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Review
Cast magnesium alloys for elevated temperature applications

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The alloy development, microstructure, properties and uses of cast magnesium alloys for elevated temperature applications are reviewed. The alloying principles and strengthening mechanisms of magnesium are discussed to identify the potential alloy systems for elevated temperature applications in automotive and aerospace industries. It is concluded that the Mg–Zr family of sand cast alloys exhibit adequate mechanical properties at both ambient and elevated temperatures for aerospace applications, and Ca-modified sand cast AS41 alloy might provide a cost-effective alternative for the Zr-containing alloys. For diecasting applications, no current alloy systems meets the requirements of good high temperature properties, acceptable castability and low cost for critical automotive components, future development is especially needed in this area. Development of dispersion strengthened magnesium alloys and improvement of current Mg–Al–RE and Mg–Al–Si systems are the potential routes to expand diecast magnesium alloys to elevated temperature applications.

1. Introduction

In the past decade cast magnesium alloys have enjoyed a renaissance in many manufacturing industries, especially the automotive and electronics industries where weight reduction is critical. The aerospace industry is also responding to the widening acceptance of magnesium. Although magnesium castings are being used in a growing number of structural applications, only a small amount of research and development has been carried out on these alloys in comparison with that which has been done on aluminum alloys. The number of the magnesium alloys that are used in casting applications is very limited. Thus it is reasonable to expect that there are still new high strength alloys based on magnesium to be discovered and certainly there remains considerable optimization to be carried out on the existing magnesium alloys.

Although the magnesium alloys offer light weight, high stiffness, excellent machinability and the best alternative for weight reduction, their use for engineering applications is restricted to a few structural parts in the automotive and other transport industries. The principal technical challenge to the widespread use of magnesium castings in structural applications is their need for improved strength and creep resistance at elevated temperatures (up to 200 °C). In sand-casting applications, Zr-refined magnesium alloys usually provide a good combination of ambient and elevated temperature properties. However, they are more expensive than the commonly used Mg–Al alloys due to the additional processing costs and their use tends to be restricted to aerospace/military applications [1].

For diecasting applications, which are more important in the automotive industry, the existing magnesium alloys do not have adequate high temperature properties. In 1975, a US NRC (National Research Council) report on the trends in usage of magnesium predicted that in the long run (15 years), higher-strength diecast alloys as well as creep-resistant alloys are expected to be developed [2]. Since then, many efforts have been made to develop creep resistant magnesium alloys and a number of Mg–Al–Si (AS series) and Mg–Al–RE (RE, rare earth) (AE series) alloys are used in diecastings. The benefits are however limited and the alloys are more difficult to cast than conventional Mg–Al alloys [1]. In addition, the higher cost associated with the rare earth elements restricts the applications of AE alloys [3]. Recently, a new family of dispersion strengthened magnesium alloys with reasonable cost and satisfactory castability is being developed for elevated temperature applications [4].

In view of the increasing interest in these alloys, this paper was prepared to review the past and current research in the cast magnesium alloys for elevated temperature applications and to identify the avenues for future development.

2. Alloy development

2.1. Mg–Al–Zn based alloys

Magnesium was first introduced as a structural material in 1909. The earliest commercial alloying elements were aluminum and zinc. Mg–Al–Zn castings were used extensively in Germany in 1914–1918, but they suffered from corrosion problems in wet or moist environments. In 1925, this serious corrosion problem was overcome by the discovery that small

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additions of manganese to Mg–Al–Zn alloys improved the corrosion resistance [5]. Alloys based on the Mg–Al–Mn system with and without zinc, such as AZ91 (Mg–9% Al–0.7% Zn–0.2% Mn) and AM60 (Mg–6% Al–0.2% Mn), have remained the principal diecast magnesium alloys for room temperature applications, such as computer housings, portable telecommunication instruments and hand tools (AZ91), passenger car seat frames and instrument panels (AM60). They constitute about 90% of all structural applications of magnesium. However, these alloys are generally unsuitable for use above 150 °C and even at this temperature considerable losses in strength are evident [6].

In 1960, a Russian paper [7] reported that the additions of calcium to sand cast Mg–Al–Zn alloys improved the tensile strength and creep resistance at elevated temperatures. Later, calcium was also found to be effective in improving the creep resistance of diecast Mg–Zn–Al alloys without adversely affecting corrosion resistance [8]. The resulting diecast alloy, ZA102 (Mg–10% Zn–2% Al–0.7% Mn–0.3% Ca), was claimed to be creep resistant at temperatures up to 177 °C. It is doubtful whether alloys of this type are being used outside Russia at the present time.

2.2. Zr-containing alloys

During the late 1930s, zirconium was shown to have a remarkable grain refinement effect in magnesium alloys containing Zn, RE, Ag, Th, etc., which led to the development of a new series of sand and permanent mould cast magnesium alloys for elevated temperature applications. The best elevated temperature properties were achieved in magnesium alloys with RE, Th and recently, Y as the main alloying elements. The first alloy in this group, MCZ (Mg–3% RE–0.7% Zr), was developed by Murphy and Payne [9] at J. Stone and Co. This was followed by a "dilute" version of the alloy in the United States, EK30 (Mg–3% RE–0.3% Zr).

The additions of zinc, up to 3%, significantly increases the room temperature tensile properties without adversely affecting the elevated temperature properties of Mg–RE–Zr alloys. Thus, Mg–RE–Zr has since largely given place to the Zn-containing quarternary alloys. The optimum combination of properties can be obtained by the choice of alloys EZ33 (Mg–3.3% RE–2.7% Zn–0.6% Zr) and ZE41 (Mg–4.2% Zn–1.2% RE–0.7%Zr). Not only does EZ33 alloy provide good long-term properties at temperatures up to 250 °C, but its castability is so good that it is frequently used for room temperature applications where pressure tightness is required [6]. This alloy was successfully used in an engine housing where the operating temperature was from 120 to 205 °C [10]. Although not intended as an elevated temperature alloy, the comparatively cheap ZE41 alloy provides attractive short-term tensile properties at temperatures up to 200 °C, and has been used at temperatures up to 160 °C in such applications as aircraft engines, helicopter and airframe components, and wheels and gear boxes [10].

For even higher temperature applications (above 250 °C), HK31 (Mg–3.3% Th–0.7% Zr) and HZ32 (Mg–3.3% Th–2.1% Zn–0.7% Zr) alloys were developed by MEL (Magnesium Elektron Ltd), in which RE was replaced by thorium. Castings of HK31 and HZ32 have been used at temperatures as high as 345–370 °C in a few applications such as missiles and spacecraft [48], they are now, however, losing favour because of environmental considerations and are generally considered to be obsolete. In Britain, for example, alloys containing as little as 2% Th are classified as radioactive materials which require special handling thereby increasing the cost and complexity of manufacture [49].

The presence of silver was found to be effective for increasing room temperature strength of magnesium alloys [11]. When RE or Th is present, along with Ag, elevated temperature strength is also increased. These findings resulted in the development of alloy QE22 (Mg–2.5% Ag–2.1% RE–0.6% Zr) at Magnesium Elektron Ltd, and the alloy has been used in more demanding aerospace applications such as aircraft engine intermediate compressor casing and generator housings [50]. The application of the alloy is, however, limited due to the higher cost associated with the silver content. Yttrium has a high solubility in magnesium (12%), and the progressive decrease in solubility with decreasing temperature permits an age-hardening response in Mg–Y based alloys. Several Mg–Y based alloys containing Zr have been reported to offer good elevated temperature properties [12–14]. Alloys WE54 (Mg–5.2% Y–3% RE–0.7% Zr) and WE43 (Mg–4% Y–3.4% RE–0.7% Zr) are the best alloys in this group, exhibiting good properties up to 300 and 250 °C, respectively. The WE54 alloy retains its properties at high temperature for up to 1000 h, whereas WE43 retains its properties at high temperatures far in excess of 5000 h. Again, the relatively higher cost of yttrium restricts application of the alloys [10]. Recently, it was reported [50] that a long-term exposure (1000–2000 h) at 200 °C led to a reduction in ductility (below 2% elongation) for alloy WE54. The alloy is no longer being considered for aerospace applications but is expected to be used in applications where high strength is critical, either for the short term or where ductility is less important (e.g. motor racing). Very recently, McDonnell Douglas incorporated a WE43 rotor transmission on its MD500 series of helicopters.

