properties, magnesium alloys are of escalating interest. The growth in magnesium alloy consumption is driven by an increasing use in automotive applications (1). The automotive industry accounts for 90% of the casting demand. In applications where ductility is important, such as safety parts, magnesium has become important. In other applications with significant weight saving potential, for instance drive train components, magnesium has so far had limited use, partly due to limited availability of die cast alloys with the appropriate property profile. This is the main area of research within alloy development today. In this paper the principles for development of creep resistant magnesium based alloys are discussed, extending also to design of ductile and high strength alloys.

Properties of Mg die cast alloys

For commercial applications of a die casting alloy a number of properties has to be in place, like:

- Competitive cost of ingot material
- Compositional stability during melting and holding
- Ease of melt handling
- Die castability
- Recyclability

Depending on the type of parts produced, various properties will be critical:
- Tensile properties at ambient temperature
- Impact strength
- Corrosion resistance
- Tensile- and creep strength at elevated temperature

All the available die casting alloys were developed with the objective of satisfying the requirements for specific applications. This paper presents some fundamental relations between composition and properties of the Mg-based die casting alloys and indicates some possible paths in the development of new alloys.

The Mg-Al-Mn system constitutes the basis for all present die casting alloys. The high-purity alloys are based on the limited solubility of iron in this system. By varying the amount of Al, and by adding additional alloying elements (like Zn, Si, Ca, Sr and RE-elements), alloys with different property characteristics are obtained.

For the moment we can divide the application areas of die cast Mg alloys in three main areas, with their specific property requirements:

- Safety parts - high ductility, energy absorption,
- Structural parts - high strength,
- Elevated temperature parts - good creep strength.

Within each group, application specific requirements (or personal preferences) give room for a variety of alloy compositions. One example is safety parts, where AM20, AM50A and AM60B are all in production.

For all the alloys the properties depend strongly on the processing parameters. Grain size, porosity distribution, segregation, oxides, casting defects, etc. all have significant impact on the properties of die cast specimens. Unless otherwise specified, the properties of different alloys referred to in this paper are from separately die cast test bars.

The microstructure of die cast Mg-Al based alloys consists of a grain interior of α- Mg(Al) solid solution, and a grain boundary zone (grain "mantle") which is eutectic Mg-Al (Al-enriched α Mg with β - $Mg_{17}Al_{12}$ embedded). All the Mg-Al based alloys also contain Mn; in the cast material this is found in the form of Al_xMn_y particles, where the stoichiometry depends on the relative amount of Al and Mn present. The additional alloying elements form a solid solution together with Al in the matrix, as well as intermetallic phases in the grain boundary zone.

Ductile alloys

Three different alloys are specified: AM20, AM50A and AM60B. However, the properties vary continuously with the compositions within the AM alloy system. Figure 1 shows the yield strength, ultimate tensile strength and the ductility of AM-alloys as a function of the Al –content. These properties are based on casting of test bars under controlled laboratory conditions. For more complex parts, the properties are also closely related to the quality of the castings, which depend on the castability. Increasing Al content improves the die filling capacity of an alloy and can yield a lower defect level in complex castings or especially large, thin-walled castings. The ductility obtained in real parts can thus be improved by increasing the Al content. Figure 2 can illustrate this. The intrinsic ductility of the AM-alloys follows the trend shown in Figure 1c. For low Al contents the ductility obtained in real parts is limited by the castability, while above a certain level the intrinsic ductility is the limit. A part that is more difficult to cast will have a higher optimum Al content than a part that is easier to cast.

Additions of elements that improve fluidity will improve the castability, but often lead to formation of more brittle intermetallic compounds at the grain boundaries, and thus reduced intrinsic ductility. A typical example is the addition of Zn, which preferentially segregates to the $Mg_{17}Al_{12}$ β-phase and increases the volume fraction of this phase. In order to significantly improve the ductility of Mg-Al based die castings with high Al contents, the brittle effect of the $Mg_{17}Al_{12}$ β-phase needs to be reduced.
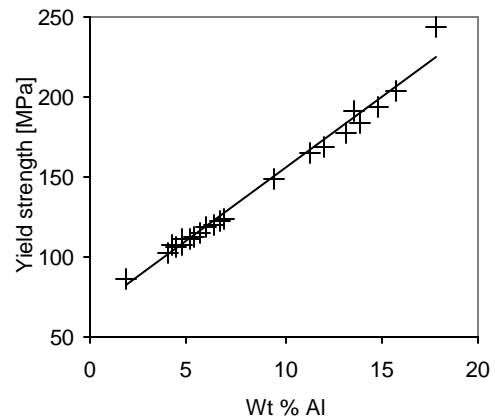

