Magnesium Alloys and Technology

Edited by K.U. Kainer

Translation by Frank Kaiser





Magnesium – Alloys and Technology

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Preface

Magnesium alloys meet the demand for a combination of low specific weight, good machinability and handling, an interesting characteristic profile, and high recycling potential. Despite this, the application of magnesium still lags behind that of competing materials. Reasons for this are the high price, the limited availability of specific, custom-made magnesium materials, and to some extent also a lack of know-how as regards the handling and machining of magnesium. The automotive industry leads the way in the growing interest in magnesium alloys since this branch in particular is under public pressure to save scarce primary energy resources and to realize their environmentally friendly use.

The German Association for Material Science (DGM) has responded to the growing interest in magnesium materials by holding a workshop on this topic. At this workshop, the present state-of-the-art in magnesium materials was extensively described. Furthermore, the lectures detailed the application possibilities and the future potential of magnesium alloys. This book has emerged from the seminars and is based on them. The main focus of the summary lies in the processing technology, although wrought alloys, which are gaining interest, are also considered. Also covered is the use of progressive processing techniques. All articles are written by experts from research and development within the field of magnesium technology. The more application-oriented topics have been covered by experts from the industry. Through their expertise, they have contributed greatly to the success of the workshop.

The following topics are dealt with:

- basics of magnesium technology
- alloying systems
- melting metallurgical processing technologies (die-casting, squeeze-casting, thixocasting)
- · extrusion, forging, sheet-metal forming
- joining (welding)
- · corrosion and corrosion resistance
- progressive technologies (powder metallurgy, spray-forming, magnesium composite materials)
- · machining
- recycling
- · economic aspects
- · application examples and future potential

This book is addressed to engineers, scientists, and technicians from the fields of material development, production, and engineering. It may also be used as a source of information on magnesium for apprentice engineers and industrial engineers.

Prof. K. U. Kainer GKSS Research Center Geesthacht GmbH January 2003

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1 The Current State of Technology and Potential for further Development of Magnesium Applications

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1.1 Introduction

High-technology companies increasingly rely on the technical and economic potential of innovative materials, as well as their workmanship and machining abilities, as a strategy for successful competition on the market. Additionally, politics and the public are demanding a more economical use of scarce primary energy sources.

One of the key goals for the next decades will be the further reduction of emissions to lower the growing environmental impact. Taking this into consideration, the use of light metals as construction materials is generally viewed as becoming of key importance in the future

Although magnesium alloys are fulfilling the demands for low specific weight materials with excellent machining abilities and good recycling potential, they are still not used to the same extent as the competing materials aluminium and plastics. One of the reasons is the fairly high priced base material, coupled with the partial absence of recycling possibilities. On the other hand, the variety of magnesium available to the consumer is still limited to a few technical alloys. Unfortunately, there is a lack of know-how in the use of magnesium, not least within the companies dealing with the machining and application of construction materials. As a result, the industry still tends to use "conventional" materials instead of magnesium alloys.

Discovered in 1774 and named after the ancient city Magnesia, magnesium is found to be the 6th most abundant element, constituting 2% of the total mass of the Earth's crust. It belongs to the second main group in the periodic table of elements (group of alkaline earth metals) and is therefore not found in elemental form in nature, but only in chemical combinations. The silicates olivine, serpentine, and talc do not play any role in refining magnesium, although they represent the most commonly occurring natural magnesium compounds. More important are the mineral forms magnesite MgCO₃ (27% Mg), dolomite MgCO₃·CaCO₃ (13% Mg), and carnallite KCl·MgCl₂·6H₂O (8% Mg), as well as sea water, which contains 0.13% Mg or 1.1 kg Mg per m³ (3rd most abundant among the dissolved minerals in sea water). Magnesium is recovered by electrolysis of molten anhydrous MgCl₂, by thermal reduction of dolomite, or by extraction of magnesium oxide from sea water. The global production of roughly 436,000 t (1997) [1] is covered by melt electrolysis to 75% and by thermal reduction to 25% [2].

Considering the total energy needed to produce magnesium from its various raw materials, it consumes a relative large amount of energy compared to other metals as long as the calculation is based on the mass. Referring it to the volume of the gained primary material magnesium shows a contrary effect: in this case, magnesium uses much less energy than

e.g. aluminium or zinc and even competes with polymers. In addition, it is assumed that the present electrical energy of 40–80 MJ/kg (25 MJ/kg would be possible in theory) needed for electrolysis can be reduced to 40 MJ/kg or less by all the big producers in the near future. This would mean that the corresponding values for producing aluminium (electrolysis of Al₂O₃ to yield aluminium consumes 47 MJ/kg) could be undercut [3]. Optimization or improvement of existing production methods and the establishment of a secondary recirculation could open new perspectives for reducing the cost of primary magnesium production.

1.2 Magnesium's Characteristic Profile

Magnesium crystallizes in the hexagonal closest packed structure and is therefore not amenable to cold forming. Below 225 °C, only {0001} <1120> basal plane slipping is possible, along with pyramidal {1012} <1011> twinning. Pure magnesium and conventionally cast alloys show a tendency for brittleness due to intercrystalline failure and local transcrystalline fracture at twin zones or {0001} basal planes with big grains. Above 225 °C, new {1011} basal planes are formed and magnesium suddenly shows good deformation behaviour, suggesting that extensive deformation only occurs above this temperature [2]. Table 1 shows the most important properties of pure magnesium.