In summary, the Zr-containing magnesium alloys offer a specific combination of elevated and room temperature properties not achievable with the Mg–Al–Zn alloys [1, 15]. However, the zirconium refined alloys are more expensive than the Mg–Al–Zn based alloys and their use are limited to gravity casting in aerospace/military applications which constitute less than 1% of the structural applications of magnesium. Recently, they have also been used in racing and competition cars [15].

2.3. Mg–Al–Si based alloys

Mg–Al–Si alloys are a recent addition to the commercial alloy list and were used by Volkswagen in the

1970s. The diecast alloy AS41 (Mg–4.3%Al–1% Si–0.35%Mn) was developed in response to a requirement of improved creep resistance up to 150 °C [16, 17]. Alloy AS41 has a creep strength slightly better than that of AZ91 and AM60 alloys at temperatures up to 175 °C; it also has good elongation, yield strength and ultimate tensile strength. Diecast AS41 was used in crankcases of air-cooled automotive engines [10], and a number of Volkswagen parts, such as the fan housing and dynamo bracket [63].

The use of this alloy, however, is limited to diecast parts because the improved elevated temperature strength of the alloy is attributed to dispersion strengthening obtained by the metallurgically stable Mg_2Si phase which is finely dispersed at the grain boundaries under the fast cooling and solidification rates of the diecasting process. The alloy has not been used in sand cast applications because under the slow cooling conditions of the sand casting process, the Mg_2Si phase assumes a coarse, brittle "Chinese script" morphology which greatly reduces ductility and tensile strength. Recently, a method for modifying and finely dispersing the Mg_2Si phase in the sand cast structure via calcium microadditions has been developed at the Institute of Magnesium Technology (ITM) in Canada. The microstructural modification thus achieved results in improved strength and ductility and renders the alloy sand castable [61].

The AS21 (Mg–1.7%Al–1.1%Si–0.4%Mn) alloy offers better creep strength than AS41. However, AS21 has lower room temperature tensile and yield strengths, and is somewhat more difficult to cast. Diecast AS21 was once reported by Foerster [8] to be used in automotive applications, despite its limited castability (fluidity) and corrosion resistance.

The Mg–Al–Si based alloys are more cost-competitive than Zr-containing alloys. They also offer improved high temperature performance over Mg–Al–Zn alloys. However, silicon increases the liquidus temperature of the alloys and necessitates a higher casting temperature which may be a disadvantage for diecasters.

2.4. Mg–Al–RE based alloys

The beneficial effects of RE elements on the strength of magnesium were discovered as early as the 1930s. In 1972–73, Foerster [18, 19] reported that 1% addition of misch metal improved the creep resistance of Mg–Al based alloys, and RE became more effective than silicon in increasing the creep strength of Mg–Al alloys, especially when the aluminum content was low. Diecast AE41 (Mg–4%Al–1%RE) and AE42 (Mg–4%Al–2%RE) provide improved creep resistance over Mg–Al–Si alloys. Although the alloys are currently being evaluated for applications in automotive powertrain components, the high cost associated with RE and the diecastability problem discourage those automakers and diecasters who demand the alloys for high volume productions.

2.5. Mg–Zn–Cu based alloys

Recently, copper additions to binary Mg–Zn alloys were found to significantly improve ductility and give alloys a good ageing response after solution heat-treatment [20, 21]. This was followed by the development of new ZCM (Zn–Cu–Mn) magnesium alloys at MEL [1]. ZC63 (Mg–5.5–6.5% Zn–2.4–3.0% Cu–0.25–0.75% Mn) was developed for sand/permanent mould casting. The alloy combines moderate ambient strength with useful elevated temperature properties up to at least 150 °C. A number of castings have been produced under practical foundry conditions using sand, permanent mould and precision casting techniques. Only limited work has been done on diecast alloys of the Mg–Zn–Cu system. Comparative trials using ZC62 (Mg–6%Zn–1.5%Cu–0.35% Mn) and AS21 alloys on cold chamber machines was done by Unsworth [1]. ZC62 alloy exhibits better ambient and elevated temperature properties than AS21.

However, it has long been known that the presence of copper has a deleterious effect on the corrosion resistance of Mg–Al–Zn alloys, and in the recent development of high purity AZ91 alloy the quantitative relationships between copper and other heavy metal contents and corrosion resistance have been established [22]. Although it has been claimed that the effect of copper additions to Mg–Zn alloys have considerably less effect than they do on Mg–Al–Zn alloys, it is evident that the corrosion resistance of Mg–Zn–Cu alloys decreases with increasing copper content [1].

2.6. Dispersion strengthened magnesium alloys

As early as 1949 [23], dispersion strengthening was found to be a promising means of extending the temperature capability of aluminum alloys far beyond the limits of conventional precipitation-hardened alloys. Since then, intensive investigations have been reported in the development of dispersion strengthened aluminum alloys [24–35]. However, no attempt has been made to date to develop dispersion strengthened magnesium alloys.

Ongoing work at ITM on the development of dispersion strengthened magnesium alloys [36] has resulted in two experimental alloys which are at this stage called ITM-B and ITM-C. Preliminary results show a fine distribution of stable particles. The dispersion strengthening effect is demonstrated by the increased hardness values of the ITM-B and ITM-C alloys over the AE42 and AM60 alloys (Fig. 1). The alloys are being evaluated for high temperature performance and the successful ones will be commercialized.

Table I summarizes the nominal chemical compositions of various important cast magnesium alloys.

3. Properties

3.1. Mechanical properties at room temperature

The mechanical properties of some cast magnesium alloys are given in Table II. The room temperature mechanical properties of magnesium alloys depend on one or more of three strengthening mechanisms,

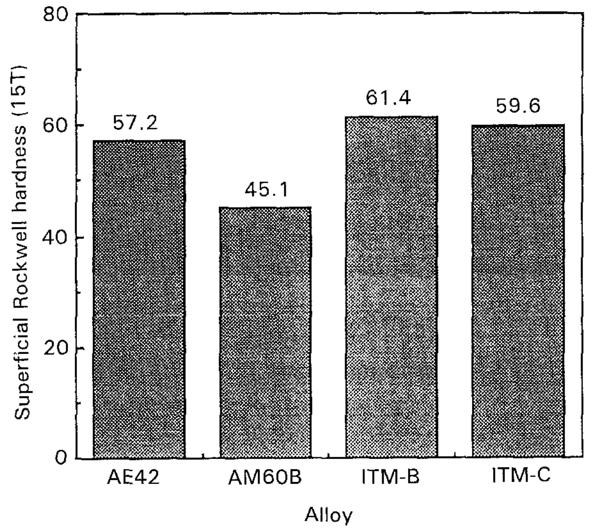

Figure 1 Hardness data for some cast magnesium alloys (permanent mould cast, as-fabricated).

namely: (1) solid solution strengthening, in which the alloying elements are completely dissolved in the base metal (magnesium); (2) precipitation strengthening, in which small particles precipitate within the magnesium matrix upon ageing; or (3) dispersion strengthening, in which insoluble and stable particles are dispersed within the matrix. The alloying behaviour and strengthening mechanisms of magnesium have been reviewed and discussed by Pekguleryuz and coworkers [3, 4, 37], and the effects of alloying elements on room temperature mechanical properties of magnesium alloys have been studied by many investigators [1, 8, 39–43]. Some of the important points are summarized as follows.

