

Mechanical properties and potential applications of magnesium alloys^①

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Abstract: Magnesium alloys, having high specific strength, with a density only 2/3 of that of aluminum and 1/4 of carbon steels, have become ideal materials for low mass applications such as automobiles and electronic devices. It was dealt with the state of the art in developing cost effective, low mass, high ductility and high creep resistance magnesium alloys that are suitable for structures and power train applications.

Key words: magnesium alloys; automobile; creep; application; mechanical properties

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1 INTRODUCTION

During the first half of the twentieth century, magnesium alloys were used extensively in civilian and military aircraft components. The neglect of magnesium alloys after world war II was represented by the slump of the production from 228.8 kt/a in 1944 to 10 kt/a after World War II. The most significant application of magnesium alloys in the second half of the twentieth century was in production of air-cooled engines and gearboxes for Volkswagen Beetle, which led the automobile industry to make a voluntary commitment to achieve 30% CO₂ emissions reduction by the year 2010^[1].

Magnesium alloys with a density only 1/4 of that of steel, only 2/3 of aluminum and specific strength far exceeding the two alloys, fulfil the role admirably as an ultralight alloy. Its use is not limited to automobiles but also extends to many other applications such as micro-electronics industry including computer components, VCD/DVD cassettes, telecommunication devices, sport goods and many more uses.

Although a wide variety of applications is assigned for magnesium alloys, their use at present is limited due to three factors: the first is that magnesium and magnesium alloys have a close packed hexagonal structure with low melting point which limits the inherent ductility, toughness and creep resistance; the second factor is due to its low corrosion resistance, consequently, the unprotected magnesium alloys dissolve rapidly in aqueous solutions; the third factor is that the price of magnesium and magnesium

alloys is still high compared with aluminum or plastics^[2].

The largest end use for magnesium is as an additive to aluminum based alloys. The second large use is in magnesium gravity and die-casting which represent 33% of the total annual production. The aim of the present work is to investigate the mechanical properties of magnesium alloys with special attention to the effect of added elements on microstructure and creep resistance.

2 PHYSICAL AND MECHANICAL PROPERTIES

Magnesium element is a nonmagnetic, and has close packed hexagonal structure with low density of 1.74 g·cm⁻³ and tensile yield strength of 70 MPa. It also has a high thermal conductivity of 156 W·m⁻¹·K⁻¹ and low electrical resistivity, as listed in Table 1.

3 EFFECT OF ALLOYING ELEMENTS ON MICROSTRUCTURE

One of the most effective ways to improve the mechanical properties of alloys is to change their microstructure. However microstructure of alloys can be altered by many ways such as addition of alloying elements, removal of impurities, heat treatment or using different production schemes. In the case of magnesium alloys all such processes can be applied to improve their performance.

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Table 1 Physical and mechanical properties of magnesium metal

Property	Data
Crystal structure	HCP
Density at 20 °C/(g·cm ⁻³)	1.74
Melting point/ °C	649
Boiling point/ °C	1 090
Electrical resistivity at 20 °C/(μΩ·cm)	4.2
Thermal emf against Pt (0-100 °C)/mV	0.44
Standard reduction potential/mV(vs. SHE)	-2.37
Harness, HV	30-45*
Tensile strength/MPa	185-232*
Yield strength/MPa	69-100*
Poisson's ratio	0.291
Tensile modulus/GPa	44.7
Linear expansion coefficient at 0-100 °C/10 ⁻⁶ K ⁻¹	26
Specific heat at 25 °C/(J·K ⁻¹ ·kg ⁻¹)	1 020
Thermal conductivity/(W·m ⁻¹ ·K ⁻¹)	156

Note: * for soft and hard metal

3.1 Effect of impurities

Iron, nickel and copper are common contaminants that can be readily introduced through poor molten-metal handling practices. These elements must be held to levels under their individual solubility limits. The presence of manganese in magnesium alloys reduces the harmful effect of iron, producing less damaging intermetallic compounds. It is recommended to keep a low iron to manganese concentration ratio in order to assure a sufficient availability of manganese^[3]. The Fe:Mn ratios lower than 0.021 and 0.032 are suggested for AM60B and AZ91D respectively, when they are produced by die casting method.

3.2 Effect of alloying elements

The development of new magnesium alloys, capable of supplying the needs of automotive industry depends mainly on improving the mechanical properties such as toughness and creep resistance.