Table 1: Properties of pure magnesium [1, 3, 6].

Crystal Structure	hdp
Density	1,738 g/cm³ at RT
-	1,584 g/cm³ at T _m
Young's Modulus	45 GPa
Ultimate Tensile Strength	80-180 MPa
Fracture Elongation	1-12 %
Melting Point	650 +/- 0,5°C
Boiling Point	1090°C
Specific Heat Capacity	1,05 kJ/(kg K)
Fusion Heat	195 kJ/kg
Heat Conductivity	156 W/(m·K) (RT)
Linear Expansion Coefficient	26·10° K1 (RT)
Shrinkage (solid-liquid)	4,2 %
Shrinkage (TRT)	ca. 5%
Specific Electrical Conductivity	22,4 m/(Ω mm ⁻²) (RT)
Normal Potential	-2,37 V

Most magnesium alloys show very good machinability and processability, and even the most complicated die-cast parts can be easily produced. Cast, moulded, and forged parts made of magnesium alloys are also inert gas weldable and machinable. Another aspect is the good damping behaviour, which makes the use of these alloys even more attractive for increasing the life cycle of machines and equipment or for the reduction of sonic emission. Pure magnesium shows even higher damping properties than cast-iron [2], although these properties are highly dependent on the prior heat treatment.

Along with the excellent properties, there are some disadvantages to the application of these alloys. As already mentioned, the cold working abilities are very poor and the corrosion resistance of magnesium alloys is very low. Besides, magnesium is very reactive. When cast, magnesium has a high mould shrinkage of approximately 4% when solidifying and of about 5% during cooling [1]. This high degree of shrinkage leads to microporosity, low toughness, and high notch sensitivity that cannot be ignored. This behaviour, as well as

the high thermal expansion coefficient (ca. 10% above the corresponding value for aluminium), is often put forward as an argument against the use of magnesium alloys.

The negative properties mentioned above deter construction engineers from accepting magnesium alloys as a competitive replacement for aluminium or steel. Therefore, attempts have been made to improve the characteristic profile of magnesium alloys by employing different alloying elements so as to achieve better precipitation and solid-solution hardening.

In this way, all the advantageous properties listed below have been realized:

- lowest density of all construction metals at 1.8 g/cm³; light construction parts possible
- high specific strength (strength/density ratio)
- excellent casting ability; steel dies may be used
- good machining ability (milling, turning, sawing) [4]
- improved corrosion resistance with high-purity (HP) alloys [5]
- · high damping properties
- · good weldability under inert gases
- integrated recycling possible

The static and dynamic mechanical properties are inferior to the corresponding values for the competing aluminium, e.g. the Young's modulus. Nevertheless, magnesium is found in all places where weight saving takes priority over the other properties, mainly because the specific strength can reach and even exceed the values for aluminium and steel.

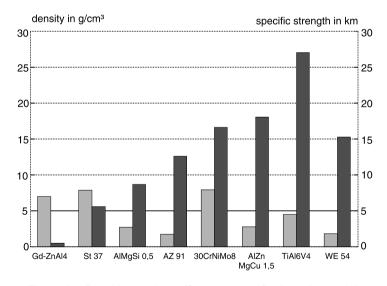


Figure 1: Densities and specific strengths of selected materials

1.3 Alloying Systems

To give a short overview of the different magnesium alloys, it is necessary to first show the identification of all kinds of alloys and the effect of each alloying element.

1.3.1 Identification of Magnesium Alloys

The identification of magnesium alloys is standardized worldwide in the ASTM norm; each alloy is marked with letters indicating the main alloy elements, followed by the rounded figures of each (usually two) weight in percentage terms. Table 2 shows the key letters for every available alloying element. The last letter in each identification number indicates the stage of development of the alloy (A, B, C,...). In most cases, these letters show the degree of purity. The alloy AZ91D, for example, is an alloy with a rated content of 9% aluminium (A) and 1% zinc (Z). Its development stage is 4 (D). The corresponding DIN specification would be MgAl9Zn1. ASTM dictates the following composition (all values weight-%): Al 8.3–9.7; Zn 0.35–1.0; Si max. 0.10; Mn max. 0.15; Cu max. 0.30; Fe max. 0.005; Ni max. 0.002; others max. 0.02. Iron, nickel, and copper have tremendous negative effects on the corrosion resistance and hence these values are strictly limited.

Abbreviation letter Alloying element Abbreviation letter Alloying element N A aluminium nickel P В bismuth lead C copper Q silver D cadmium R chromium S Ē rare earths silicon F Т iron tin Н W thorium yttrium K Y zirconium antimony Z L lithium zinc M manganese

Table 2: ASTM codes for magnesium's alloying elements.

1.3.2 Alloying Elements [3, 6, 11, 12]

Since the advent of magnesium alloys, there has been a lot of effort to influence the properties of pure magnesium with different alloying elements. The main mechanism for improving the mechanical properties is precipitation hardening and/or solid-solution hardening. While solid-solution hardening is determined by the differences in the atomic radii of the elements involved, the effectiveness of precipitation hardening mainly depends on a reduced solubility at low temperatures, the magnesium content of the intermetallic phase, and its stability at application temperature. Magnesium forms intermetallic phases with most alloying elements, the stability of the phase increasing with the electronegativity of the other element.