1. When the mechanical properties of a series of binary Mg alloys are examined under comparable conditions, it is seen that alloying elements fall into three main catagories [39]:
   (a) Those that increase both strength and ductility. These elements, in the order of effectiveness, are:

   Al, Zn, Ca, Ag, Ce, Ga, Ni, Cu, Th
   (strength criteria);
   Th, Ga, Zn, Ag, Ce, Ca, Al, Ni, Cu
   (ductility criteria).

   (b) Those which provide little strengthening, but increase ductility, which are Cd, Tl and Li.
   (c) Those which may confer considerable strengthening but at the cost of ductility, which are Sn, Pb, Bi and Sb.

   The above information provides a better understanding of the mechanical properties in Table II, and it is not surprising that the most common alloys which have been developed are based on Mg–Al, Mg–Zn, and Mg–Al–Zn systems.
2. For alloys based on the Mg–Al–Zn system, the 3% Zn addition gives the best ductility and the 9% Al addition provides maximum strength. Where a compromise needs to be made between strength and ductility, a 6% Al addition offers the acceptable strength, while a 5% Zn addition shows reasonable elongation.
3. Zirconium addition to magnesium alloys was of outstanding interest in promoting strength and ductility in castings. However, this is significant only in the alloys without aluminum or manganese, which are usually inevitable alloying elements added for various other properties such as castability and corrosion resistance.

3.2. Mechanical properties at elevated temperatures

Elevated temperatures have adverse effects on mechanical properties of cast magnesium alloys, which are evaluated by considering [10]:

1. The strength as determined by bringing the test specimen up to temperature and testing immediately (short-time test);

TABLE I Nominal chemical compositions of various important cast magnesium alloys [1, 8, 10]

System	Alloy	Casting method[a]	Al (%)	Zn (%)	Mn[b] (%)	Zr (%)	RE (%)	Other (%)
Mg–Al–Zn	AZ91	S, P, D	9.0	0.7	0.13	–	–	–
	AM60	D	6.0	–	0.13	–	–	–
	ZA102	D	2.0	10.0	0.7	–	–	0.3 Ca
Zr-containing	EZ33	S, P	–	2.7	–	0.6	3.3	–
	ZE41	S, P	–	4.2	–	0.7	1.2	–
	HK31	S, P	–	–	–	0.7	–	3.3 Th
	HZ32	S, P	–	2.1	–	0.7	–	3.3 Th
	QE22	S, P	–	–	–	0.7	2.1	2.5 Ag
	WE54	S, P	–	–	–	0.7	3.0	5.2 Y
	WE43	S, P	–	–	–	0.7	3.4	4.0 Y
Mg–Al–Si	AS41	D, S	4.3	–	0.35	–	–	1.0 Si
	AS21	D	1.7	–	0.4	–	–	1.1 Si
Mg–Al–RE	AE41	D	4.0	–	–	–	1.0	–
	AE42	D	4.0	–	–	–	2.0	–
Mg–Zn–Cu	ZC63	S, P	–	5.5–6.5	0.25	–	–	2.4–3.0 Cu
	ZC62	D	–	6.0	0.35	–	–	1.5 Cu

[a] D, diecasting (pressure); P, permanent mould (gravity die) casting; S, sand casting.
[b] Minimum.

TABLE II Room temperature mechanical properties of some cast magnesium alloys [1, 8, 10, 44, 45]

Alloy	Condition[a]	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Shear strength (MPa)	Impact toughness (J)
AZ91	D, F	150	230	3	140	1.5
AM60	D, F	115	205	6	–	–
ZA102	D, F	172	221	3	–	–
EZ33	S, T5	110	160	2	145	–
ZE41	S, T5	140	205	3.5	160	–
HK31	S, T6	105	220	8	145	–
HZ32	S, T5	90	185	4	140	–
QE22	S, T6	195	260	3	–	–
WE54	S, T6	172	250	2	–	–
WE43	S, T6	165	250	2	–	–
AS41	D, F	150	220	4	–	2.8
AS21	D, F	130	240	9	–	–
AE41	D, F	103	234	15	–	4.3
AE42	D, F	110	244	17	–	4.5
ZC63	S, T6	125	210	4	–	–
ZC62	D, F	119	226	11	–	–

[a] D, diecast; S, sand cast; F, as-fabricated; T5, artificially aged only; T6, solution heat-treated and artificially aged.

TABLE III Effect of elevated temperature on the ultimate tensile strength (MPa) of sand/permanent mould cast magnesium alloys [10]

Alloy	Tested at exposure temperature (°C)					Tested at room temperature (°C) after 1000 h exposure at:	
	Exposed 10 min at:			Exposed 1000 h at:			
	20	150	315	205	315	205	315
EZ33-T5	160	145	83	130	70	170	180
ZE41-T5	218	167	77	–	–	–	–
HK31-T6	215	195	125	180	62	240	180
HZ32-T5	200	145	83	115	76	220	235
QE22-T6	266	208	80	–	–	–	–
WE54-T6	280	255	184	235	–	272	217
WE43-T6	265	243	163	–	–	250	–
ZC63-T6	242	179	–	–	–	–	–

TABLE IV Effect of elevated temperature on creep stress and elastic modulus of sand/permanent mould cast magnesium alloys [10]

Alloy	Creep stress[a] (MPa) at:		Elastic modulus (GPa) at	
	205 °C	315 °C	205 °C	315 °C
EZ33-T5	38	6.9	40	38
ZE41-T5	31	–	41	24
HK31-T6	64	14	40	39
HZ32-T5	52	22	40	39
QE22-T6	55	–	37	31
WE54-T6	132	–	41	36
WE43-T6	96	–	39	37
ZC63-T6	49	–	–	–

[a] Stress to produce 0.2% creep strain in 1000 h.

2. The strength at temperature after prolonged heating at elevated temperature;
3. The effect on room temperature properties of heating at elevated temperature for short or long times;
4. The deformation produced by prolonged heating under load (creep test).

Tables III and IV show the effects of elevated temperature on the ultimate tensile strength, creep stress and elastic modulus of sand/permanent mould cast magnesium alloys. For diecast alloys, the temperature at which 0.1% creep strain was produced within 100 h under a load of 34.5 MPa was measured and defined as the creep resistant temperature by Foester [8, 19]. Based on Foerster's results, the creep resistant temperatures for several important diecast magnesium alloys are shown in Fig. 2.

Creep can be defined as the time-dependent plastic strain under a constant stress and temperature. Metals and alloys normally show three stages of creep, namely, primary or transient creep, secondary or steady-state creep, and tertiary creep (Fig. 3). Only primary and secondary creep curves are of interest for engineering design, and they can be described by the following equations:

$$\text{Primary creep strain} = at^b$$

$$\text{Secondary creep strain} = c + dt$$

The creep strain coefficients a, b, c and d for several important diecast magnesium alloys under different

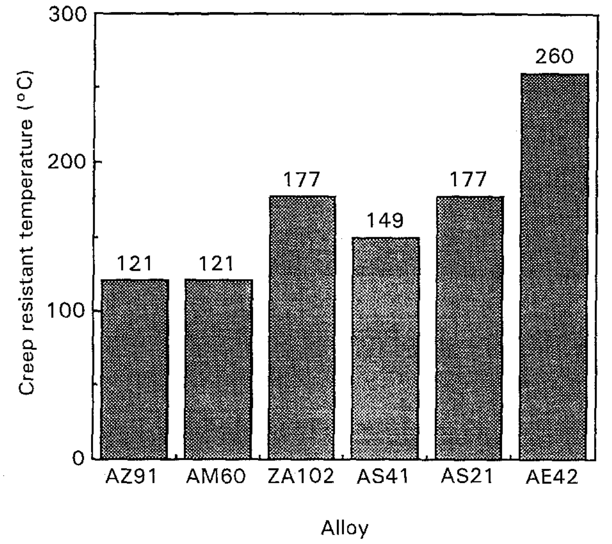

Figure 2 Creep resistant temperatures for some diecast magnesium alloys.