Magnesium alloys can be improved in the following background: the alloying elements should show sufficient solubility, in magnesium at high temperature, which decreases with decreasing temperature so that age hardening become possible through precipitation from the super saturated solution^[4]. Reducing the amount of alloying elements can be achieved by having precipitates containing a high magnesium con-

centration and formation of high melting point precipitates that can improve the creep resistance. Table 2 lists the most important precipitates and their melting points.

Table 2 Precipitates of different elements added to magnesium alloys

Group	Metal	Precipitates(melting point/ C°)
1	Al	Mg ₁₇ Al ₁₂ (BCC 455)
	Mn	Mn ₁₇ Al ₁₂ Fe, Mn ₁₇ Al ₁₂ Cu (in the presence of Al and Fe or Cu)
	Zn	MgZn ₂ , MgZn ₃ , β-Mg ₇ Zn ₃
	Si	Mg ₂ Si (1 085)
2	Ce	Mg ₁₂ Ce, Mg ₁₂ (La _{0.4} Ce _{0.5}), Al ₂ Ce(1 480)
	Sb	Mg ₃ Sb ₂ (1 228)
	Ca	Al ₃ Ca(FCC 1 079)
	Sc	MgSc, Mg ₂ Sc
	Nd	Mg ₃ Nd, Mg ₁₂ Nd
	Gd	MgGd
	Th	Mg ₃ Th, Mg ₂ Th, Mg ₂₃ Th ₆

3.2.1 Magnesium-aluminum alloys

The magnesium-aluminum alloys (containing 2%-9% Al, mass fraction) comprise the majority of the current magnesium die casting alloys such as AZ91, AM60, AM50 (Table 3). These alloys are classified as a dual phase alloys: the α Mg-Al or α Mg-Al-Zn solid solution with the same crystal structure (HCP) as pure magnesium; and the β precipitate, consisting of the intermetallic Mg₁₇Al₁₂. The typical microstructure has β phase at α grain boundaries^[5,6] as shown in Fig. 1.

The β intermetallic structure is incoherent with the α magnesium matrix, exists over a composition range of 48%-52% Al and has a low melting point of 458 °C. This may explain the low creep resistance of this alloys. Miller^[9] found that die cast AZ91 alloy creeps even at room temperature through a dislocation climb mechanism.

It appears that the addition of aluminum to magnesium improves fluidity and tensile strength through solid solution strengthening^[10] as well as corrosion resistance. On the other hand, the presence of aluminum leads to formation of the β phase (with low melting point) which has an adverse effect on creep resistance.

Addition of zinc to magnesium enhances its room temperature strength as well as fluidity and creep resistance, by increasing the rupture time^[11,12]. However increasing the zinc content above 3% (mass fraction) can cause hot cracking.

Table 3 Composition and mechanical properties of magnesium die cast alloys used in automobile and electronic applications

Alloy	Composition/ %	σ_y / MPa	σ_s / MPa	ϵ / %	ρ / (g•cm ⁻³)	Creep*
AZ91D	9Al, 0.7Zn, 0.17-0.4Mn	230	160	3	1.81	3
AM60B	6Al, 0.2Zn, 0.15-0.5Mn	220	130	6-8	1.78	3
AM50A	5Al, 0.2Zn, 0.28-0.5Mn	220	110	6-10	1.78	3
AM20	2Al, 0.23Mn	210	90	12	1.78	3
RZ5	4.2Al, 1.2Re, 0.7Zr	218	148	4	1.78	3
MEZ	2.5Al, 1.2Re, 0.35Zn	172	145	5	1.78	2
ZAC8506	8Zn, 5Al, 0.6Ca	219	146	5	1.8	2
AMC5006	5Al, 0.6Ca, 0.32Mn	156	95	8.5	1.78	2
MRI 151		277	175	7.5		2
MRI177	Under patent process	275	177	6.7		2
Noranda Al		202	145			2
A380	9Si, 3.5Cu, 3Zn, 2Fe	324	160	3.5	2.68	

Note: * all ratios are relative, 1.0 is the best; MRI 151 see project of Israel; Noranda Al: trademark of Canada.

