Cite this article

Tan Q, Yin Y, Mo N, Zhang M and Atrens A (2019)
Recent understanding of the oxidation and burning of magnesium alloys.
Surface Innovations **7**(2): 71–92, <https://doi.org/10.1680/jsuin.18.00062>

Invited Feature Article

Paper 1800062
Received 06/12/2018; Accepted 11/01/2019
Published online 30/01/2019

Keywords: alloys/oxidation/thin films

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Recent understanding of the oxidation and burning of magnesium alloys

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This paper reviews the following for magnesium (Mg) alloys: (a) fundamentals of oxidation and burning; (b) influence of alloying on oxidation; (c) theoretical models for improved oxidation resistance through alloying with calcium (Ca), beryllium (Be), strontium (Sr) and rare earth elements; (d) recent research on the improved oxidation resistance of beryllium-containing magnesium alloys; and (e) the recent proposed oxide reinforcement model. The oxidation resistance of magnesium alloys is closely related to the protective incubation period, which is mainly controlled by the crack resistance of the initially formed surface oxide layer. Cracking of the initially formed surface oxide facilitates the vapor phase diffusion of magnesium and results in catastrophic oxidation and eventual burning of magnesium. According to the oxide reinforcement model, an oxide layer with increased mechanical strength and hardness (such as the (Mg,Be)O layer on beryllium-containing alloys) can better withstand the internal tensile stress arising during the oxidation process and therefore can delay oxide layer cracking and extend the oxidation incubation period. This model provides guidance on developing new oxidation-resistant magnesium alloys.

Notation

a	lattice parameter
c	mole atomic concentration
d	layer thickness
d	interplanar distance of a crystallographic plane (Å)
H	hardness
H_l	hardness of the oxide layer
H_s	hardness of the substrate
h	indenter penetration depth
hkl	Miller indices of a crystallographic plane
M	atomic or molecular mass
n	number of metal atoms in one molecule of the oxide
p	partial pressure of oxygen
R	gas constant
R_a	surface roughness
R_{PB}	Pilling–Bedworth ratio
r_s	Wigner–Seitz radius
T	reaction temperature (K)
T_i	ignition temperature
V_m	volume of the elementary cell of the metal
V_{ox}	volume of the elementary cell of the metal oxide
X	element
X_{Re}	reactive element
X_{Sa}	surface-active element
α	activity
ΔG^0	standard Gibbs free energy of formation
ρ	density

1. Introduction

The urgent demand for lighter materials in the automobile, railway and aerospace industries to enable higher fuel efficiency and less greenhouse gas emissions has been driven by the current shortages in energy and fuel and increasing carbon dioxide (CO₂) emissions. As the lightest structural metallic material, magnesium (Mg) alloys are gaining increasing interest because of their high specific strength, high stiffness, good castability and good damping capacity.^{1–5} Consequently, the global production of primary magnesium has increased each year in the past decade and reached 1.1 Mt in 2017.⁶ At present, the application of magnesium alloys has included components in vehicles such as steering wheels, instrument panels, seats and gearboxes and parts in aircraft such as the thrust reverser cascade, wheels, drive train components and transmission casings.^{7–10} However, the widespread application of magnesium alloys is restricted because of their limited cold workability, poor creep resistance and low wear resistance,^{7,11} particularly compared with steels and aluminium (Al) alloys.

Furthermore, magnesium has high chemical reactivity, which causes susceptibility to aqueous corrosion and oxidation in air at elevated temperatures.^{12–19} The magnesium oxide (MgO) layer initially formed on magnesium alloys during air oxidation has an incompact structure with a low Pilling–Bedworth (P–B) ratio (R_{PB}) of 0.81,^{13,20,21} unlike the protective oxide layers on aluminium, stainless steel or titanium (Ti) alloys. Thickening of the magnesium

oxide layer during oxidation in air at high temperatures is accompanied by an increase in the internal tension stress, leading to layer cracking and subsequent rapid oxidation.¹³

The major problems caused by the low oxidation resistance of magnesium alloys are (a) surface degradation during long-term exposure at elevated temperatures and (b) easy burning when in contact with a sufficiently strong heat or flame, particularly when the magnesium alloy is in the form of fine powder or fragmented chips, although resistance is much higher for larger sections.^{12,13,22} Consequently, magnesium alloys have long been restricted from use in aircraft interiors, in particular the passenger cabin, due to concerns with magnesium burning,^{23,24} in contrast to other lightweight metals, such as titanium- and aluminium-based alloys. A recent full-scale simulated test conducted by the Federal Aviation Administration (FAA) indicated that most commercial magnesium alloys, such as AZ31, AZ80 and ZE41, were unable to meet the survivability requirement in the passenger cabin, whereas some rare-earth (RE)-containing magnesium alloys were significantly better than existing aluminium alloys.²⁵ Hence, it is of critical significance to develop magnesium alloys with improved oxidation resistance for their wider applications.