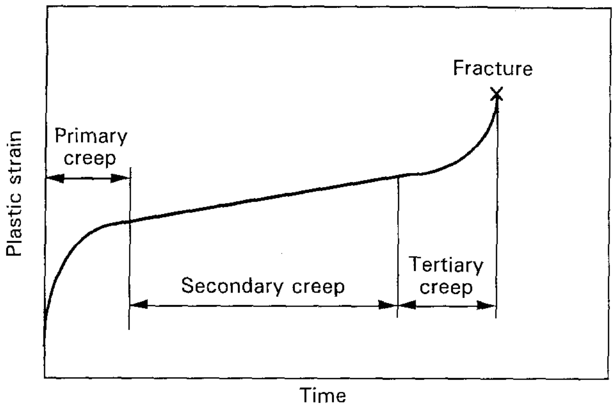

Figure 3 Typical creep curve for metals and alloys.

temperature and loading conditions are given in Table V, based on the experimental results (Fig. 4) of Aune and Ruden [45]. The results in Fig. 4 and Table V indicate that the AS41 and AE42 alloys show improved creep resistance over the AZ91 and AE41 alloys, while alloy AE42 provides the best properties of all these alloys.

3.3. Castability

Magnesium alloys generally offer good castability and can be produced by nearly all of the conventional casting methods, including sand, investment, permanent mould and diecasting. For cast magnesium alloys, properties related to castability are fluidity, resistance to shrinkage microporosity and hot-tearing, as well as oxidation resistance during melting and casting.

Castability increases with increasing aluminum content due to the improvement of fluidity, however, aluminum also increases the tendency for shrinkage microporosity due to the increase in freezing range. Zinc also improves fluidity, but high levels of zinc can lead to hot cracking and microporosity problems. The diecastablity of the Mg–Al–Zn system is shown in Fig. 5 [8]. Magnesium alloys containing up to 10% Al and less than 2% Zn are diecastable. As the level of zinc increases there are potential problems with hot-cracking. A Dow Chemical research report [46] in 1973 revealed that at still higher zinc levels (5–12%, depending on aluminum content), the magnesium alloy again became castable and ductile. At much higher zinc levels embrittlement problems occurred in the castings.

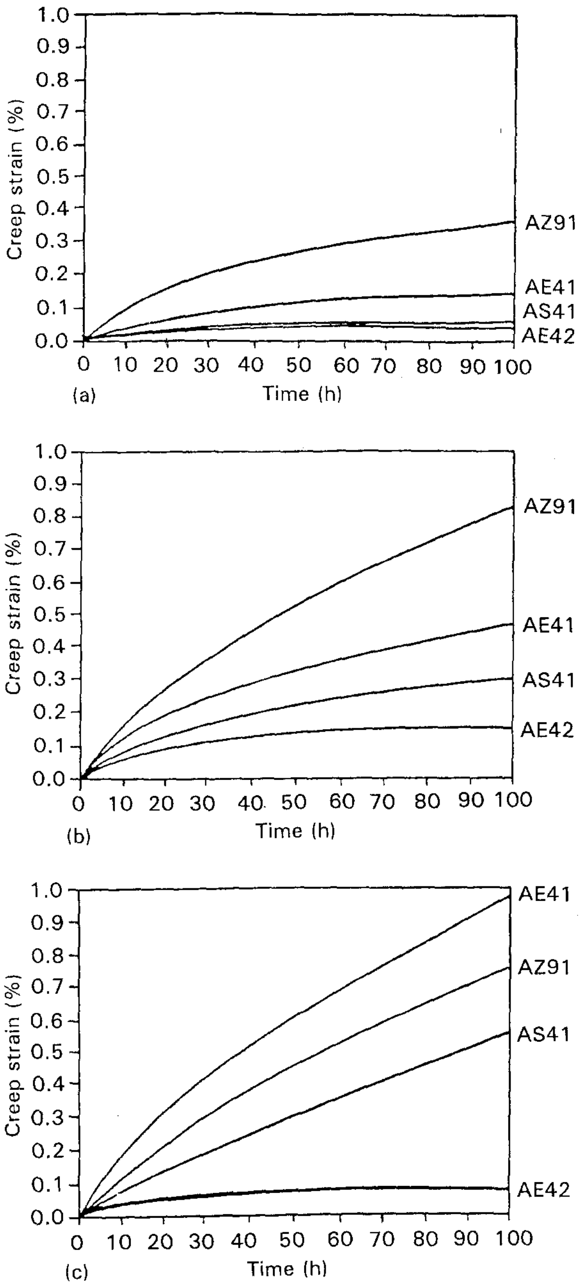

Figure 4 Creep curves for some diecast magnesium alloys. (a) 150 °C, 100 MPa; (b) 150 °C, 50 MPa; (c) 200 °C, 30 MPa [45].

RE elements and thorium can improve fluidity and resistance to microporosity and hot-tearing, but they also result in susceptibility to oxidation problems during melting and casting. These problems can be partially solved by trace additions of beryllium (10–30 p.p.m.) which improve the oxidation resistance by forming a microscopic surface layer of oxide inhibiting further oxidation of the molten magnesium alloys

TABLE V Primary and secondary creep coefficients for several cast magnesium alloys [45]

Alloy	Condition					
	Temperature (°C)	Stress (MPa)	a	b	c	d
AZ91	100	100	0.078	0.45	0.280	0.0028
	150	50	0.078	0.58	0.280	0.0092
	200	30	0.064	0.69	0.310	0.0096
AS41	100	100	0.036	0.65	0.116	0.0021
	150	50	0.032	0.28	0.076	0.0019
	200	30	0.007	0.37	0.133	0.0041
AE41	100	100	0.049	0.49	0.113	0.0037
	150	50	0.168	0.39	0.395	0.0061
	200	30	0.058	0.63	0.069	0.0105
AE42	100	100	0.042	0.40	0.117	0.0003
	150	50	0.083	0.37	0.243	0.0015
	200	30	0.015	0.18	0.053	0.0002

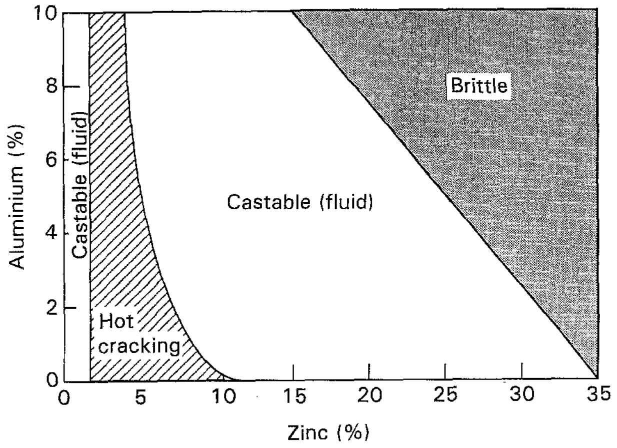

Figure 5 Diecastability of Mg–Al–Zn alloys [8].

[47]. In addition, the RE-containing alloys (AE41 and AE42) tend to stick to the dies and are therefore more difficult to diecast. Alloying magnesium with zirconium, even in the form of fluorozirconate (such as K_2ZrF_6), usually requires high temperature melting (800–900 °C), which induces an unacceptably high level of iron, which in turn has adverse effect on the corrosion resistance.

Diecastability of magnesium alloys has been of considerable interest to both magnesium diecasters and end-users. The overall castabilities and costs of important diecast magnesium alloys are summarized in Table VI. Since magnesium has a low latent heat (89.1cal/g), magnesium diecastings solidify very quickly and the shot speed can be higher for magnesium parts than for aluminum. Magnesium castings are less likely to stick in the dies since iron does not alloy readily with magnesium. Table VI also shows that there is a wide difference in the freezing ranges for different alloys, which greatly affects the castability. AZ91 and AM60 alloys can be readily cast in thin sections without major problems due to hot-cracking or lack of feeding. However, AS41 has lower aluminum contents and less fluidity, and hence is not easily diecast. Although this alloy has been used by Volkswagen in Europe for diecastings, it has seen little use in North America, because of the castability problems and the negligible improvement over AZ91 it provides in creep resistance. With lower Al content AS21 is even more difficult to diecast.