By the 1920s, aluminium had already become the most important alloying element for significantly increasing the tensile strength, specifically by forming the intermetallic phase Mg₁₇Al₁₂. Similar effects can be achieved with zinc and manganese, while the addition of silver leads to improved high-temperature strength. High percentages of silicon reduce the

castability and lead to brittleness, whereas the inclusion of zirconium forms oxides due to its affinity for oxygen, which are active as structure-forming nuclei. Because of this, the physical properties are enhanced by fine grain hardening. The use of rare earth elements (e.g. Y, Nd, Ce) has become more and more popular since they impart a significant increase in strength through precipitation hardening. Copper, nickel, and iron are very rarely used. All these elements increase susceptibility to corrosion, as established by the precipitation of cathodic compounds when they solidify. In contrast to regular cases, where a magnesium oxide or -hydride layer protects the metal and lowers corrosion rate, these elements increase the corrosion rate. This is one of the reasons why alloy development has been directed towards "high-purity" (HP) alloys with very little use of iron, nickel, or copper.

Below are the most important alloying elements in alphabetical order:

Al	The improvement of the physical properties with aluminium was already established in the 1920s. These alloys containing Al were sold as "Elektron". Aluminium increases the tensile strength and the hardness, although the hardness effect caused by the precipitated phase $Mg_{17}Al_{12}$ is only observed up to 120 °C. These alloys are usually heat treated (T6), except under die-cast conditions, which hardly allow for heat treatment. Besides these improvements of the mechanical properties, there is the big advantage of better castability (eutectic system, $T_{\rm E} = 437$ °C). This is the main reason why most technical alloys – especially casting alloys (mainly AZ91) – contain a high percentage of aluminium. The disadvantage is a higher tendency for microporosity.
Ве	Beryllium is only supplied to the melt in small amounts (<30 ppm); the melt oxidation can be reduced dramatically.
Ca	Calcium has a positive effect on grain refining and aids creep resistance. On the other hand, calcium can lead to sticking to the tool during casting and to hot cracking [9].
Li	Lithium leads to solid-solution hardening at ambient temperatures, reduces density, and increases ductility. However, it has strong negative effects on the burning and vapour behaviour of the melt. Corrosion behaviour gets worse. Above 30% Li-content, the lattice structure changes to fcc.
Mn	Above 1.5 weight-% manganese, the tensile strength is increased. Alloying with manganese results in better corrosion resistance (Fe content is controlled by lowering the solubility), grain refinement, and weldability.
RE	All rare earth elements (including yttrium) form eutectic systems of limited solubility with magnesium. Therefore, precipitation hardening is possible and makes sense. The precipitates are very stable and raise the creep resistance, corrosion resistance, and high-temperature strength. Technical alloying elements are yttrium, neodymium, and cerium. Due to the high costs, these elements are mainly used in high-tech alloys.
Si	Silicon lowers the castability, but the creep resistance can be raised by stable silazide formation.
Ag	Silver, together with the rare earth metals, strongly increases the high-temperature strength and creep resistance, but also leads to low corrosion resistance.
Th	Thorium is the most effective element for increasing high-temperature strength and creep resistance of magnesium alloys. Unfortunately, however, it is radioactive and is therefore substituted by other elements.
Zn	Zinc induces the same behaviour as Al in terms of castability and strengthening. By adding up to 3% zinc, shrinkage can be compensated and tensile strength is raised. As with aluminium, there is a tendency towards microporosity, and on adding more than 2% hot cracking can also occur.
Zr	Addition of zirconium leads to an increase in tensile strength without a loss of ductility, because of its affinity for oxygen. The formed oxides are structure-forming nuclei and aid grain refining. Zirconium cannot be added to melts containing aluminium or silicon.

1.3.3 Casting Alloys

Aluminium is, as already described, the most frequently used alloying element for magnesium, with contents varying between 3 and 9 weight-%. These alloys have good mechanical properties and excellent corrosion resistance. The more aluminium the melt contains (eutectic system, $T_{\rm E} = 437$ °C; Al content ~33%), the better the castability. The most widely used of magnesium die-casting alloys is AZ91 because of its superb castability even for the most complex and thin-walled parts. Table 3 gives a short overview of available alloying systems for pressure die-casting.

Table 3: Overview of all available casting alloys.

The most important die-casting alloy groups:

AZ alloys

- good room temperature properties
- low heat resistance and creep resistance
- limited ductility

AM alloys

- lower Al content and elimination of zinc improves ductility
- limited room temperature properties and castability

AS alloys

- significantly higher heat and creep resistance through Mg-RE precipitations
- only casting is possible
- limited castability

Consumption of the European automobile industry:

2004	AZ: 61%	AM: 32%	AS/AE: 7%
1999	AZ: 67%	AM: 29%	AS/AE: 4%

As mentioned above, the negative effect of a high aluminium content is the formation of the interdentritic grain boundary phase $Mg_{17}Al_{12}$. It lowers the strength within the fine-grained crystal structure and leads to limited ductility of the alloy, as is also found for zinc components.