The present paper reviews (a) the fundamentals of the oxidation of magnesium alloys, (b) the current models of the effect of alloying elements on the oxidation resistance of magnesium alloys, (c) recent research on the oxidation behaviour of beryllium (Be)-containing magnesium alloys and (d) the new oxide reinforcement (OR) model that provides a new theoretical basis for the development of new oxidation-resistant magnesium alloys.

2. Oxidation

2.1 Oxidation kinetics

Magnesium alloys are easily oxidised when exposed to air at high temperatures, due to a high affinity to oxygen (O₂).²⁶ The chemical reaction between magnesium and oxygen is as follows²⁷

As oxidation progresses, the oxide layer thickens and the weight increases.²⁸ The weight gain of the magnesium alloy specimen is equivalent to the mass of oxygen taken into the oxide layer according to Equation 1. Hence, the oxidation kinetics can be characterised by measuring the weight gain of the magnesium alloy specimen, because it has been experimentally found that the oxide layer remains on the alloy surface.

Figure 1 presents typical weight gain–time curves, as measured by thermogravimetric analysis (TGA), for AZ91 in air at different temperatures.²⁹ At 197°C, the overall specific weight gain was as low as ~0.02 mg/cm², indicating slow oxidation. Higher temperatures above 400°C facilitated oxidation and caused a significantly increased weight gain. After oxidation at 487°C

Figure 1. The weight gain–time curves for as-cast Mg–9Al–1Zn in air at 197, 437, 472 and 487°C measured by TGA. At 197°C, the overall weight gain was small, indicating a slow oxidation. Increasing the temperature to over 400°C led to accelerated oxidation stages after the incubation periods. Redrawn from Czerwinski²⁹ and used with permission from Elsevier

for ~19 min, the specific overall weight gain of AZ91 was 0.44 mg/cm², which was over 20 times higher than that at 197°C.

High-temperature oxidation of magnesium alloys in air typically involves an initial oxidation stage with parabolic kinetics and a subsequent oxidation stage with accelerated kinetics which are linear or power-law kinetics.^{13,30} The parabolic growth stage is considered as an oxidation incubation period, during which a compact protective oxide layer forms and isolates the magnesium substrate from the oxygen in air.^{13,29} Within the incubation period, the oxidation is mainly dominated by ionic diffusion and the oxidation rate decreases with increasing layer thickness.²⁸ In contrast, the accelerated oxidation stage represents non-protective oxidation, which is attributed to the breakage of the initially formed surface oxide layer.^{27,29,31} During the accelerated oxidation stage, the oxidation rate is independent of the oxide layer thickness, and oxidation proceeds with linear or power-law kinetics.^{28,32} Hence, the oxidation resistance of magnesium alloys is closely associated with the incubation period. As shown in Figure 1, the weight gain of the AZ91 followed parabolic kinetics within the entire test period at 197°C, indicating that the surface oxide provided sufficient protection to the alloy at this relatively low temperature. In contrast, at a temperature higher than 400°C, there was an accelerated oxidation stage after the incubation period. At 437°C, AZ91 had an oxidation incubation period of ~25 min. Increasing the temperature to 472 and 487°C shortened the incubation period to ~15 and ~13 min, respectively. The rapid oxidation with linear kinetics at both 472 and 487°C indicated the occurrence of fast oxidation.

The oxidation kinetics of magnesium alloys thus has a critical temperature, which ranges from 400 to 450°C depending on the

alloy composition.¹³ Below the critical temperature, there is a slow oxidation rate and a small weight gain. In contrast, above the critical temperature, the weight gain accelerates and follows linear or power-law kinetics after the incubation period. A higher oxidation temperature results in a higher oxidation rate and a shorter incubation period.^{30,33,34}

The published data on incubation periods of magnesium alloys at various temperatures are summarised in Table 1.^{13,21,30,33–55} Pure magnesium had an incubation period of 440 min at 500°C. The alloying elements aluminium, zinc (Zn), tin (Sn), copper (Cu) and manganese (Mn) shorten the incubation period for magnesium alloys. Commercial magnesium alloys such as AZ31, AZ91, AM60, ZC63

Table 1. Summary of the incubation period of various magnesium alloys at various temperatures