Figure 1a. Yield strength vs. Al content in AM alloys.
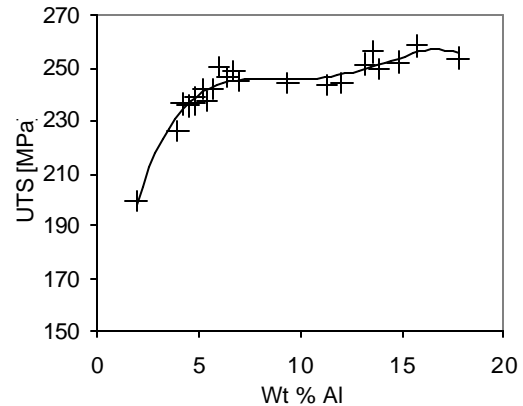

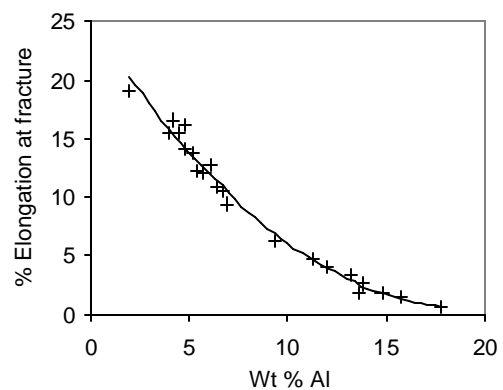Figure 1b. Ultimate tensile strength vs. Al content in AM alloys.

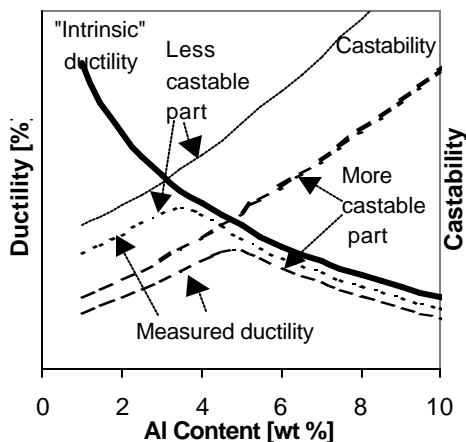Figure 1c. Fracture elongation vs. Al content in AM alloys.

Figure 2. Ductility relative to castability for real parts. A part that is difficult to cast has its optimum ductility at higher Al content than a part that is easier to cast.

Creep resistant alloys

The dominating creep mechanisms vary with stress and temperature (2). For Mg die casting alloys under practical application conditions, creep deformation is relevant in the temperature range 100 – 200 °C, and with mechanical stresses in the range up to the yield strength of the alloys. However, creep deformation at ambient temperature has also been reported (3-4). Adapting creep data for Mg die cast alloys to power law creep calculations reveals $n>1$ for the test conditions where creep deformation is significant. (5-9) This indicates that dislocation processes are the dominating deformation processes (10).

There is a significant compression-tension asymmetry in the creep response of Mg die cast alloys, with higher deformation rates in tension than in compression. (6, 7,11). This is explained in two ways. First, the precipitation reaction of supersaturated α Mg(Al) to $\alpha + \beta$ results in a lattice dilation and will be enhanced under tension and suppressed under compression. Second, the strain induced by the precipitation reaction will increase the creep strain measured in tension and decrease it in compression. In addition there may be a cavity growth in tension, which will be suppressed in compression. The majority of the creep data reported in the literature is from tensile creep tests.

Creep tests of homogenised permanent mold cast Mg-Al binary alloys with 0 – 9 % Al at 150 °C show a reduction in creep rates with increasing Al content (12). This indicates that the grain interior of die cast Mg-Al alloys has a lower creep resistance than the grain mantle. However, in the grain mantle there will be discontinuous precipitation, which is reported to be contributing in the creep deformation process (13). Die cast Mg-Al binary alloys also show a reduction in creep rates with increasing Al-content. AM, AS and AE-alloys all have their minimum in creep rate vs. Al content around 2 % Al. This indicates that intermetallic particles have a significant effect on creep in these

alloys. The effect of these intermetallic particles is reduced when the Al content increases into the range 2 – 6 %, since the intermetallic particles are then increasingly embedded in eutectic Mg-Al. This is illustrated in Figure 3 for Mg-Al, AM and AS alloys, where the creep rates after 100 hours at 150 °C under 50 MPa tensile stress is shown vs. Al content.