To improve the deformation behaviour of magnesium alloys, the Al content is decreased, the alloying with zinc is completely abandoned, and manganese is added instead. These alloys of the magnesium–aluminium–manganese family, e.g. AM20, AM50, AM60 (Mn contents between 0.2 and 0.4%) show lower strength at ambient temperature, but they are less brittle than the Al/Zn-based alloys. AMx alloys exhibit better deformation behaviour, but the low aluminium content limits their castability.

One of the most important criteria for magnesium alloys is the high-temperature and creep behaviour. For this reason, in earlier years attempts were made to reduce the aluminium content in the melt and to use different materials for alloying. During production of the VW-Beetle, the addition of silicon had already been established [13]. The resulting alloys, AS21 and AS41, were found to possess a much greater high-temperature strength and creep resistance than AZ91. The mechanism whereby high-temperature and creep behaviour is improved is based on a reduction of the aluminium content and the formation of the intermetallic phase Mg_2Si ($T_m = 1085$ °C), which shows good stability even at high temper-

atures. In this context, the AE alloys have to be taken into consideration, although they cannot be produced by die-casting because very stable Al-RE precipitates are formed on slow cooling. An overview of the tensile strength as a function of temperature for the most frequently used alloying systems is given in Fig. 2:

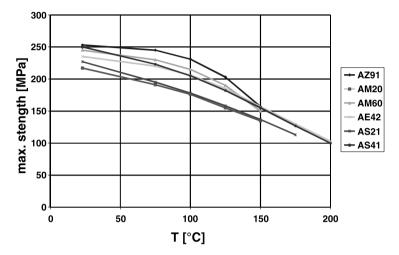


Figure 2: Tensile strengths of the most important Mg die-casting alloys as a function of temperature [2]

Applications at temperatures beyond 200 °C demand properties that can only be served by alloys containing silver and/or rare earths (Table 4). Specifically, this means the QE alloy group, which exhibit remarkable high-temperature properties, and the high-tech alloys WE-x, which allow applications up to 300 °C. The disadvantage of both series of alloys is their low castability; the production method is limited to sand and gravity casting. Additionally, the high costs have to be considered as a reason for many not to use them (e.g. 13 €/kg for QE22, 25 €/kg for WE54; compared to 2–3 €/kg for an AZ or AM alloy). For this reason, these alloys are mainly used in special applications such as in the aircraft and spacecraft industries. The falling prices for rare earths in the international markets may lead to a change in this trend in the future.

Table 4: Overview of the rare earth containing casting alloys (mostly sand/gravity casting).

```
Rare earth containing casting alloys
History:
1937: good heat resistance Mg/Ce
1947: influence of zirconium (EK, EZ, ZE series)
1949: influence of La < Ce < Nd
1959: influence of Ag (QE, EQ series)
1979: system Mg-Y (WE series)
Important alloys applied today:
            ZE41
            EZ33
            EQ21
            OE22
            WE43
            WE54
The WE series represents the current stage of the material development:

    good castability

    highly heat resistant

            - highly creep resistant

    ageing resistant

    good fatigue strength

    corrosion resistant
```

1.3.4 Wrought Alloys

The poor cold workability of the hexagonal lattice structure and the formation of twins have resulted in a very limited usage of magnesium as a wrought material. Therefore, the range of available wrought alloys is still limited. Tables 5 and 6 give an overview of the compositions and properties of selected alloys. The Mg/Al series of alloys (AZ31, AZ61, AZ80) plays the most important role, being used on a scale comparable to that of the casting alloys.

Table 5: Summary of available magnesium wrought alloys [3]

alloy	Al	Ca	Zn	Mn	Cu	Zr	Υ	Nd	Th
AZ21X1	1,6-2,5	0,1-0,25	0,8-1,6	0,15	0,05				
				max.					
AZ31	3,0		1,0	0,3					
AZ31B	2,5-3,5	0,04	0,7-1,3	0,20-1,0	0,05				
		max.							
AZ61A	5,8-7,2		0,40-1,5	0,15-0,5	0,05				
AZ80	8,5		0,5	0,12					
AZCOML	2,0-3,6	0,04	0,3-1,5	0,15 min	0,10				
		max.							
AZM	6,0		1,0	0,3					
ZC71			6,5	0,7	1,2				
ZK40			3,5-4,5			0,45 min			
ZK60A			4,8-6,2			0,45 min			
ZM21			2,0	1,0					
ZW3			3,0			0,6			
HM21				0,8					2,0
HM31						0,7			2,0
WE43						0,5	4,0	4,0	
WE54						0,5	5,25	3,5	

Alloy/condition	Tensile Strength [MPa]	0,2%-Yield Strength [MPa]	Fracture Elongation [%]	0,2%- Compression Strength [MPa]
Solid Profile				
AZ31B-F	262	193	14	103
AZ61A-F	317	228	17	131
AZ80-T5	379	276	7	241
HM31A-T5	303	269	10	172
ZK60A-T5	365	303	11	248
Tubes/Hollow Profiles				
AZ31B-F	248	165	16	83
AZ61A-F	283	165	14	110
ZK60A-T5	345	276	11	200
Sheets/Bands			•	
AZ31B-H24	290	221	15	179
AZ31B-0	255	152	21	110
HK31A-H24	262	207	9	159
HK31A-0	228	200	23	97
HM21A-T8	248	193	11	145

Table 6: Mechanical properties of various magnesium wrought alloys [3]

Alloys such as ZC71, ZW3, and ZM21 [12] are available, but are not used to any great extent. Wrought alloys are hot-worked by rolling, extrusion, and forging at temperatures above 350 °C. Additional cold-working procedures can be applied afterwards with low deformation rates to prevent the formation of cracks [3]. Since magnesium is envisaged for use in parts with high safety concerns, there has been a noticeable increase in interest in wrought alloys. The behaviour during crashing is an important criterion in such considerations.