Alloy	Incubation period at various temperatures: min							Reference
	400°C	430°C	450°C	500°C	550°C	600°C	700°C	
Pure magnesium				440				Aydin <i>et al.</i> ³⁵
AZ31				55				Yu <i>et al.</i> ⁵¹
AZ61	350							Lee ⁵²
AZ91	150							Tan <i>et al.</i> ⁴⁵
	180		20					Medved <i>et al.</i> ³³
				55				Barrena <i>et al.</i> ⁵⁴
AM50	>700		95	85				Medved <i>et al.</i> ³³
			41					Lin <i>et al.</i> ⁴⁸
AM60	>700		80	75				Medved <i>et al.</i> ³³
			60					Aydin <i>et al.</i> ³⁵
AE42	>700		130	95				Medved <i>et al.</i> ³³
AM50–0.28Y			>60					Lin <i>et al.</i> ⁴⁸
AM50–1Y			57					Lin <i>et al.</i> ⁴⁸
AM60–10SiC			>300					Aydin <i>et al.</i> ³⁵
AS21				140				Tan <i>et al.</i> ⁵⁵
AZ31–0.3Ca			>1200	>1200				Lee ³⁸
AZ31–0.75La			36					Zhao <i>et al.</i> ⁴⁴
AZ61–0.5Ca				>1200	60			Lee ⁵²
AZ91–1.5Ca	270							Cheng <i>et al.</i> ³⁷
AZ91–1.5Ca–0.5Y	>300							Cheng <i>et al.</i> ³⁷
AZ91–10SiC		>300	90					Nguyen <i>et al.</i> ⁴⁷
AZ91–20SiC		>300	>300					Nguyen <i>et al.</i> ⁴⁷
AZ91–2Ca							55	Choi <i>et al.</i> ⁴⁹
AZ91–5Ca							>60	Choi <i>et al.</i> ⁴⁹
AZ91–5SiC		120	60					Nguyen <i>et al.</i> ⁴⁷
AZ91–60 ppm (wt) beryllium	>300							Tan <i>et al.</i> ⁴⁵
Mg–0.3Nd				480				Aydin <i>et al.</i> ³⁵
Mg–0.5Nd				670				Aydin <i>et al.</i> ³⁵
Mg–0.5Y					>100	60		Yu <i>et al.</i> ²¹
Mg–1.5Ca				>300				You <i>et al.</i> ³⁶
Mg–1.5Y				>160				Yu <i>et al.</i> ⁵¹
Mg–1.7Ca(OH) ₂				>300				Jang and Kim ⁵³
Mg–1.7CaO				>300				Jang and Kim ⁵³
Mg–10Gd–3Y	>90		>90	>90	>90	>90		Wang <i>et al.</i> ⁴²
Mg–1Y					>100	90		Yu <i>et al.</i> ²¹
Mg–2.5Nd				>700				Aydin <i>et al.</i> ⁴³
Mg–2.5Sr				>700				Aydin <i>et al.</i> ⁴⁶
Mg–2Sn				60				Yu <i>et al.</i> ⁵¹
Mg–2Zn				30				Tan <i>et al.</i> ⁵⁵
Mg–3.08Y–0.68Ce	>140			>140		16		Fan <i>et al.</i> ⁴⁰
Mg–3.7Y					>100	>100		Yu <i>et al.</i> ²¹
Mg–5.13Y–0.25Zn–0.32Zr	>16 200							Ning <i>et al.</i> ⁴¹
Mg–6Nd				>700				Aydin <i>et al.</i> ⁴³
Mg–6Sr				>700				Aydin <i>et al.</i> ⁴⁶
Yttrium-surface-implanted magnesium				>90				Wang <i>et al.</i> ³⁹
ZC63				15				Tan <i>et al.</i> ⁵⁵
ZC63–10SiC		90	55					Lee <i>et al.</i> ³⁴
ZE41	>330		>330	90				López <i>et al.</i> ³⁰
ZK20				20				Tan <i>et al.</i> ⁵⁵

Chemical compositions are represented by mass fraction. The prefix ‘>’ indicates that the oxidation test was terminated within the incubation period. Reproduced from Tan *et al.*¹³ and supplemented with updated data^{21,30,33–55} and used with permission from Elsevier

and ZK20 exhibited incubation periods shorter than 80 min at 500°C, indicating low oxidation resistance of these alloys. In contrast, alloying with calcium (Ca), strontium (Sr), beryllium, REs and silicon carbide (SiC) nanoparticles suppress oxidation of magnesium alloys by extending the incubation period.

2.2 Evaporation-enhanced magnesium oxidation

The non-protective oxidation of magnesium alloys is also closely related to the high evaporation rate of magnesium at high temperatures,^{35,56} as the temperature approaches the melting temperature of the magnesium alloy. Magnesium exhibits a much higher tendency to evaporate during high-temperature oxidation than aluminium, titanium and iron (Fe), as driven by the higher vapour pressure. For example, at 500°C, the equilibrium vapour pressure of magnesium is 10.2 Pa, which is 1.9×10^{11} , 5.0×10^{15} and 1.9×10^{20} times larger than that of aluminium, iron and

titanium, respectively.⁵⁷ The magnesium vapour pressure also increases as the temperature exceeds the melting temperature of thermally unstable microconstituents, such as eutectic microstructures.^{32,33,58} The vigorous magnesium vapourisation contributes to the breakage of the surface oxide layer and to the accelerated oxidation.⁵⁶

Figure 2 provides a schematic diagram of the evolution of the oxide layer on magnesium alloys during high-temperature oxidation. During the initial oxidation stage – that is, during the incubation period – the thin magnesium oxide layer is considered to be crack-free and therefore provides some protection to the alloy by isolating the substrate metal from oxygen,^{32,56} as shown in Figure 2(a). As the magnesium vapour diffusion is retarded by the continuous surface layer, oxidation occurs mainly by the ionic diffusion of magnesium ions (Mg^{2+}) through the surface layer,