The solid solubility of Al in Mg at 150 °C is 1.8 % (14). This is the level of Al found in the grain centres of die cast AM50. For alloys with Al contents above this, the whole microstructure will be supersaturated at typical creep conditions, while alloys with lower Al contents will have grain interiors with Al below the solubility limit. In regions of the microstructure where the Al content is above the solubility limit, precipitation processes will be active under creep conditions. The continuous precipitation will inhibit dislocation motions, while the discontinuous precipitation will form α - β interfaces which are sites for dislocation annihilation and generation. A T4 treatment leads to increased creep rates, while a further T6 treatment reduces the creep rates for alloys high enough in Al to respond to a T6 treatment.
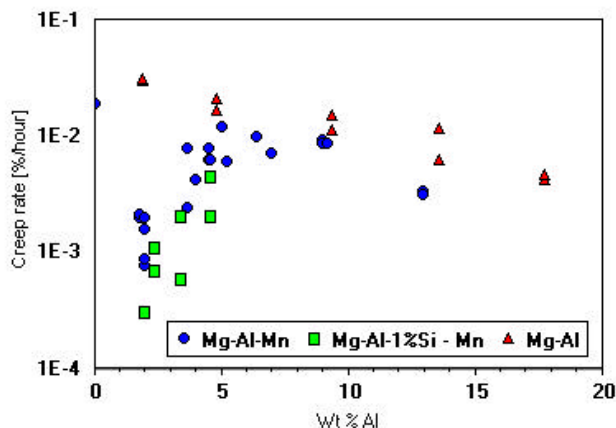
Figure 3. Creep rates vs. Al-content for Mg-Al, AM and AS alloys after 100 hours at 150 °C, 50 MPa.

The creep resistant alloys within the Mg-Al base system thus obtain their creep resistance by a relatively low content of Al, and addition of elements that form stable intermetallic phases within the grain mantle. AS41 and AS21 contains around 1 % Si, which forms Mg_2Si particles. AE42 contains 2-3 % Cerium-rich Mischmetal (RE), which forms $Al_{11}RE_3$. In both cases the intermetallic phases are distributed in the grain boundary zone, and their effect on creep is primarily to inhibit grain boundary sliding. In the case of Mg-Al-RE, the formation of $Al_{11}RE_3$ also reduces the effective amount of Al, which otherwise would lead to Al-enrichment in the grain boundary zone. The grain interior is not significantly influenced by the addition of either Si or RE.

Alternative alloys are developed with Ca and/or Sr as alloying elements in order to obtain creep resistance. The metallurgical

principles are the same as for AE42, i.e., the addition of elements forming stable intermetallic compounds in combination with Al. All the elements marked with black in Figure 4 have a similar effect; the differences are the morphologies of the compounds formed.

Another option is to use alloying elements from groups IVA or VA in the periodic table, which form phases with Mg. Among these, only silicon has been exploited in commercial alloys AS21 and AS41B. Addition of Si is limited by the liquid solubility to 1.7 % at normal melt handling temperatures. However, additions above 1.2 % (Mg-Si eutectic level) lead to the formation of coarse, blocky intermetallic particles that have no significant impact on the mechanical properties of the alloy. The other elements can be added in higher amounts, the maximum levels are more limited by alloy density and cost considerations. The effect of some of these elements is also limited due to formation of coarse intermetallic particles.

All these alloys can be principally divided into two groups, based on the phase formation in the Mg-Al system. In Figure 4 the alloying elements forming significant amounts of intermetallic phases in the Mg-Al system are shown.

The elements of group IIA and IIIB are forming phases with Al, while the elements of groups IVA and VA are forming phases with Mg. The mutual liquid solubility of the elements within each group can be significant, while it may be limited between the elements from different groups. Thus, it is possible to mix, e.g., Ca, Sr, La, Ce in significant quantities, while the addition of RE-elements to AS-alloys is limited to 0.1 – 0.2 %, depending on the temperature.

The morphology and distribution of the phases vary significantly between the various alloying elements, and the effect on the mechanical properties varies to some extent accordingly.

Figure 4. Elements forming stable intermetallic phases in the Mg-Al base system.

High strength alloys

Since die cast Mg alloys are used in the as-cast condition, the relevant strengthening mechanisms are solid solution strengthening, grain size/grain boundary effects and to some extent dispersion hardening. The basic requirement for solid solution strengthening is to obtain a significant amount of

elements in solid solution. Investigating the binary Mg-based phase diagrams identifies the candidate elements, see Figure 5.

The elements showed in Fig. 5 are grouped according to their position in the periodic table. It is seen that cadmium (Cd) from group 2b is the only element showing continuous mutual solubility with Mg in the liquid phase. Sc, Ti, Zr and Mn have a larger solubility in solid state than in liquid (peritectic systems). While Sc show liquid solubility of 15 wt% and Mn and Zr have liquid solubilities in the order of 1wt%, the liquid solubility of Ti is too small to be interesting for traditional liquid alloy processing. The other binary alloys are eutectic systems.