1.4 Applications

In the past, the driving force behind the development of magnesium alloys was the potential for lightweight construction in military applications. Nowadays, the emphasis has shifted towards saving weight in automobile applications in order to meet the demands for more economic use of fuel and lower emissions in a time of growing environmental impact.

It is interesting to note that the use of magnesium in cars is by no means a recent innovation. As early as the 1930s, it was common to include magnesium cast parts in automobiles, with the VW-Beetle as the most famous example. Since the start of its production in 1939, more and more parts, such as the crank case, camshaft sprocket, gearbox housing, several covers, and the arm of an electric generator, were added until the total magnesium weight reached 17 kg in 1962, which meant a reduction of 50 kg in total mass compared to steel. The production of the VW-Beetle used almost 21,000 t of magnesium alloys in 1960 [19] and the Volkswagen Group reached a total consumption of 42,000 t of magnesium alloys in 1972 [13], until the change from air-cooled to water-cooled engines dramatically reduced the use of magnesium alloys.

Other manufacturers used magnesium in their technical applications, as well as in complex parts such as tractor hoods made of die-castings (dimensions: 1250 mm × 725 mm × 480 mm; weight 7.6 kg), main gear boxes for helicopters (casting weight 400 kg, machined 200 kg), crank cases for zeppelin engines, air intake cases for propjet engines (weight 42 kg), frames, rims, instrument panels, fan blades for cooling towers (weight 169 kg), etc.

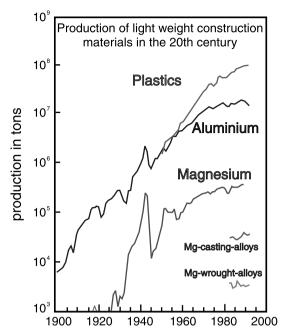


Figure 3: Production of materials with low density in the 20th century [3]

Why the trend of utilizing magnesium alloys did not continue in a straightforward manner is hard to explain today. A main factor was certainly the limited capacity of the few magnesium producers, as a result of which a low and constant price on the world market was not attained.

The development of high purity (HP) alloys, with their much improved corrosion resistance, contributed to a rapidly expanding production. In the past, the corrosion behaviour of available alloys had often been the overriding factor preventing their application. A further factor favouring magnesium use is that it counts as a substitute for polymers for which no satisfactory recycling solution has yet been found.

With regard to the processing of magnesium alloys, pressure die-casting is preferred in view of its advantages in the processing of aluminium and zinc, which are both amenable to this type of casting. Besides the specific properties of magnesium mentioned above, further favourable factors are its low casting temperature (650–680 °C, depending on the alloy) and the relatively low energy needed for melting. The energy needed for AZ91 (2 kJ/cm³) is about 77% of that required to melt the aluminium alloy AlSi12CuFe [3]. The high price of magnesium usually refers to its mass not its volume, and the lower density coupled with other factors can actually make it cheaper in real terms. Thus, the low thermal content allows the casting process to be 50% faster than with aluminium; a high clock cycle of parts is possible, maintaining high precision and good surface quality.

On freezing, the crystal structure is very fine grained, which results in good mechanical properties at room temperature but also leads to poor creep resistance. Moreover, the microstructure can be porous due to turbulences at high mould-filling speeds; subsequent heat treatments are useless since the pores would break apart. Magnesium does not attack iron moulds as much as aluminium does; the moulds can have steeper walls and the

potential savings in terms of tools can be as much as 50% compared with the use of aluminium [21]. Machine endurance is much higher as well (less retooling). The typical microstructure of an AZ91 alloy is shown in Fig. 4.

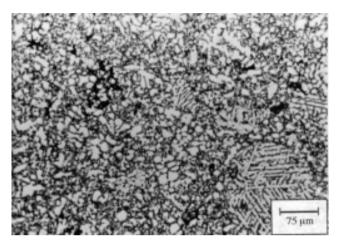


Figure 4: Microstructure of a die-cast AZ91 alloy

The automotive industry is by far the major user of magnesium alloys on a large scale, due to the possibility of mass-producing series parts by pressure die-casting with high quality at reasonable costs. Examples of magnesium parts in vehicles include:

- gearbox housing, e.g. in the VW Passat, Audi A4
- the inner tailgate in the Lupo ("3-liter car"), which is made of AM50 (3.2 kg)
- tank cover in the Mercedes-Benz SLK
- cylinder head caps, e.g. made of AZ91HP by cold-chamber casting, and having a weight of 1.4 kg [17]
- dashboard, e.g. in the Audi A8 and in the Buick Park Avenue/Le Sabre [22]
- seat-frames [23]
- steering wheels, e.g. in the Toyota Lexus, Celica, Carina, and Corolla [22]
- rims, e.g. in the Porsche Carrera RS (9.8 kg AM70 HP; low-pressure ingot casting) [17]