Figure 2. Schematic evolution of the oxide layer on magnesium alloys at high temperatures: (a) the formation of a thin magnesium oxide layer within the incubation period; (b) layer cracking within the magnesium oxide layer; (c) the formation of oxide ridges on the magnesium oxide layer; (d) nodular growth of the magnesium oxide at the outer surface

which is driven by the activity gradient of magnesium ions across the oxide layer.²⁸ This is a relatively slow process.^{59–61} However, due to the low P–B ratio (R_{PB}) of magnesium oxide/magnesium of 0.81, an internal tensile stress is generated within the layer.²⁰ Thickening of the magnesium oxide layer and the evaporation of underlying magnesium simultaneously cause the internal stress to increase, leading to the formation of cracks within the oxide layer,^{32,56} as illustrated in Figure 2(b). Thereafter, magnesium vapour and oxygen can easily transport through the cracks and react with each other to form porous magnesium oxide at the alloy/oxide layer interface, within the cracks and at the outer surface.^{27,62} As a result, the initially formed flat and continuous oxide layer is replaced by a ridge morphology, as shown in Figure 2(c). The vapour phase transport of magnesium is no longer restricted by the surface oxide layer, and the oxidation follows linear or power-law kinetics.^{13,30,32} As the non-protective oxidation continues, the growth of magnesium oxide exhibits a nodular morphology at the outer surface, as presented in Figure 2(d). This is attributed to the rapid reaction between the magnesium vapour and oxygen at the outer surface.^{59,62}

Recently, Zhang *et al.*⁶³ further confirmed the evaporation-enhanced mechanism of magnesium oxidation by studying the oxidation and evaporation behaviour of single-crystal magnesium nanoparticles at 130 and 200°C using an in situ environmental transmission electron microscope. An ~2 nm thick preformed monocrystalline magnesium oxide layer had been formed on the sample surface prior to the oxidation test. The orientation relationship between the magnesium matrix and the magnesium oxide was $(0001)_{Mg} \parallel \sim 2^\circ$ from $(1\bar{1}1)_{MgO}$, $[2\bar{1}\bar{1}0]_{Mg} \parallel [001]_{MgO}$.⁶³ The thin magnesium oxide surface film formed at ambient temperature was crystalline, in contrast to the previous assumption that amorphous magnesium oxide formed at room and at low temperatures.^{32,60} Increasing the temperature to 130 and 200°C led to a quick increase in the layer thickness and to the formation of magnesium oxide lamellae on top of the preformed oxide layer. After the initial stage, layer thickening was barely noticeable even after 243 s at 130°C, indicating slow oxidation at this temperature. In contrast, irregular oxide bubbles formed at the magnesium/magnesium oxide interface after oxidation at 200°C for 12 s.⁶³ The bubble growth of the oxide layer was attributed to the intensified magnesium evaporation at 200°C. Further oxidation resulted in oxide layer cracking and the subsequent growth of large magnesium oxide dendrites, indicating the occurrence of non-protective oxidation.⁶³

2.3 Effect of surface roughness

An isothermal oxidation test in a TGA apparatus is often used as a standard method to characterise the high-temperature oxidation behaviour by measuring the specific weight gain (mg/cm^2) of the specimen.²⁸ The specimen area is typically taken to be the apparent area computed from the measured macroscopic specimen dimensions, without consideration of surface roughness.^{30,46,48,52} However, even a macroscopically smooth surface has a certain amount of surface roughness.⁶⁴ Previous studies^{64–68} indicated that

increasing specimen surface roughness significantly increased the initial oxidation rates of iron and nickel (Ni)-based superalloys.

The authors' recent work⁶⁹ found that the initial oxidation rate of magnesium alloys also increases with increasing specimen surface roughness. Figure 3 presents the TGA results⁶⁹ for the oxidation in air at 400°C, for AZ91 specimens with increasing surface roughness (R_a) values of 0.05, 0.49 and 0.85 μm . The weight gain increased with increasing surface roughness. After oxidation at 400°C for 5 h, the polished specimen, with $R_a = 0.05 \mu\text{m}$, had the lowest overall weight gain of 0.12 mg/cm^2 . The weight gain increased to 0.58 mg/cm^2 with increasing R_a to 0.49 μm and to 0.73 mg/cm^2 for the specimen with R_a of 0.85 μm . The increase in the surface roughness also led to a decrease in the incubation period. The incubation period of the polished specimen ($R_a = 0.05 \mu\text{m}$) was ~150 min, whereas the ground specimens with R_a values of 0.49 and 0.85 μm exhibited an incubation period of ~70 min.

The higher oxidation rate of AZ91 with higher surface roughness was associated with the crests and grooves on the rougher surface.⁶⁹ The crests and grooves facilitated oxidation at the initial stage by providing additional facets and sharp edges exposed to air for oxidation.^{65–68} In addition, the stress relaxation within the initially formed oxide layer was significantly restrained by the wavy geometry on the sharp edges, promoting layer cracking and the accelerated oxidation.^{28,65} Hence, compared with the polished specimen, the ground specimens with rougher surfaces exhibited higher oxidation rates and shorter incubation periods, as shown in Figure 3.