3.4. Corrosion resistance

The corrosion behaviour and corrosion protection techniques for magnesium alloys have been reviewed by a number of authors [38, 51–55]. The early magnesium alloys were susceptible to heavy corrosion in moist conditions. This was attributed to the "micro-galvanic" impurities, particularly iron, copper and nickel, which were present in the magnesium. These impurities acted as microscopic cathodes which destroyed the protective oxide film on the metal surface. Both manganese and zirconium additions to molten magnesium precipitate iron, nickel and other harmful impurities from solution, thus greatly improving the corrosion resistance of modern alloys [38]. In normal atmospheres magnesium alloys exhibit good surface stability and are used without surface protection, or with at most a thin chemical finish in a number of commercial applications. When environments corrosive to magnesium are expected in service, a variety of chemical and anodic treatments, paint systems, and electroplating techniques have been developed to make magnesium parts serviceable [38].

There are generally two test methods used in the magnesium industry to evaluate the corrosion resistance of the alloys: (1) salt-spray test in which plate specimens are tested in a salt-spray corrosion cabinet according to ASTM standard B117-90 which requires the use of neutral 5% NaCl test solution and a chamber temperature of 35 °C; (2) immersion test which involves a natural immersion in 5% NaCl solution at room temperature. Table VII summarizes the corrosion rates obtained from the salt-spray tests

TABLE VI Castabilities and costs of important diecast magnesium alloys [5, 10]

Alloy	AZ91	AM60	AS41	AS21	AE42	AE41
Liquidus (°C)	595	615	620	630[a]	625[a]	625[a]
Solidus[b] (°C)	470 (425)	540 (504)	565	610[a]	575[a]	575[a]
Freezing range[b] (°C)	125 (170)	75 (111)	55	20	50	50
Diecastability	Excellent	Excellent	Good	Good–fair	Fair–poor	Fair
Cost	Low	Low	Low	Low	High	High

[a] Temperatures obtained from the Mg–Al binary phase diagram.

[b] Equilibrium solidus. Non-equilibrium solidus temperatures and resultant freezing ranges are given in parenthesis.

for some magnesium alloys available in Metals Handbook [10]. Regardless of laboratory results, it is suggested that the final selection of magnesium alloy for a specific application should be based on tests under actual service conditions.

Using both the salt-spray and immersion tests, Lunder *et al.* [64] systematically studied the corrosion behaviour of diecast Mg–Al alloys and concluded that the corrosion rate of diecast magnesium alloys in a chloride environment decreased rapidly with increasing Al content up to 4% and that further Al additions up to 9% gave only a modest improvement in the corrosion resistance (Fig. 6). The beneficial effect of Al on the corrosion resistance of magnesium alloys can be explained by the lower corrosion rate of β ($Mg_{17}Al_{12}$) precipitates which cover and protect the grain boundaries which are usually susceptible to chemical attack. Fig. 7 shows the corroded surface of an AZ91 specimen after a 100 h salt-spray test. It is evident that the magnesium matrix (marked MG) with a lower Al concentration corrodes at a faster rate than that of grain boundary β-phase (marked β) with a much higher Al content, as shown in the EDS spectra in Fig. 7. Electrochemical studies [65] have shown that the corrosion resistance of the β-phase is related to its passive behaviour within a much wider pH range than its pure components.

TABLE VII ASTM B177-90 salt-spray corrosion rates of some magnesium alloys [10]

Alloy	AZ91	AM60	WE54	AS41
Corrosion rate ($mg\ cm^{-2}\ day^{-1}$)	< 0.13	< 0.13	0.1–0.2	< 0.25

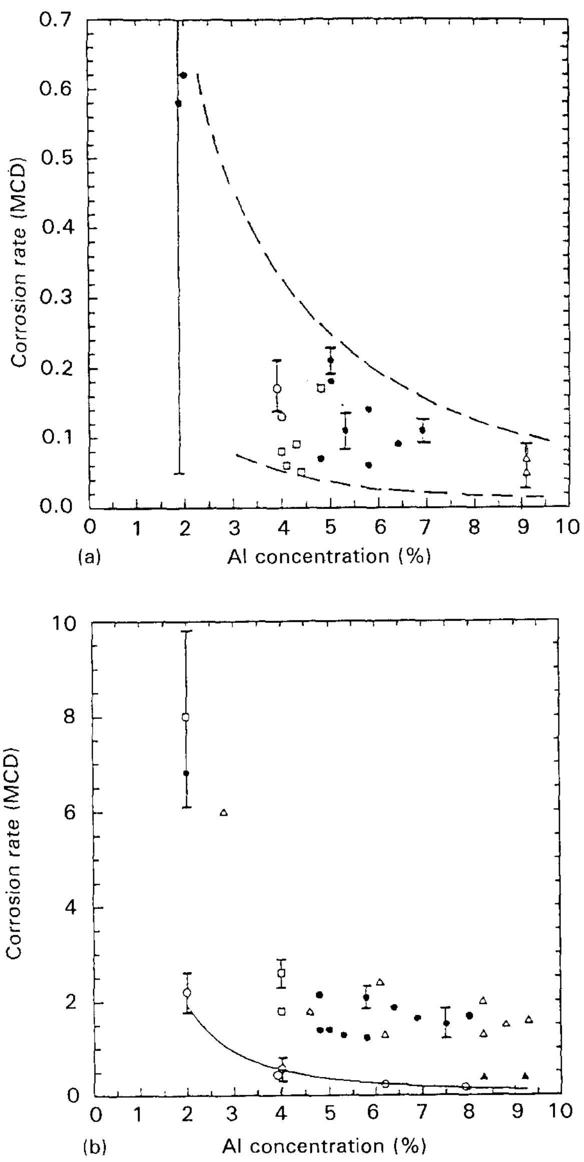

Figure 6 Corrosion rate of diecast magnesium alloys as a function of their aluminium content during (a) salt-spray test (ASTM B117-90) for 10 days, data points are the average of five duplicate experiments; (b) immersion in 5% NaCl solution for three days, data points are the average of three duplicate experiments [64]. △, ▲, AZ; ●, AM; □, AS; ○, AE

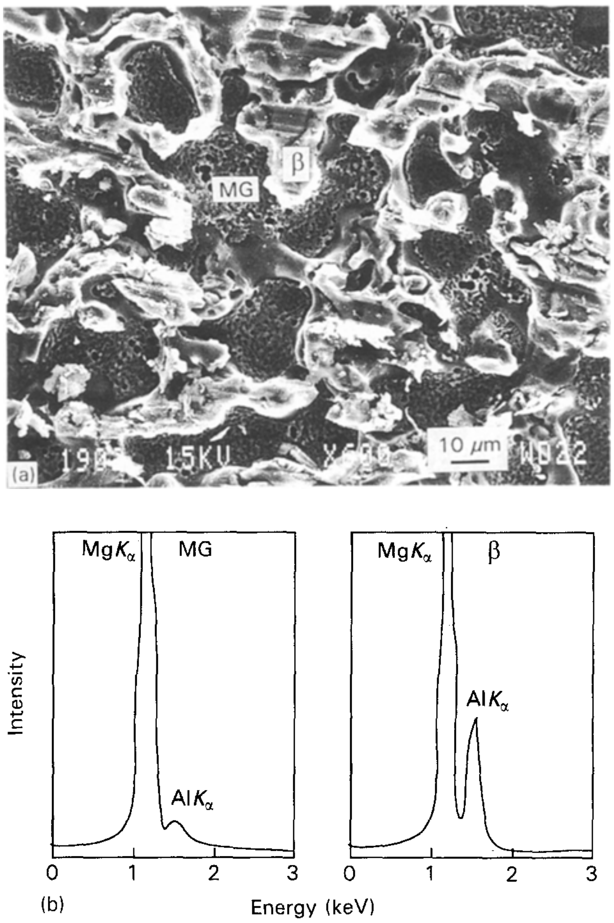

Figure 7 (a) SEM micrograph and (b) EDS spectra for corroded surface of an AZ91 specimen after 100 h salt-spray test (MG, magnesium matrix; β, $Mg_{17}Al_{12}$ phase).