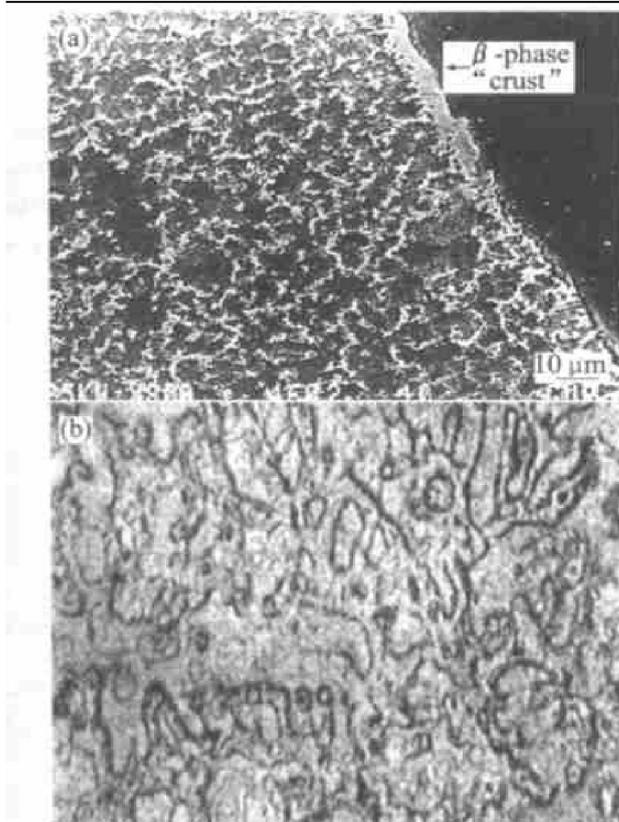


Fig. 1 Microstructures of AZ91(a)^[7] and AM60(b)^[8]

Magnesium-aluminum zinc alloy (AZ91) represents the magnesium alloy for automobile industry and electronic applications. It has the same yield strength and ductility as its aluminum counter part A380. The VW/Audi car company has lunched the B80 gear box housing made of AZ91 in 1996 with mass saving of 20% as compared to aluminum alloys^[13]. This company also produces manual transmission cases for use in VW Passate, Audi A4/A6^[14], and Santana model

built in China. The operating temperatures for these applications are below 120 °C.

Another important alloy in this class is the AZ31 alloy with a microstructure mostly of α phase because of low aluminum content as illustrated in Fig. 2(a). It is the wrought alloy of extruded sheets offers slightly lower strength, but a higher ductility (15%), than the commonly used AlMg alloys such as 5182 and 5052.

At present magnesium sheets are not capable

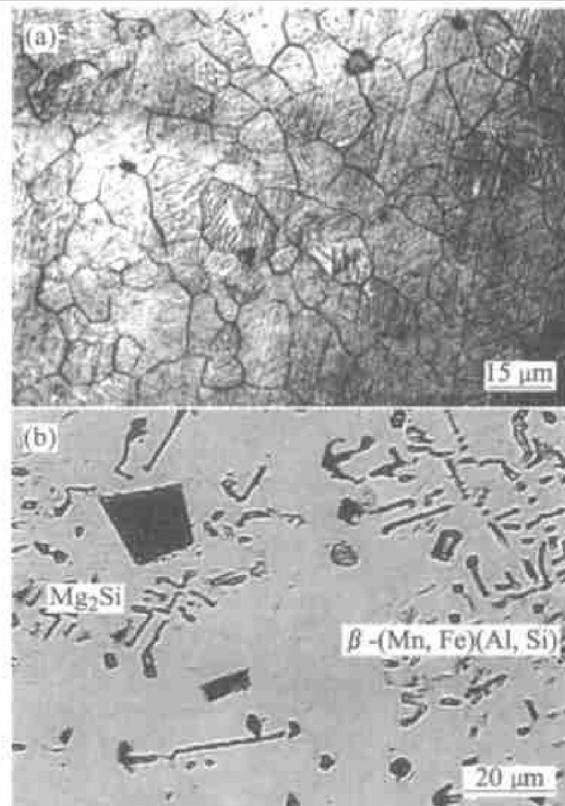


Fig. 2 Microstructures of AZ31(a) and AS21(b)^[15] magnesium alloys

of meeting the requirements for bending stresses (buckling stiffness) needed for body components such as doors, boot and bonnet. They also cannot meet the corrosion resistance and surface finish requirements of the vehicles body.

The alloys AM50 and AM60 (with low aluminum additions) reveal less β -phase at grain boundaries as shown in Fig. 1. Both alloys have good combination of tensile strength, ductility (elongation 10%–15%), energy absorption and castability. Their impact strength is better than that of aluminum die cast A380.