For magnesium oxidation, the specific weight gain represents the amount of oxygen absorbed into the oxide layer and is proportional to the layer thickness.²⁸ In contrast, the incubation period indicates the protectability of the oxide layer and thereby the oxidation

Figure 3. The isothermal oxidation kinetics of AZ91 in air at 400°C for 5 h for samples with different surface finishes. A higher surface roughness (R_a) led to a more rapid oxidation rate at the initial oxidation stage. Reproduced from Tan *et al.*⁶⁹ and used with permission from Elsevier

resistance.⁵⁶ The incubation period ends because cracking occurs in the initially formed magnesium oxide layer and non-protective fast oxidation begins. Reducing the surface roughness by 17 times led to a significant decrease in the weight gain but provided a relatively small extension to the incubation period. This indicated the low oxidation resistance of AZ91. Once the crests and grinding grooves on the outmost surface were completely consumed by oxidation, it would be expected that all specimens exhibit the same oxidation rate.

3. Burning

Continuing oxidation at a high temperature can result in ignition and subsequent burning of the magnesium alloy component or specimen. Similar to other metals, the burning of a magnesium alloy specimen can be understood by means of the concept of heat balance within the specimen during oxidation.⁷⁰ During oxidation at a high temperature, heat can be input into the specimen by (a) the external heat energy from heating in a furnace or in a flame and (b) the heat energy released by the exothermic oxidation. On the other hand, heat can be extracted from the magnesium alloy specimen by means of (a) radiation, (b) conduction, (c) convection and (d) melting and evaporation of the alloy. When the heat input exceeds the total heat extracted, exothermic oxidation becomes self-sustaining and ignition occurs.⁷⁰ In contrast, burning extinguishes when heat extraction dominates. As mentioned, oxidation of magnesium alloys is accompanied by vigorous magnesium evaporation, particularly for semi-solid and molten conditions. The magnesium vapour significantly expands the contact area between oxygen and magnesium, promotes exothermic oxidation and favours ignition and subsequent burning.⁷¹ Hence, ignition of magnesium alloys is prone to occur at oxide layer cracks that are

saturated with magnesium vapour.^{13,23} One typical feature of magnesium burning is the epitaxial growth of the oxide protuberances with a cauliflower morphology, which results from the outward diffusion of magnesium vapour, followed by direct reaction with oxygen at the oxide/air interface.^{23,27,29,72}

3.1 Ignition temperature

The term 'ignition temperature' (T_i) represents the temperature at which a magnesium alloy initiates burning.^{12,73,74} The continuous heating test is used to measure the T_i of magnesium alloys because of its ease of use, its reproducibility for a particular experimental set-up and its high precision, but there are large variations between different experimenters.^{75,76} In this test, the magnesium alloy specimen is heated in a furnace at a constant heating rate in a dry air atmosphere and the T_i is evaluated as the lowest temperature associated with a sharp rise in the specimen temperature due to the significant emission of heat after the onset of burning of the magnesium alloy.^{13,23,75} One should be aware that, although the T_i quantifies the burning resistance of a magnesium alloy, it is not an intrinsic parameter.²³ Experimental conditions such as the specimen geometry, heating rate, air velocity, humidity and foreign metal contact all influence the measured T_i value.^{12,13,23} For example, the T_i of an AZ91 bulk specimen was measured to be 600°C,⁷⁶ whereas AZ91 powders exhibited a much lower ignition temperature of 484°C.⁷⁷ Details on these factors influencing the T_i of magnesium alloys can be found in the paper of Tekumalla and Gupta.¹²

Figure 4 summarises published T_i data for magnesium alloys in the form of bulk specimens.^{35,37,38,50,52,74,76,78–101} The grid patterns on the columns indicate the T_i variations, which result from different

Figure 4. Ignition temperatures (T_i) of some magnesium alloys in the form of bulk from published data.^{35,37,38,50,52,74,76,78–101} The grid patterns in the columns indicate the temperature variations according to different tests. Aluminium, zinc, manganese, copper and silicon decrease the T_i of magnesium alloys, whereas calcium, strontium, beryllium and REs improve the T_i . Alloys with high ignition temperatures over 700°C, marked by the dashed line, are associated with high concentrations of calcium, strontium and REs of over 2 wt.%

testing conditions. Pure magnesium bulk ignites at temperatures between 615 and 660°C,^{35,78–82} which is close to or above its melting temperature of 650°C.¹⁰² Figure 4 indicates that the alloying elements aluminium, zinc, manganese, copper and silicon (Si) decrease the T_i of magnesium alloys, attributed to the decrease in the solidus temperature and/or the formation of microconstituents with low melting temperatures with those solutes.^{13,34,36,80,103} For example, alloying magnesium with aluminium leads to the formation of the magnesium–Mg₁₇Al₁₂ eutectic microconstituent with a low melting temperature of 437°C along the grain boundaries of α -magnesium.^{72,103–105} High-temperature oxidation causes preferential melting of the eutectic microconstituent, promoting magnesium evaporation along the grain boundaries and thereby leading to ignition of the alloy prior to bulk melting.^{13,27,33} Hence, commercial magnesium–aluminium-based alloys, such as AZ61, AZ91 and AM60, exhibit relatively low T_i as shown in Figure 4. Alloying elements that increase the T_i of magnesium alloys are calcium, strontium, beryllium and RE elements such as yttrium (Y),

gadolinium (Gd) and neodymium (Nd). Such an increase is ascribed to the formation of a protective oxide layer on the alloy surface.¹³