Figure 5. Liquid and solid solubilities of some elements in binary magnesium alloys in units of weight %. Note that the left axis is exponential. Max. liquid solubility is the same as the concentration at the eutectic. The eutectic temperatures are indicated on the right axis. (14,18)

Elements having a partition ratio coefficient in the 0.1-1 range include Li (1b), Al, Ga, In (3a), Sn, Pb (4a), Ag (1b), Y and Gd (3b). The heavy rare earths or heavy Lanthanide series from Gd and onwards (Tb, Dy, Ho, Er and Tm) are also interesting, as these elements have solid solubilities in Mg in the range 4.5-6.9 at%, roughly corresponding to 20-30 wt%, at the eutectic temperatures. The partition ratio coefficients for these elements are all fairly close to 1, similar to that of Gd. The high solid solubilities, falling with decreasing temperature, make the Mg-heavy RE alloys amenable to age hardening. A series of alloys containing these elements has been developed (15-17). Common features of these are high strength and excellent creep properties obtainable by heat treatment processes. However, with the restrictions discussed initially, there are very few elements remaining as candidate alloying elements.

With the rapid solidification of the die casting process, a relatively fine grain size normally is obtained. There are, however, alloy dependent differences. E.g., increasing Al content leads to decreasing grain size. The grain boundary phases also has a significant effect on the yield strength, with a positive contribution from a distribution of intermetallic phases with high strength and good matrix bonding. The morphology and phase distribution will be important parameters, which normally just can be found by practical empirical work. Again using Al as example, increasing Al content leads to an increasing content of $Mg_{17}Al_{12}$, which will act as a hardening phase.

Figure 1 shows the tensile strength of AM-alloys vs. Al-content. The yield strength increases linearly with increasing Al-content all through the investigated composition range. This is an effect of both increasing solid solution, decreasing grain size, and increasing content of grain boundary intermetallic phases. Addition of elements like Zn, Si, Ca, Sb and Rare Earth elements seems to improve the yield strength above that obtained with Al alone. Figure 6 shows the relations between the total content of alloying elements and the yield strength for a large number of alloys, including the above mentioned additions to AM-alloys. Binary Mg-Al, Mg-Zn, Mg-Sn, Mg-Bi and Mg-RE are also included in the figure. Elements forming strong intermetallic phases well distributed along the grain boundaries seem to have a very strong effect on the yield strength, indicating that the grain boundary strengthening effect is important for these alloys.

The data presented in Figure 6 shows that in order to obtain die cast alloys with high yield strength, the total amount of alloying elements must be relatively high. In a plot of the ductility vs. amount of alloying elements, Figure 7, it can be seen that high yield strength and ductility will be opposing properties.
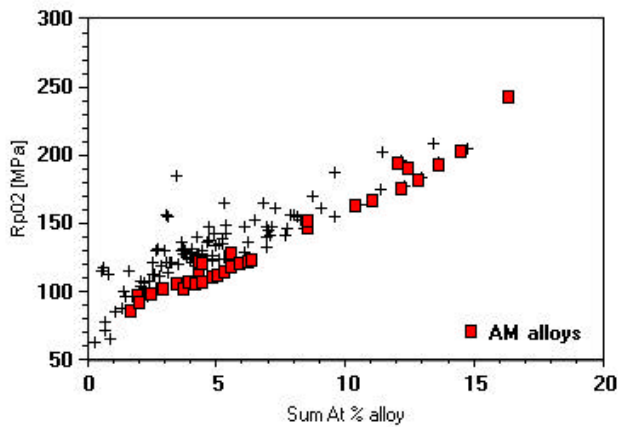
Figure 6. Yield strength vs. at % alloying elements for various experimental Mg alloys.
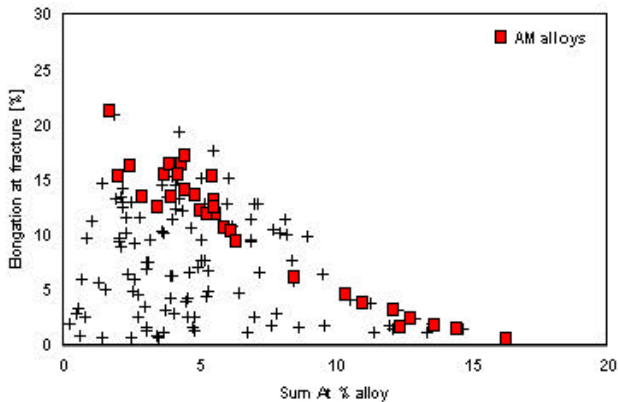
Figure 7. Elongation at fracture vs. at. % alloying elements in various experimental Mg alloys.