4. Microstructure

In the microstructure of cast magnesium alloys, there are three major features which are important to the elevated temperature properties of the castings – grain structure, precipitation structure and dispersion structure. The grain structure of magnesium castings depends mainly on the solidification rate which varies with the casting process employed. Fig. 8 shows the as-cast microstructures for sand cast AS41, permanent mould and diecast AE42 alloys. The sand cast AS41 sample (Fig. 8a) shows a large grain size and coarse precipitates (Mg_2Si). The permanent mould and diecast structures (Fig. 8b and c) for AE42 alloy are much finer grained due to the rapid solidification rates during casting.

The diecast structure also exhibits more microporosities (black interdendritic voids, shown in Fig. 8c) than the permanent mould cast structure. A major portion of microporosity in conventional cold- and hot-chamber diecastings usually results from the trapped air and sometimes from die lubricants. Although this porosity is finely distributed in diecastings it adversely affects the mechanical properties, especially the ductility and impact toughness, it also means that the diecastings are usually not heat-treatable or weldable. This is because the pores expand and blister the surface if the casting is reheated. New processes such as pore-free diecasting, squeeze casting and vacuum-assisted diecasting may provide the answers to this problem. In addition, there exists microporosity that originates from microshrinkage which can be interconnected and give rise to pressure tightness problems in applications such as wheels and intake manifolds. ITM is currently investigating the effects of trace elements, such as Sr, on microshrinkage porosity.

4.1. Precipitation structure

Precipitation hardening, which is an important strengthening mechanism in magnesium alloys, occurs when the solid solubility decreases with decreasing temperature. In magnesium alloys containing more than 2% aluminum, β ($Mg_{17}Al_{12}$) precipitates appear as an intergranular phase (Fig. 8b and c) and contribute to the room-temperature mechanical properties of the alloys. The β-phase may have different sizes and morphologies depending on the cooling or solidification rate. Solution treatment at around 420 °C results in the dissolution of the intergranular phase, leading to solid solution strengthening whereby both the tensile strength and ductility are significantly improved. Ageing at 150–250 °C results in some precipitation of $Mg_{17}Al_{12}$ within the grain and a further small increase in tensile strength [6]. Unfortunately, the above heat-treatments cannot be applied to diecast parts due to the blistering problem.

Furthermore, the β-precipitate has a cubic crystal structure incoherent with the h.c.p. Mg matrix. It also has a low melting point (437 °C) and can readily soften and coarsen with temperature due to accelerated diffusion. Since the precipitate weakens the grain boundaries at elevated temperatures, it has been determined to be the key factor accounting for the low creep resistance of these alloys [56]. In diecast parts the microstructure is further characterized by a very fine grain size and a massive grain boundary β-phase which multiplies the grain boundary area available for easy creep deformation.

There are a number of potential routes for the microstructural modification of Mg–Al based diecast and gravity cast alloys to improve the high temperature properties. A valuable future research area would be to study the effect of trace elements on the structural modification of the β-phase to make it coherent with the Mg matrix or to increase its melting point. Another route would be to affect grain coarsening in the diecast structure to reduce the grain boundary area available for creep deformation. It has been reported [57] that Sr, Li, Ca, Ba and Bi can modify the β-phase or change the grain size of the AZ91 alloy. Further studies need to be carried out to determine the effect on creep resistance and high temperature strength.

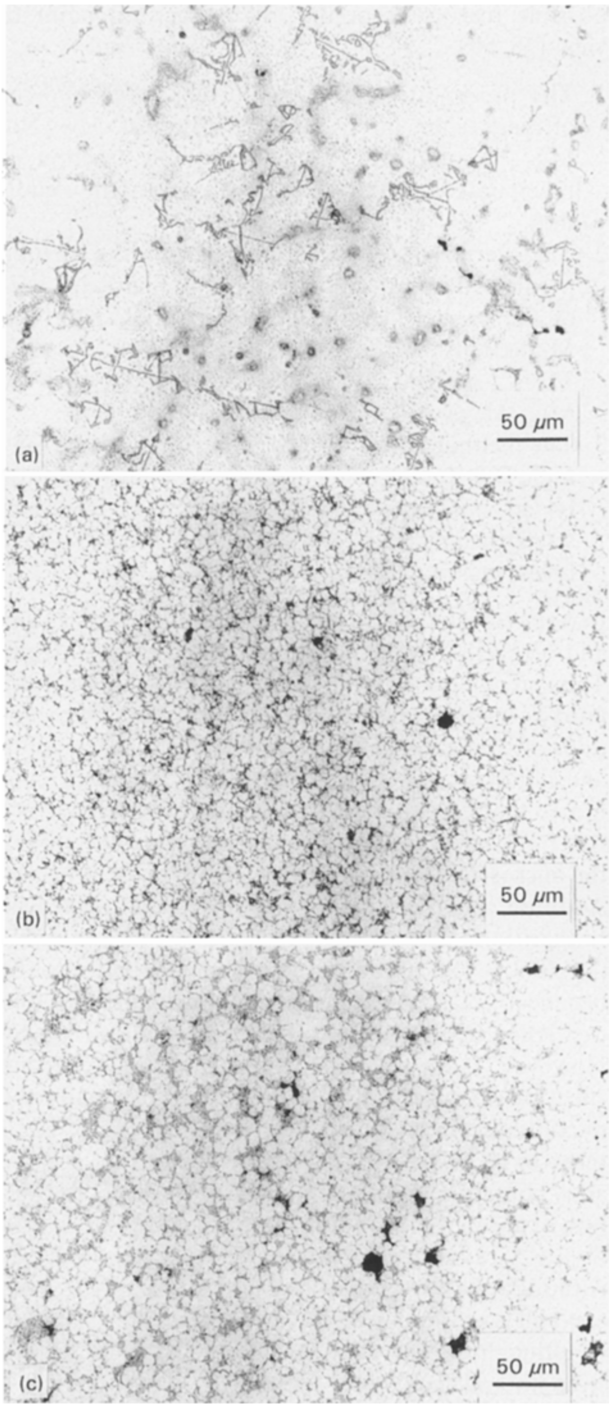

Figure 8 As-cast microstructure of (a) AS41, sand cast; (b) AE42, permanent mould cast; (c) AE42, diecast.

The Zr-containing magnesium alloys with third element additions of RE, Th and Y have shown good elevated temperature properties. There are several possible reasons from the microstructural point of view [58, 59].

1. The precipitates formed involve a large number of magnesium atoms, such as $Mg_{12}Ce$, $Mg_{12}Nd$, $Mg_{23}Th_6$ and $Mg_{24}Y_5$. The volume fraction of precipitate is therefore high for a given alloy addition.
2. The thermal stability as indicated by the melting point (or decomposition temperature) in Table VIII of the precipitate is high. The melting point for $Mg_{12}Ce$ is 611 °C, $Mg_{12}Nd$ 560 °C, $Mg_{23}Th_6$ 772 °C and $Mg_{24}Y_5$ 620 °C; whereas that of $Mg_{17}Al_{12}$ is 437 °C and MgZn 347 °C.
3. The melting points of RE, Th and Y are relatively high, 798–1663 °C, and they diffuse relatively slowly in magnesium while the more common strengthening additions, such as Al and Zn, have lower melting points.