Figure 4 indicates that the ignition-proof magnesium alloys with high T_i of over 700°C (marked by the horizontal dashed line) contain large amounts of calcium, strontium or REs of over 2 wt.%. This leads to an increase in the alloy cost and significant embrittlement particularly in magnesium–calcium-based alloys.^{37,106–109} Thus, development of new ignition-proof magnesium alloys with lower concentrations of these alloying elements is of technological and practical significance.

3.2 Flammability

The term ‘flammability’ describes the tendency of a magnesium alloy specimen to burn when in contact with a flame or similar heat source and after heat source removal.^{12,13,23} A high resistance to flammability requires the alloy to self-extinguish easily when the heat source is removed.¹¹⁰

Prasad *et al.*^{90,111} used a torch test as schematised in Figure 5 to study the flammability of high-purity (HP) magnesium, a range of magnesium– X binary alloys (X = aluminium, calcium, silicon, tin, strontium, lanthanum (La), manganese, zinc, zirconium (Zr), yttrium, cerium (Ce), gadolinium and neodymium) and commercial AZ61 and AZ91. The specimen tip was heated in a liquefied-petroleum-gas (LPG) flame until melted. For all studied alloys, burning started after some melting of the specimen tip. As melting of magnesium alloys significantly enhances magnesium evaporation, this result indicates that the magnesium vapour is the burning species for maintaining the flame.^{90,111}

Figure 6 shows the typical burning behaviours of AZ61 and Mg–5Y using the torch test as illustrated in Figure 5.⁹⁰ Figure 6(a) shows that the AZ61 tip melts and partially ignites after being subjected to the LPG flame for some time. Continuous heating in the LPG flame results in a more prominent burning of the specimen tip and the formation of oxide protuberances with cauliflower morphology on the attached molten blob, as illustrated in Figure 6(b). A blob of molten magnesium alloy often separates

Figure 5. Schematic top view of the torch test. One end of the horizontal cylindrical magnesium alloy specimen was exposed to the flame from LPG at ~1190°C, which was measured by a thermocouple (TC_{flame}) placed in the flame at a 50 mm distance from the mouth of the nozzle. The specimen was typically 20 mm in diameter and 200 mm in length. The embedded thermocouples (TC_1 and TC_2) were used to monitor the temperature at the ends of each specimen. Reproduced from Prasad *et al.*⁹⁰ with permission from Elsevier

Figure 6. Burning behaviour of AZ61: (a) melting and partial ignition of the specimen tip after exposure to the LPG flame; (b) subsequent burning of the specimen tip; (c) burning of the detached blob after removal of the LPG flame. Burning behaviour of Mg–5Y: (d) melting and minor ignition of the specimen tip in the LPG flame; (e) extinguished ignition even in the presence of the LPG flame. Reproduced from Prasad *et al.*⁹⁰ with permission from Elsevier

from the specimen tip after melting and burning for a period. When the LPG flame is removed, as shown by Figure 6(c), the burning of the specimen tip ceases, whereas the separated blob of molten AZ61 continues to burn until consumed completely. Similar results are also found for HP magnesium, AZ91 and aluminium-, silicon-, tin-, strontium-, manganese-, zinc- and zirconium-containing binary magnesium alloys, indicating the insufficient flammability resistance of those alloys.^{90,111}

In contrast, for Mg–5Y, there is only minor ignition at the specimen tip after melting, as shown in Figure 6(d). Then, burning self-extinguishes even in the presence of the LPG flame, as shown in Figure 6(e). In addition, the separated molten blob remains unignited within the entire test period. This result indicates that the Mg–5Y exhibited a considerable flammability resistance compared with AZ61, which is attributed to the formation of a protective yttrium-containing surface oxide layer.⁹⁰ High flammability resistance is also found for calcium-, gadolinium-, cerium-, lanthanum- and neodymium-containing binary magnesium alloys, of which the detached molten blob does not burn during the test period.¹¹¹ This result is consistent with the fact that alloying with calcium and REs significantly increases the T_i of magnesium alloys, as shown in Figure 4.

Similar observations were reported by Marker²⁵ from the FAA for commercially used magnesium alloys, including AZ31, AZ80, ZE41, ZE10, EV31, Elektron 675 (Mg–6Y–7Gd–0.5Zr) and WE43. Alloys with high concentrations of REs, typically WE43, EV31 and Elektron 675, exhibit a considerably higher tendency to self-extinguish after flame removal compared with other alloys. Geometrical factors, such as the specimen thickness, significantly affect the flammability resistance of magnesium alloys.²⁵ The WE43 specimen with section thickness of 0.6 inch (15.2 mm) self-extinguishes instantaneously after flame removal, whereas the specimen with section thickness of 0.4 inch (10.2 mm) continues to burn for ~2 min. Hence, the geometric requirement in the component design is a significant factor determining the high-temperature applicability of magnesium alloys. Magnesium alloys with thin sections could be melted readily and have a higher tendency to ignite when contacting with sufficient heat.