Previous study by Iskandre et al^[16] has shown that the tearing modulus measured for AM60B (the amount of energy that would be required to propagate a flow) is a stable-tearing mode, which means the energy input needed to propagate crack extension provides some warning of structural failure (non-catastrophic failure). During this study they found that the energy necessary to initiate a flow in the cast AM60B alloy is about the same as that for wrought aluminum alloy 6061-T651, and the tearing modulus of AM60B is better than that of 6061-T651. AM and AZ alloys are used in manufacturing of low temperature structural applications such as instrument panels, steering system, seating structures and wheels.

For applications that require higher ductility and toughness, AM20 alloy could be used although this alloy exhibits poor castability. However the AM and AZ magnesium alloys have low creep resistance^[17] which limits their use for high temperature applications.

3.2.2 Magnesium-aluminum-silicon alloy

The addition of silicon to magnesium-aluminum alloys leads to formation of an intermetallic compound, Mg_2Si precipitates at grain boundaries and within the grains in the Chinese script form^[15]. The presence of manganese leads to formation of $MnSi_3$ and aluminum forms the eutectic phase ($Mg_{17}Al_{12}$), and β -Mn(Al, Si) as shown in Fig. 2(b). The intermetallic Mg_2Si exhibits a high melting point (1085 °C) and hence better creep resistance than AZ and AM alloys does. This intermetallic phase is very stable with low density (1.9 g/cm³), high hardness (HV 460) and low thermal expansion coefficient ($7.5 \times 10^{-6} K^{-1}$). Therefore Mg_2Si can act as an excellent heat resistant strengthening phase in light metals^[18,19].

Silicon is one of the inexpensive alloying elements that can provide creep resistance alloys^[20], and it is one of the promising elements to have alloys with BCC structure. The two well known Mg-Al-Si alloys are the AS41 (Mg-4% Al-1% Si) and AS 21 (Mg-2% Al-1% Si) which offer a creep resistance slightly higher than AZ alloys does, with good combination of strength, ductility and fair castability. These alloys

were developed by VW car company and used in 1970 for manufacturing of air-cooled engines and gearboxes.

Unfortunately, it should be pointed out that these alloys are found limited use at present in automotive industry because the silicon phases act as a pit initiation site for magnesium alloys corrosion^[21,22].

3.2.3 Effect of calcium addition

The creep resistance of magnesium-aluminum alloys increases substantially with increasing calcium content. The improved creep resistance results from the precipitation of an intermetallic Al_2Ca phase with a FCC crystal structure at α magnesium grain boundaries^[23,24], as shown in Fig. 3(a). This phase has a melting point of 1079 °C, which is considerably higher than that of β - $Mg_{17}Al_{12}$. The first attempt to add calcium to Mg-Al based alloys for improving creep resistance was reported in a British patent^[25] as early as 1960. This patent disclosed that calcium addition of 0.5%–3% improves creep resistance of magnesium alloys containing up to 10% Al, 0.5% Mn and a possible Zn content up to 4%.

Recent research^[26] related to the addition of calcium to AM alloys has shown that β - $Mg_{17}Al_{12}$ is completely suppressed in the presence of calcium. They conclude that the Al_2Ca phase at grain

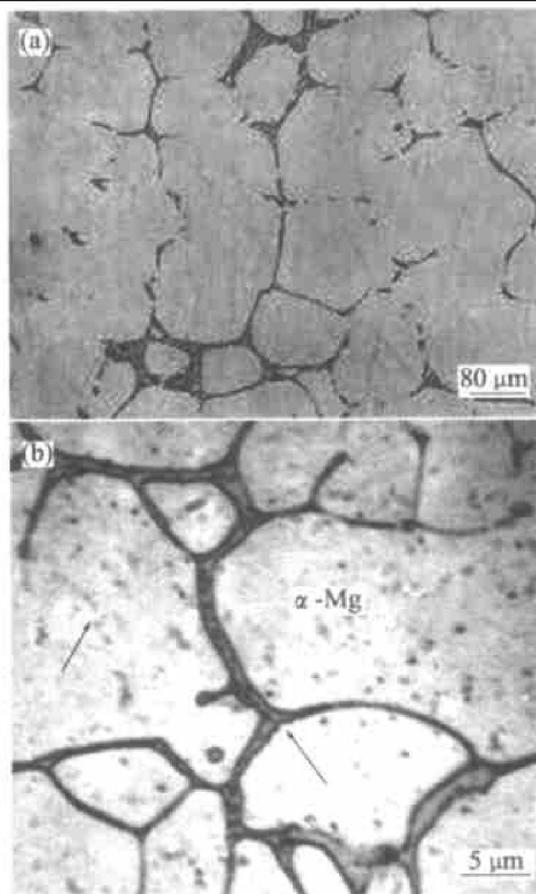


Fig. 3 Microstructures of Mg-5Al-0.7Ca(a)^[28] and MEZ alloy(b)^[36]

boundary is likely to impede grain boundary sliding and diffusion-related dislocation climb at high temperature, and that can partially explain the improved creep resistance.