In hypoeutectic sand cast Si-containing alloys (AS41 and AS21) there is another precipitate present, Mg_2Si. This precipitate assumes a coarse "Chinese script" morphology (Fig. 9a), due to the slow cooling conditions of sand casting, which results in reduced ductility and fluidity. Ongoing work at ITM [3, 61] has confirmed that Ca additions in the range of 0.11–0.13% to AS41 alloy render the alloy sand castable by refining the microstructure of the brittle Mg_2Si phase (Fig. 9b). Addition of Ca at 0.11% can bring the as-cast tensile properties of sand cast AS41 close to those of AZ91 (Table IX). The refining effect of Ca may also be beneficial for elevated temperature properties of diecast AS41 by inhibiting the coarsening of the Mg_2Si. However, Table IX also shows that the beneficial effect of Ca on the tensile properties, especially the ductility, of the alloy is lost at higher levels of additions (0.14 and 0.18%). The microstructure for the alloy containing 0.18% Ca (Fig. 10) shows the formation of another precipitating phase containing Ca and Si (see X-ray dot-mapping for Ca and Si in Fig. 10). Although the Mg_2Si particles (marked B in Fig. 10a) are still well-modified, the needle-like Ca–Si phase resulting from the excess Ca is detrimental to the strength and ductility of the alloy.

For Mg–Al–RE based alloys (AE alloys), Foerster [18, 19] has attributed the improved elevated temperature properties to the solid solution strengthening of RE elements. The solidification rate of AE alloys during diecasting is high enough to prevent extensive formation of equilibrium Al–RE compounds and sufficient RE is retained in the magnesium matrix. Recent studies of Wei [5] suggest that no RE-containing precipitates are formed in AE alloys containing 1% RE after solution and ageing treatment, and RE elements are strongly bound in the intergranular Al_4RE which is thermally stable during solution treatment even at temperatures as high as 500 °C.

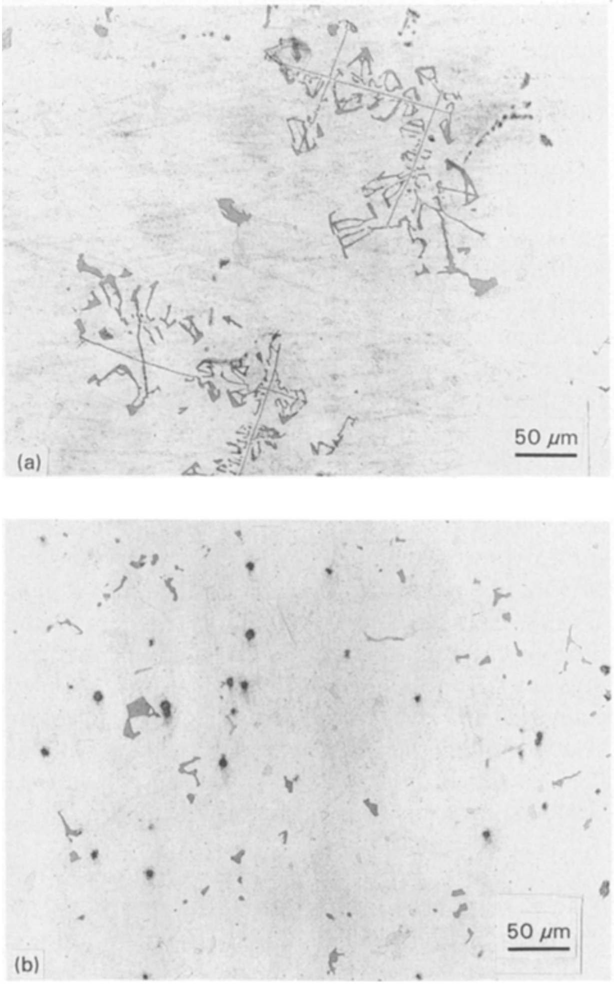

Figure 9 As-cast microstructure of sand cast AS41 alloy. (a) "Chinese script"; (b) 0.1% Ca-modified structure.

TABLE VIII Precipitation characteristics of some binary magnesium alloy systems [59, 60]

System	Maximum solubility (wt %)	Precipitate	Melting point (°C)
Mg–Al	12.7	$Mg_{17}Al_{12}$	437
Mg–Zn	8.4	MgZn	347
Mg–Ca	2.2	Mg_2Ca	714
Mg–Ce	0.74	$Mg_{12}Ce$	611
Mg–Nd	3.6	$Mg_{12}Nd$	560
Mg–Th	5.0	$Mg_{23}Th_6$	772
Mg–Y	12.0	$Mg_{24}Y_5$	620

4.2. Dispersion structure

The precipitation strengthening effect, which can be maximized by solution and ageing treatments, is limited in diecast magnesium alloys since the parts are not heat-treatable and only F temper can be utilized. Another disadvantage of the precipitated particles in magnesium alloys is that as the temperature rises they can coarsen, producing greater spacing, reaction with the matrix and eventually dissolved in the matrix. Dispersiods differ from precipitates in their thermal stability due to its much higher melting point and limited (or not) solubility in the magnesium matrix. The mechanical properties of dispersion strengthened alloys may then be retained to temperatures well above the normal softening temperature because dislocations are impeded, and softening by recrystallization or grain growth is prevented by the pinning effect of the dispersiods. The creep properties are therefore improved.

TABLE IX Tensile properties of unalloyed and calcium alloyed AS41 compared to AZ91 (sand cast test bars, F- temper)

Alloy	UTS (MPa)	YS (MPa)	Elongation (%)	Elastic modulus (MPa)
AS41 unalloyed	138 ± 8 (11)[a]	72 ± 19 (11)	3.5 ± 1.4 (11)	39 ± 12 (11)
AS41 + 0.08% Ca	155 ± 2 (16)	85 ± 2 (16)	4.5 ± 0.7 (15)	46 ± 2 (16)
AS41 + 0.11% Ca	171 ± 9 (8)	74 ± 4 (18)	6.8 ± 1.1 (8)	44 ± 10 (8)
AS41 + 0.14% Ca	159 ± 15 (3)	74 ± 3 (3)	5.4 ± 1.6 (3)	35 ± 2 (3)
AS41 + 0.18% Ca	145 ± 3 (3)	72 ± 5 (3)	3.7 ± 0.4 (3)	34 ± 5 (3)
AZ91C [10]	160–220 {130 min}[b]	90–120 {80 min}	2–5 {1.0 min}	

[a] Values in paranthesis indicate the number of samples tested.

[b] Values in braces indicate the minimum values to be considered for design purposes up to 15 mm wall thickness.