The ultimate tensile strength increases from around 200 MPa for AM20, to a constant level of around 250 MPa for all Al contents above 5 %. Within this level, the UTS will primarily depend on the defect content of the casting.

Since the combination of yield strength and ductility is of interest for the application of a material, the combination of these is plotted in Figure 8. In this figure there is an upper limit for the combination of yield strength and ductility. In order to obtain yield strength significantly higher than AZ91, some ductility has to be sacrificed. It can also be seen that AZ91 is not at the upper limit of the property combination; other compositions may have better combinations of yield strength and ductility. For practical application of such new alloys, the total property profile needs to be appropriate: castability, corrosion resistance and production cost.
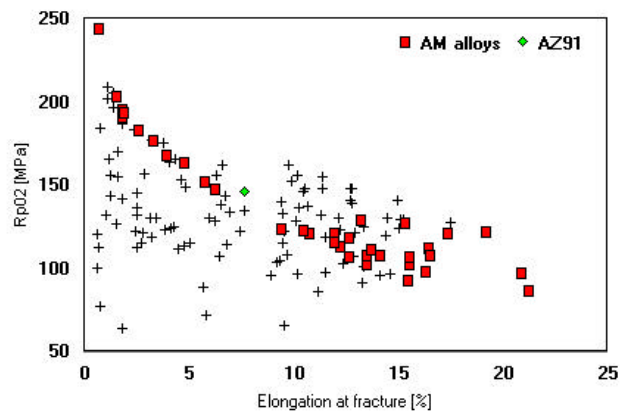

Figure 8. Relation between ductility and yield strength for a number of experimental alloys.

Corrosion

The corrosion mechanism of magnesium is attributed to microgalvanic corrosion cells between magnesium matrix and the more noble intermetallic particles or the $Mg_{17}Al_{12}$-phase. Thus, the galvanic potential of the phases formed in an alloy will have to be considered, and this will limit the number of alloying elements available for practical alloys. As an example, some Mg-Ni compositions are die castable and have good creep resistance, but will completely disappear in standard corrosion tests.

Sticking to the Mg-Al base system, the addition of Mn is limiting the solubility of Fe, and thus modifies the galvanic potential of the Fe-containing particles that are formed. This is the basic principle for the high purity alloys. With decreasing Al content, the solubility of Mn and Fe increases, and the corrosion resistance of the AM alloys decreases with decreasing Al content. The presence of additional elements will influence on the solubility of Mn and Fe, and can have significant effects on the corrosion rates. One example is the addition of 1 % Si. Mg_2Si has a galvanic potential very close to the potential of the Mg matrix and has no effect on the corrosion. However, AM20 contains 0.5 % Mn, while the liquid solubility in AS21HP is 0.2 % at normal

melt handling temperatures. This reduces the amount of AlMn-type particles and can explain the improvement in corrosion resistance from AM20 to AS21HP. An additional improvement is obtained by exchanging some of the Mn with rare earth elements, which is done with AS21X. This has further reduced the amount of AlMnFe type particles, in exchange for particles with lower galvanic potential and a further improvement in the corrosion resistance.

Similar considerations have to be made in the development of new alloy systems; the galvanic potential of the intermetallic phases formed is vital for the corrosion properties.

Conclusions

The Mg-Al-Mn system is the basis for all present die casting alloys: ductile alloys, creep resistant alloys as well as high strength alloys.

In order to obtain alloys with good elevated temperature properties, the element(s) added must:

1) Cause formation of a strengthening phase that is thermodynamically stable,
2) Facilitate a stabilised matrix structure.

The precipitated phase(s) must have a favourable morphology, facilitating locking of grains at the grain boundaries.

As die cast Mg alloys are used in the as-cast condition, the relevant strengthening mechanisms are solid solution strengthening and grain size/grain boundary effects. Stabilisation of the matrix requires a certain solid solubility in Mg.

The intrinsic ductility decreases with increasing Al content. The castability is improved with increasing Al content hence depending on the complexity there is an optimum ductility at a certain Al content. Additional elements may improve the castablilty without reducing the ductility.

The galvanic potential of the intermetallic phases is vital to the corrosion properties. Elements forming phases with significantly higher galvanic potential than the matrix can not be utilised in alloys for practical applications. Exploiting the mutually limited solubility of various alloying elements can pave the way for improved corrosion properties.

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