More recently, it was found that small additions of calcium (0.2%–0.4%) to Mg–2% Si and Mg–4% Si alloys can modify the dendritic morphology into finely dispersed round particles^[27]. Calcium additions can also improve the castability of Mg–Si alloys via increased fluidity and reduction of oxidation of the melted alloy at temperature up to 900 °C. The excellent high temperature properties and wear resistance of Mg–Si–Ca alloys suggest that they are promising for the development of magnesium pistons.

According to the last finding many magnesium–aluminum–calcium alloys were designed and tested for improving creep resistance such as AMC5003 (4.4% Al, 0.32% Mn, and 0.25% Ca), AMC5006 (4.4% Al, 0.32% Mn and 0.56% Ca)^[28], AX506 (4.5% Al, 0.24% Mn and 0.6% Ca) and AX51 (4.6% Al, 2.4% Mn, 1% Ca)^[26].

3.2.4 Effect of rare earth metals

The beneficial effect of rare earth elements on the strength of magnesium alloys was discovered in 1930's^[29]. During the past fifty years many magnesium alloys containing rare earth metals were developed for aerospace applications, such as EZ33A (2.5% Re, 3.2% Zn, 0.75% Zr), ZE41A (4.2% Zn, 0.7% Zr, and 1.25% RE (RE: 53% Ce, 25% La, 17% Nd and 5% Pr)).

These alloys do not contain aluminum as the primary alloying ingredient, and zirconium is added to refine the grain structure. Both alloys have moderate strength and ductility at room temperature but improved properties at high temperature, with enhanced creep resistance^[30]. Another historically important rare earth zirconium alloy is QE22A (2.5% Ag, 2.2% RE, 0.7% Zr). It has high tensile strength, high creep resistance and good weldability, and it is used for aircraft gearboxes and missile housings. However, these alloys are much expensive to be used in automobile industry.

In 1972, it was reported that 1% addition of rare earth elements in the form of misch metal improves the creep resistance of Mg–Al based alloys^[31], especially when the aluminum content is less than 4%. This led to the development of AE series alloys (AE41, AE42 and AE21) which contained 2%–4% aluminum. The ternary AE die-casting alloys have only the thermally stable intermetallic $Al_{11}RE_3$ compound and $Mg_{17}Al_{12}$ precipitates. The AE alloys have improved creep resistance over aluminum zinc alloys, and the best of this group is AE42 which is viable for use in power train components^[32].

A recent study by Powell et al^[33] indicated that instability of intermetallic precipitates may persist above 150 °C, and they suggested that a decomposition of $Al_{11}RE_3$ to Al_2RE_3 and $Mg_{17}Al_{12}$ occurs at 175 °C, therefore, the presence of aluminum in rare earth alloys may reduce creep resistance at elevated temperature.



Further development of rare earth alloys was done by Magnesium Electron Ltd (MEL)^[34]. The new composition MEZ alloy consists of Mg–2.5% RE, 0.35% Zn, 0.3% Mn which does not contain aluminum. The alloy shows superior creep resistance compared with AE42 and good mechanical properties up to 177 °C.

The most recent research^[35,36] of the microstructure of MEZ alloy indicated that the intermetallic phase at grain boundaries is $Mg_{12}(La_{0.43}Ce_{0.57})$ as illustrated in Fig. 3(b). The capability of this alloy to produce automotive parts such as gearbox housings has been reported. However, the alloy remains expensive as it has an even higher content of rare earth elements than AE42 alloy has.

3.2.5 Effect of thorium, yttrium, scandium additions

Thorium was the most effective alloying element known to improve the high-temperature properties of magnesium alloys significantly. This was shown to be as a result of the high thermal stability of the equilibrium phase $Mg_{23}Th_6$ with FCC structure.

The two important alloys used extensively in aircraft engines and missiles are the HK31A containing 3.2% Th and 0.7% Zr and HZ32A which composes of 3.2% Th, 0.7% Zr and 2% Zn. They have high creep resistance for long time usage. Indeed, the radiation of thorium has resulted in its exclusion as an alloying element.