4. Theoretical models

The low oxidation resistance of magnesium alloys has been attributed to (a) the high vapour pressure of magnesium at elevated temperatures and (b) the non-protective nature of the magnesium oxide layer. The high vapour pressure is a thermodynamic property of magnesium and is difficult to overcome owing to the low binding energy of magnesium atoms.¹¹² The non-protective magnesium oxide layer has received considerable attention in the attempts to produce better protection through alloying magnesium alloys with the elements calcium, REs, strontium and beryllium.^{13,113}

This section analyses (a) the theoretical models that have been proposed for the mechanisms of how these alloying elements improve oxidation resistance and (b) the applicability of

the models to various oxidation-resistant magnesium alloys. The effects of alloying elements have been previously reviewed^{12,13,23,60,74} and therefore are not discussed herein.

4.1 P–B ratio

Pilling and Bedworth²⁰ indicated that the protectability of an oxide layer can be assessed by the volume ratio between the oxide formed and the corresponding metal consumed – that is, the P–B ratio (R_{PB})

$$R_{PB} = \frac{V_{ox}}{V_m} = \frac{M_{oxide}\rho_{metal}}{nM_{metal}\rho_{oxide}}$$

where V_{ox} is the volume of the elementary cell of the metal oxide, V_m is the volume of the elementary cell of the corresponding metal, M is the atomic or molecular mass, n is the number of metal atoms in one molecule of the oxide, ρ denotes density and the subscripts are self-explanatory.

In this model, $R_{PB} < 1$ indicates that tensile stresses are generated within the oxide so that the oxide layer has a high susceptibility to cracking due to the internal tensile stresses and is therefore expected to be non-protective. In contrast, $R_{PB} > 1$ indicates a complete coverage of the substrate by the oxide and a compressive stress within the oxide. However, $R_{PB} > 2$ indicates a large compressive stress that may cause oxide buckling and spalling, resulting in protection failure.²⁰ Hence, the formation of a continuous surface oxide layer with R_{PB} between 1 and 2 is a critical factor in improving the high-temperature oxidation resistance of magnesium alloys.¹¹³

The R_{PB} value of magnesium oxide/magnesium is 0.81, indicating that the magnesium oxide layer has an incompact structure with an internal tensile stress.

Table 2 lists the R_{PB} values of the oxides of common alloying elements.^{13,20} The oxides aluminium oxide (Al_2O_3), zinc oxide

Table 2. Commonly used alloying elements in magnesium alloys and the R_{PB} of their corresponding oxides^{13,20}

Element	Oxide	R_{PB}
Magnesium	Magnesium oxide	0.81
Aluminium	Aluminium oxide	1.29
Zinc	Zinc oxide	1.59
Silicon	Silicon dioxide	1.89
Calcium	Calcium oxide	0.65
Copper	Copper (I) oxide	1.64
Zirconium	Zirconium (IV) oxide	1.56
Strontium	Strontium oxide	0.66
Yttrium	Yttrium (III) oxide	1.13
Cerium	Cerium (III) oxide	1.14
	Cerium (IV) oxide	1.15
Neodymium	Neodymium (III) oxide	1.13
Gadolinium	Gadolinium (III) oxide	1.23
Lanthanum	Lanthanum (III) oxide	1.11
Beryllium	Beryllium oxide	1.70

(ZnO), silicon dioxide (SiO₂), copper (I) oxide (Cu₂O), zirconium (IV) oxide (ZrO₂), beryllium oxide (BeO) and all RE oxides exhibit R_{PB} values between 1 and 2, indicating a possibly protective oxide.

Thermodynamics can be used to assess the conditions that can lead to the formation of a surface XO oxide on a given alloy magnesium– X . The possible reactions on the alloy surface during oxidation are^{13,28}

The change in Gibbs free energy, ΔG , of these reactions are^{13,28}

$$\begin{aligned} \Delta G_{MgO} &= \Delta G_{MgO}^0 + RT \ln \frac{\alpha_{MgO}^2}{\alpha_{Mg}^2 p_{O_2}} \\ &= \Delta G_{MgO}^0 + RT \ln \frac{1}{c_{Mg}^2 p_{O_2}} \end{aligned}$$

5.

$$\begin{aligned} \Delta G_{XO} &= \Delta G_{XO}^0 + RT \ln \frac{\alpha_{XO}^2}{\alpha_X^2 p_{O_2}} \\ &= \Delta G_{XO}^0 + RT \ln \frac{1}{c_X^2 p_{O_2}} \end{aligned}$$

6.