The list of magnesium parts in cars can be continued, e.g. in refs. [1,21,24], since new examples are constantly being added. Two recent applications of magnesium are illustrated in Figs. 5 and 6. The Mercedes-Benz SLK fuel tank cover is used as an example to show the consequences resulting from converting the construction from conventional materials to magnesium alloys. The part supports the car body's web and serves as a separation between the trunk and the back seats. Previous solutions consisted of a welded conduit frame. The first alternatives were steel and aluminium weldings (7–8 kg each) and a magnesium cast part. The magnesium casting could be established as a serial part with a total weight of 3.2 kg, a decreased spatial requirement, and fewer components. Moreover, no post-processing was necessary and the part could be used uncovered. The use of magnesium in the gearbox housing in the VW Passat is also primarily based on the weight savings achieved on replacing aluminium alloys. The use of the AZ91 alloy instead of aluminium led to a

total weight reduction of almost 25%, and the geometry and production equipment remained identical. Since the introduction of repetitive work in 1996, 600 parts are manufactured at VW in Kassel per day [10]; an output of 1200 parts/day is projected for the future.

Magnesium's low density, its shielding against electromagnetic radiation, and the possibility of producing thin-walled parts has led to further use of die-cast parts in the computer industry [25], in mobile phones (Figs. 7 and 8), and in hand tools (e.g. chainsaws).

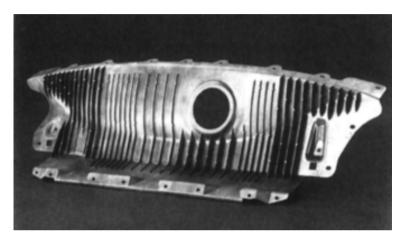


Figure 5: Fuel-tank cover (Mercedes-Benz AG)

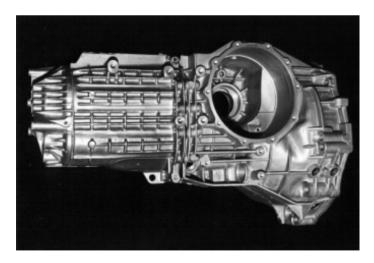


Figure 6: Gearbox housing in the VW-Passat (Volkswagen AG)

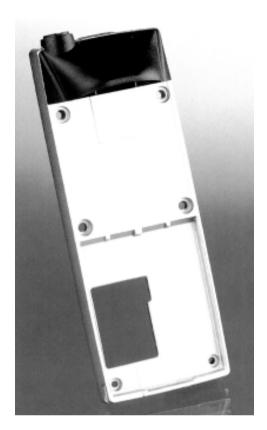


Figure 7: Mobile-phone case (Unitech Company)

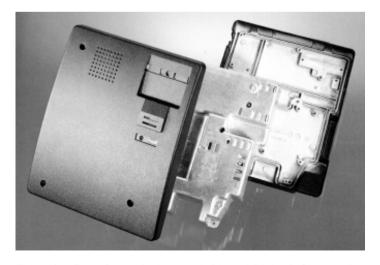


Figure 8: Parts for a telephone switchboard (Unitech Company)

1.5 Main Focuses in Research and Development

The main focuses within research and development are currently:

- · alloy development
- · rapid solidification
- production technology
- composites
- · corrosion and its prevention
- · recycling

1.5.1 Alloy Development

Having its golden years between 1930 and 1950, alloy development has again become one of the main focuses of contemporary research. One reason is magnesium's growing market segment, realized by the introduction of the corrosion resistant HP-alloys in the mid-1980s and followed by a demand for further alloys with specific characteristic profiles. Better creep and corrosion resistance, as well as even lower density, are the main targets for these alloys. The development of alloys with improved ductility and toughness and specific wrought alloys could support a growing magnesium market. The effect of different alloying elements and also micro-alloying, which has a tremendous effect on other materials, needs to be researched systematically.

1.5.2 Rapid Solidification

The technology of rapid solidifying plays an important role when it comes to materials with extraordinary profiles. A whole new series of structural effects can be observed when a metallic melting bath is cooled beyond its thermodynamic equilibrium extremely rapidly, as, for example, on sputtering.

This usually leads to an oversaturation of alloying elements, metastable phases within the microstructure, homogeneous distribution of elements and phases, an extremely fine-grained microstructure as well as minimized eliquations, and a high purity of the materials. Figure 9 shows two WE54 alloy microstructures that illustrate the difference between gravity casting and gas sputtering. Rapid solidification offers a link between production technology and alloy development since the development of new alloys, which cannot be accomplished by classical metallurgical procedures, is now possible. At the same time, the corrosion resistance is improved through a more homogeneous element distribution and a low eliquation microstructure.

Spray-forming is an attractive new technology for producing parts and near-complete products in almost final outline. Tubes, discs, rods, or sheets can technically be produced directly in one working step. The process is divided into the sputtering of a metal bath and the deposition of partly frozen drops on a substrate material. This technology is used successfully on an industrial scale for aluminium and copper alloys, and has recently been applied to steels as well. It is an advanced technology in wich it offers a greater variety of alloying elements with different concentrations. At the same time, spray-forming allows any given solid particle portable within the gas flow to be introduced into the sputter-zone.