Yttrium has a relatively high solubility in magnesium. It is an effective solid solution hardener. The addition of rare earths to yttrium magnesium alloys enables both solid solution hardening and precipitation hardening. The intermetallic phases exhibit little diffusivity and good coherence to the matrix^[37].

The most technically important alloys of this group are the WE43 (4% Y, 3% RE, 0.5% Zr) and WE54 (5% Y, 4% RE). They have high creep resistance^[38], tensile strength and corrosion resistance. WE54 has slightly better creep resistance and ductility, and this alloy has been used by BMW car company for manufacturing wheels, once again WE group has even more rare earth elements, and it can not be used economically in car industry.

An attempt to increase the creep resistance of magnesium alloys and exclude the expensive rare

earth metals was a point of research during the last few years^[39,40]. Scandium was selected as a low density metal of 1 g cm^{-3} and a higher melting point of $1541 \text{ }^\circ\text{C}$ as compared to rare earths. The main disadvantage of Mg-Sc alloys is that they are difficult to melt due to formation of high melting point phase and they suffer from grain growth. The quantity of scandium used (6% - 15%) is not economically feasible for mass production of alloy which will be used in automotive industry. Further attempts to reduce the price or increase the creep resistance by addition of Ce, Y or Gd^[41], has ended with better creep resistance than WE43 with no significant reduction in the cost.

Finally antimony was added at different contents to magnesium alloy AZ91. The main effect on microstructure is the refinement of $\beta\text{-Mg}_{17}\text{Al}_{12}$ and formation of rod-shaped precipitates of Mg_3Sb_2 at grain boundaries. Guangyin et al^[42] concluded that small amount of antimony additions to AZ91+ 0.35% Sb results in increase of yield strength to 177 MPa, and creep resistance up to $200 \text{ }^\circ\text{C}$, with elongation of 24%.

4 EFFECT OF MOLDING METHODS ON MAGNESIUM ALLOYS

The world of magnesium alloys molding is dominated for the last five years by pressure die casting. It represents more than 70% of all magnesium production processes. In 2001, magnesium die casting takes a share of 33% of the world production of magnesium metal.

This adoption of die casting is due to its high productivity, high precision, high quality surface and possibility to produce thin walled and complex structures. The main disadvantage of die casting is the presence of entrapped gas and shrinkage defects.

In an attempt to improve the casting products in substitution to the widespread high pressure die casting, new methods were introduced such as vacuum pressure die casting, squeeze casting and semi-solid processing (Thixomolding). Thixomolding is the most promising method for production of high quality magnesium parts. The resultant component of this process displays a much more uniform microstructure than conventional die cast component does and does not suffer from porosity to the same extent, as well as lower shrinkage^[4].

Mathieu et al^[43] investigated the microstructure and corrosion of AZ91D alloy produced by semi-solid casting. They found that the process leads to a structure with large rounded grains of α phase solid solution higher in aluminum concentration of (3%, mass

fraction), whereas die cast alloys are more homogeneous, and the α phase contains less aluminum of 1.8%.

5 DISCUSSION

The need for mass reduction in micro-electronic devices, and automotive applications has stimulated the metals industry to renew its interest in using magnesium alloys.

It appears that improvement of mechanical properties of magnesium alloys can take many strategies, such as development of low cost Mg-Al-Si, Mg-Al-Ca and Mg-Al-Sb alloys that have high creep resistance at temperature higher than $150 \text{ }^\circ\text{C}$ in order to produce automotive engine parts. The second is, inventing new alloys with FCC or BCC microstructure (similar to thorium-magnesium alloys) so that metal forming operations such as stamping and drawing can be used to produce wrought sheets for structural parts. The third way is by reducing the cost of the semi-solid casting processes which is an adequate production method for high quality magnesium products. It is also interesting to know that, the studies on improvement of mechanical properties of magnesium alloys such as effect of core and surface heat treatments are minimal, and the practical data on creep, and fatigue is rather scarce.

6 CONCLUSIONS

The future applications of magnesium alloys are not realistic with the currently available alloys, and further improvement of alloys and production methods is needed as follows:

- 1) Production of new alloys with BCC or FCC structures, so that metal forming processes can be used.
- 2) Improvement of the available alloys toward higher creep resistance and yield strength.
- 3) Investigation of the mechanical properties such as fatigue strength and fracture toughness of the currently used alloys.

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