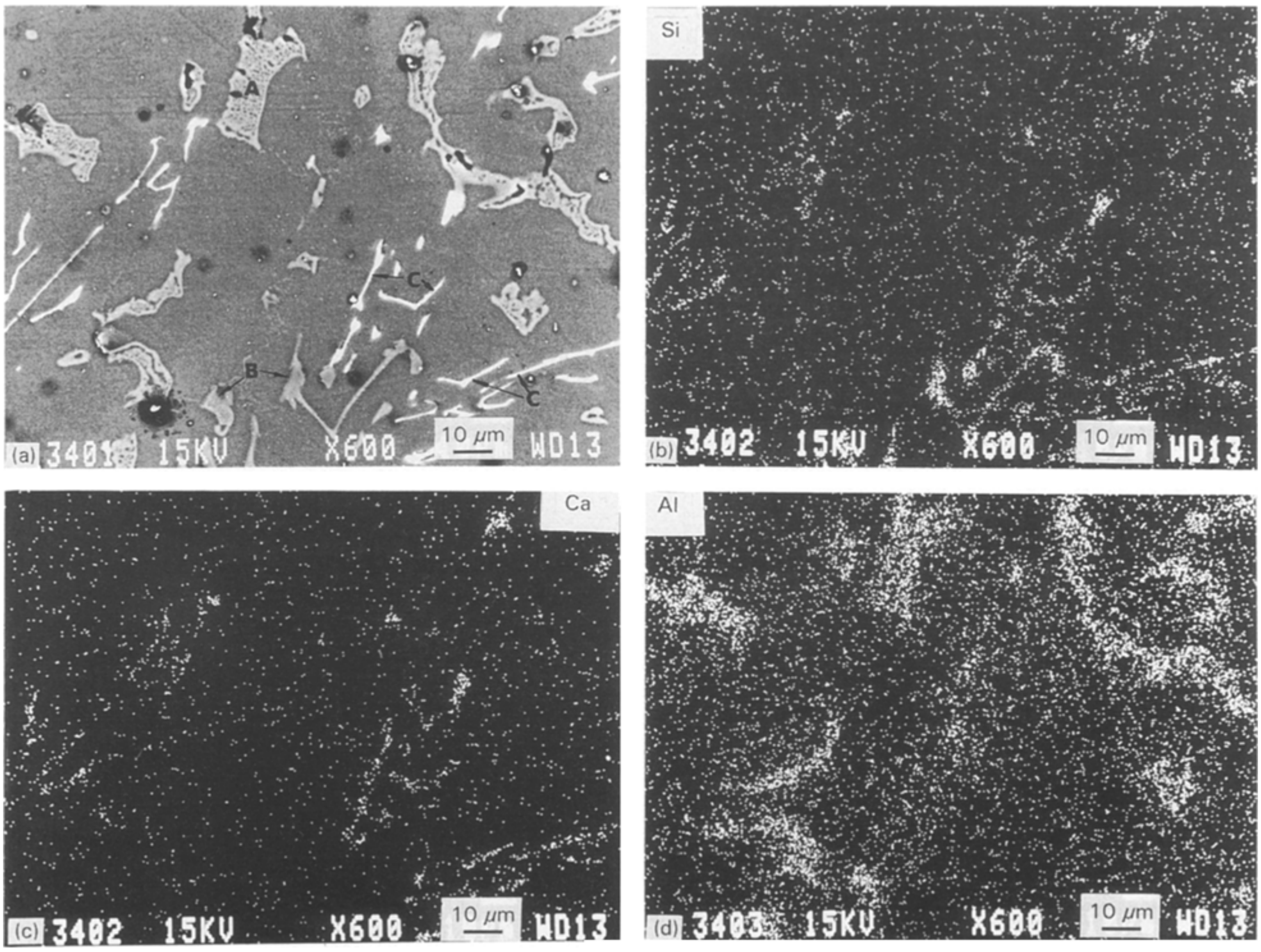

Figure 10 SEM micrographs showing the microstructure of sand cast AS41 alloy containing 0.18% Ca. (a) Backscattered electron image; (b)–(d) X-ray dot-mapping for Si, Ca and Al, respectively (A, $Mg_{17}Al_{12}$; B, Mg_2Si; C, Ca-Si)

Fig. 11 shows the as-cast microstructure of dispersion strengthened magnesium alloy ITM-B, in which the dispersion of intermetallic particles is evident. The SEM micrograph (Fig. 11b) also shows the precipitation of $\beta(Mg_{17}Al_{12})$-phase in the matrix. The strengthening mechanism of a dispersion strengthened alloy is schematically illustrated in Fig. 12, where dispersiods and precipitates are distributed in the alloy matrix. Upon room temperature deformation both precipitates and dispersiods can act as barriers to slip behaviour (dislocation movement) and strengthen the alloy. At elevated temperatures the soluble precipitates will be coarsening and softening and gradually losing the strengthening effect, but the "thermal-stable" dispersiods would continue resisting slip and provide the high temperature strength. It seems important that the dispersiods should be wetted by the matrix, otherwise, on deformation, separation of the matrix at the interface will occur causing premature ductile fracture, resulting in poor ductility [62].

5. Future developments and concluding remarks

At present, the existing demand, particularly from the aerospace industry, for lightweight sand castings with

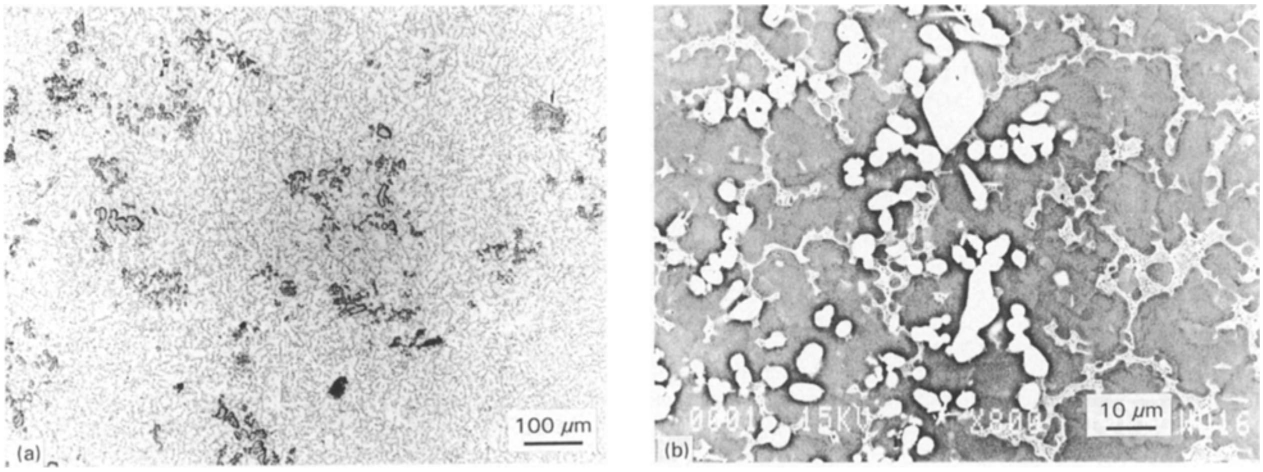

Figure 11 As-cast microstructure of ITM-B alloy (permanent mould cast) showing distribution of intermetallic dispersiods. (a) Optical; (b) SEM.

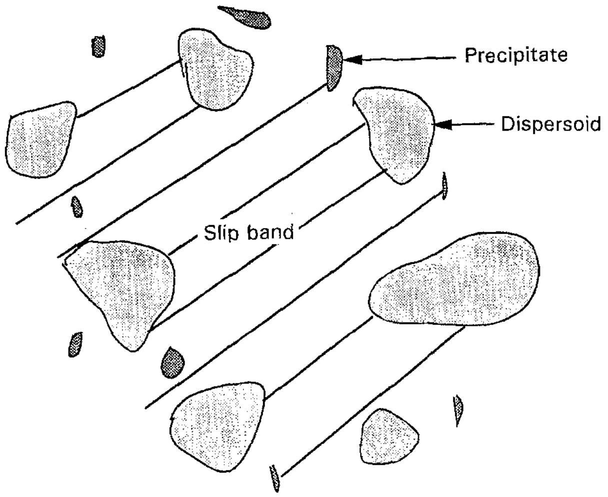

Figure 12 Schematic diagram showing strengthening mechanism in dispersion strengthened magnesium alloys.

excellent mechanical properties at both ambient and elevated temperatures is leading to continuous alloy development of the Mg–Zr family of sand cast alloys. The automotive industry, on the other hand, requires more cost-effective alloys for its gravity cast applications. With Ca modification, sand cast AS41 alloy may find some automotive or aerospace applications. Further work is needed to evaluate the elevated temperature properties of sand cast AS41 alloy with Ca microadditions.

For diecasting applications, no current alloy systems meet the requirements of good high temperature performance, adequate castability and low cost of critical automotive components. Future development is especially needed to develop or modify magnesium alloys for these types of applications. Development of dispersion strengthened magnesium alloys and improvement of existing Mg–Al–RE and Mg–Al–Si systems are the potential routes to expand diecast magnesium alloys to high temperature applications.

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