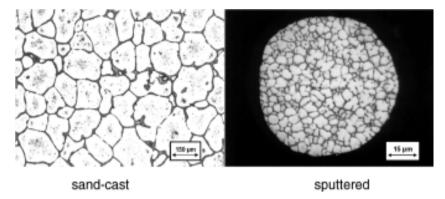


Figure 9: Comparison of the microstructures of sand-cast and sputtered WE54 [26]

In this way, composite materials with a homogeneous particle distribution (e.g. SiC, Al₂O₃) can be produced. Another possible application could be an in situ observation of the reaction between sputtered magnesium melts and nozzle gas components or injected materials for producing dispersion strengthened magnesium alloys. The development of magnesium wrought alloys also has tremendous potential in combination with rapid solidifying.

1.5.3 Production Technology

Another main emphasis of the research and development work towards magnesium alloys is their production technology. The main production methods, such as casting, joining, disconnection, and moulding, have been adapted without any material-specific optimization towards their use with magnesium. Material development (e.g. new alloys and composites) and the development of innovative procedures for producing and machining magnesium (primarily for automotive applications) represent a major part of magnesium's overall potential. For aluminium, these new procedures (e.g. squeeze-casting, rheo-casting, thixo-casting, thixo-forming, etc.) have already been successfully brought onto the market. Besides conventionally produced parts, pressure-cast or spray-formed aluminium materials are used in repetitive series production. Magnesium still lags behind this growth, but with further optimization of the process and the ongoing development of the materials, there will be a growth of magnesium die-cast parts unprecedented for any other metal.

Other innovative methods have been partly tested in research and development and it is assumed that they too will soon become established since the acceptance of magnesium alloys within the consuming industry is increasing. The possibilities of extending the applications of light metals will surely grow with the help of these new methods and materials.

1.5.4 Composite Materials

Metal composites based on magnesium offer well-defined material properties, such as high tensile strength, hot working abilities, or creep resistance; the Young's modulus or abrasion resistance may be directly matched to the required application profile. The reinforcement

of magnesium alloys with ceramic fibres (short or long fibres; usually made of aluminium oxide, silicon carbide, or carbon) or ceramic particles (mostly SiC [27], Fig. 10) must be mentioned first. These materials may be produced by squeeze-casting (preform infiltration from the reinforcement phase), by stirring during the reinforcement phase, or by sprayforming, each technique having its own advantages.

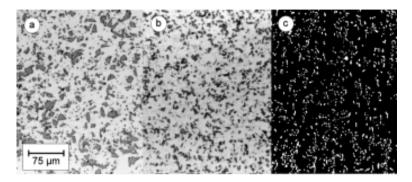


Figure 10: Micrographs of an SiC particle reinforced alloy QE22, produced by p/m methods [27]:

- a) AZ91 + 15 vol.% SiC (31 mm), cross-section polish (optical microscope)
- b) AZ91 + 15 vol.% SiC (8 mm), longitudinal polish (optical microscope)
- c) AZ91 + 15 vol.% SiC (8 mm), longitudinal polish (SEM)

1.5.5 Corrosion and its Prevention

The susceptibility of the surfaces of conventional alloys to corrosion has already been significantly lowered with the introduction of the HP alloys. The reduction of the critical contents of Ni, Fe, and Cu influenced the application of the alloys in a positive way (Fig. 11), but they still lack a passivating ability and a 'self-healing' passivating layer. In both the alloying and manufacturing steps, efforts need to be directed towards reducing the susceptibility to corrosion of Mg alloys. The process of rapid solidifying might offer advantageous features in this context.

With respect to appropriate organic or inorganic coatings, protection measures have been selected corresponding to those used for aluminium. The minimization of corrosion by surface conditioning or coating has given satisfactory results in some applications, but a systematic evaluation of the physical and chemical basis is still required for a full optimization.

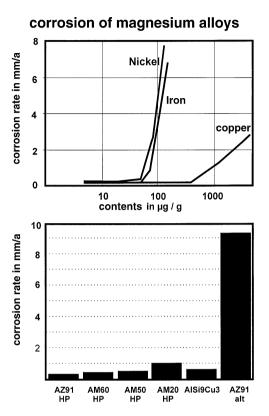


Figure 11: Influence of impurities on the corrosion behaviour of the alloy AZ91 (top) [3]; corrosion behaviour of various magnesium alloys compared to that of the aluminium alloy AlSi9Cu3 (bottom) [17]

1.5.6 Recycling

The recycling of conventional magnesium alloys is straightforward; scrap and melt residues can be directly reinserted into the process of the respective foundry, although contaminated or painted parts present bigger problems. A lot of magnesium leftovers have hitherto been used for steel desulfurization, but since magnesium has become a mass product, its secondary cycling is arousing interest on the part of producers and processors of magnesium. This is the reason why recycling activity has increased considerably in the last years. The recovery of the expensive rare earth metals is another important aspect, and this needs to be analyzed extensively.

It is assumed that all the aforementioned research and development work will yield further positive effects for the use of magnesium in the coming years. Therefore, an accelerated growth in its use can be expected.

1.6 Summary and Conclusion

Despite the evident advantages of magnesium parts, magnesium has yet to fulfil its full market potential. The advantages and limitations of its application, as described herein, are summarized in Fig. 12.

The driving force for an increasing use of magnesium alloys is still the automotive industry on the consumer side, urged by the public to meet the demands for a reasonable and limited exploitation of resources and primary energy, so as to reduce emissions and to stop further environmental impact. In the past, structural drive unit concepts and low aerodynamic drag were at the forefront of considerations for saving energy, while light construction remained a secondary concern. Figure 13 displays the average fuel consumption (values for passenger cars in Germany; Otto engines only) proving this fact. For a complete picture, however, the trend of vehicle weights shown in Fig. 14 needs to be taken into consideration. It becomes clear that, despite increasing vehicle weights, the average fuel consumption has been lowered significantly. The demand for a "3-litre-car" is growing and an increasing proportion of alternative materials are used to achieve this goal. This effect is clearly evident, for the industry is more interested in using magnesium – especially in the field of die-casting – and the magnesium market is growing. In this regard, the North American market is far ahead of the European one: the market for magnesium die-casting experienced an annual growth of more than 17% between 1984 and 1994 and a growth rate of 33% in 1994. At present, an annual growth of 12–20% is envisaged [31, 32].

The potential use of magnesium parts has been studied in more depth in [33]. The analysis showed that the following amounts of magnesium alloys could now be used, whereby the weight savings indicated would be realized (Fig. 15):

Table 7: Summary of the most important pros and cons of the construction material magnesium.

Characteristic Profile of Magnesium Alloys lowest density of all metallic construction few optimized alloys materials hardly any wrought alloys high specific strength low ductility and toughness at room temp. good castability and suitability for pressure die- limited high-temperature properties (heat – casting resistance, creep resistance) easy machining with high cutting speeds high chemical reactivity good weldability under inert gases high shrinkage highly improved corrosion resistance no comprehensive recycling concepts high availability lack of knowledge in terms of combustibility, compared to plastics: corrosion behaviour, and handling better mechanical properties limited number of producers, no low and stable price ageing resistant better electrical and thermal conductivity recyclability

Characteristic Profile of Magnesium Alloys

- lowest density of all engineering metals
- high specific strength
- good castability including die casting
- good machinability at high cutting speeds
- good weldability with inert gas
- highly improved corrosion resistance
- high availability
- compared to plastics:
 - better mechanical properties
 - aging resistant
 - better electrical and thermal conductivity
 - recyclable

- few optimized alloys
- wrought alloys
- low deformability at room temperature and low toughness
- limited high temperature properties (heat and creep resistance)
- high chemical reactivity
- high shrinkage
- no extensive recycling concepts available
- mind barriers with respect to handling, corrosion behaviour and burning
- limited number of producers, no stable and low price

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Magnesium Alloys

Figure 12: Progress of the average fuel consumption in Germany (passenger car figures; Otto engines) [29]

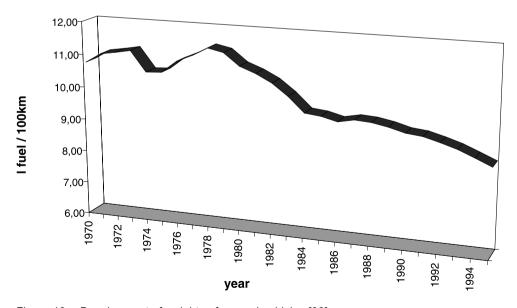


Figure 13: Development of weights of several vehicles [30]

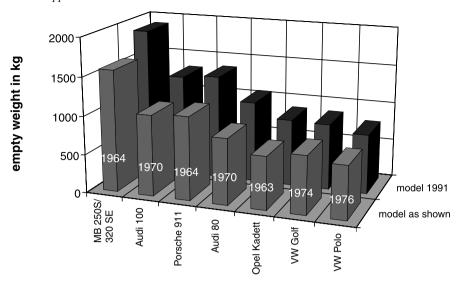


Figure 14: Possible application of Mg alloys in different vehicle classes and the projected weight savings [33]

In time, it will be possible to overcome the prevailing lack of knowledge and reservations concerning the application of magnesium alloys and to raise their acceptance in important fields of use. Research work must address the following goals:

- low and constant costs for the primary material.
- extended variety of alloys, with emphasis on better creep resistance, wrought alloys, and decreasing the specific weight,
- the use of new and innovative production methods,
- extension of the production variety (e.g. squeeze-casting, thixo-forming),
- further increase of the corrosion resistance by self-healing layers or improved coatings,
- exploitation of the rapid solidification process,
- · development of application-optimized composites,
- comprehensive recycling concepts with the establishment of secondary cycling.

Once these goals are met, magnesium and its market will grow like no other material has grown before.

1.7 Literature

- /1/ Byron B.: "Global Overview of Automotive Magnesium Requirements and Supply & Demand", Automotive Seminar der International Magnesium Association (IMA); Aalen, 09.10.1997.
- /2/ Norsk Hydro Datenbank "NHMg.db (ext.)", Norsk Hydro Research Centre Porsgrunn, 1996.