where ΔG^0 is the standard Gibbs free energy of formation, T is the reaction temperature (in kelvins), R is the gas constant, α represents the activity, p is the partial pressure of oxygen and the subscripts are self-explanatory. Oxides, magnesium oxide and XO are regarded as pure solids, so both α_{MgO} and α_{XO} are equal to 1.¹¹⁴ For metals, α_{Mg} and α_X can be approximated by their mole atomic concentrations c_{Mg} and c_X , respectively.^{13,28}

The thermodynamic feasibility of the formation of XO ($\Delta G_{XO} < \Delta G_{MgO}$ ²⁸) can be represented as

$$7. \quad \frac{c_{Mg}}{c_X} < \exp \frac{\Delta G_{MgO}^0 - \Delta G_{XO}^0}{2RT}$$

In binary alloys, c_{Mg} can be expressed by $1 - c_X$, yielding

$$8. \quad \frac{1}{c_X} < \exp \frac{\Delta G_{MgO}^0 - \Delta G_{XO}^0}{2RT} + 1$$

Equation 8 can be satisfied for (a) a highly negative value of ΔG_{XO}^0 and (b) a high concentration of X , c_X , on the alloy surface.

The first point is determined by the chemical activity of the alloying element X , while the second point requires a substantial accumulation of X on the alloy surface, which is closely related to the maximum solubility of X in magnesium.^{12,28} Kim *et al.*¹¹³ suggested that an alloying element that may improve the oxidation resistance of a magnesium alloy requires (a) a high solubility limit (>2 at.%) in magnesium, (b) a high chemical reactivity and (c) an appropriate R_{PB} value (between 1 and 2).

This model allows understanding of the improved oxidation resistance of most RE-containing magnesium alloys.^{21,39,115–117} REs such as yttrium, gadolinium, dysprosium (Dy) and erbium (Er) have high solid solubility (>2 at.%) in magnesium so that surface accumulation can be easily achieved during oxidation, leading to the formation of an RE oxide layer with the appropriate R_{PB} on the alloy surface to isolate the alloy from oxygen. Yu *et al.*²¹ reported a dense, compact and continuous yttrium (III) oxide (Y₂O₃) layer ($R_{PB} = 1.3$) on the surface of a Mg–5.5Y alloy that protected the alloy from oxidation at 600°C for over 100 min. Wu *et al.*¹⁰⁰ developed a non-flammable Mg–15.3Gd–1.9Ag–0.3Zr (GQ152K) alloy that was able to withstand a flame at 930°C for over 6 min. The high flammability resistance was attributed to the coverage of the entire alloy surface by a gadolinium (III) oxide (Gd₂O₃) layer ($R_{PB} = 1.23$). Similar results were reported for magnesium–neodymium, magnesium–dysprosium and magnesium–erbium in both solid and molten conditions.^{35,93,113}

Although this model allows understanding of the oxidation resistance of RE-containing magnesium alloys, it is not applicable to alloys such as magnesium–calcium, magnesium–strontium and in particular magnesium–beryllium. Calcium oxide (CaO)/calcium and strontium oxide (SrO)/strontium have low R_{PB} values of 0.65 and 0.66, which should indicate a highly incompact layer.²⁰ Moreover, the solid solubilities of calcium and strontium in magnesium are limited to 0.65 and 0.66 at.%, respectively, indicating difficulty in obtaining sufficient surface accumulation of both solutes.¹¹³ However, alloying with calcium and/or strontium significantly improves the oxidation resistance and increases the T_i of magnesium alloys.^{36,38,46,84,92,118} For magnesium–beryllium, although the solid solubility of beryllium is almost zero in magnesium,¹⁰³ alloying with beryllium at parts per million (ppm) concentrations greatly enhances the oxidation resistance of magnesium alloys.^{83,114,119–121} Houska¹¹⁹ showed an increase of 200°C in the T_i of pure magnesium through alloying with 10 ppm (wt) beryllium. Czerwinski¹²⁰ reported a decrease in the oxidation rate at 487°C of AZ91 containing 10 ppm (wt) beryllium. Owing to the high affinity of beryllium to oxygen and the appropriate R_{PB} value of beryllium oxide/beryllium (1.70), such an improvement has long been ascribed to the formation of a continuous protective beryllium oxide layer on the alloy surface.^{20,121} However, beryllium oxide has not been observed. Moreover, the authors' previous work⁴⁵ confirmed that the formation of beryllium oxide on magnesium alloys was not thermodynamically feasible at ppm concentrations. Thus, this model needs refinement.

4.2 Surface-active elemental effect

Surface-active elements, X_{Sa} , are solutes that decrease the surface energy and surface tension of a liquid metal and exhibit a tendency to segregate to the melt surface.^{122,123} Such surface segregation alters the surface composition, evaporation behaviour and oxidation rate of the liquid metal, resulting in the ‘surface-active elemental effect’ (SAEE).^{13,84} Yamauchi¹²⁴ proposed that in a binary substitutional-solid solution, the solute element with a larger Wigner–Seitz radius, r_s , tends to segregate to the surface of the solvent metal and to reduce the surface energy. Figure 7 presents the r_s values of some alloying elements in magnesium,^{84,125} which implies that sodium (Na), calcium, cerium, neodymium, tin and strontium are surface-active elements in a magnesium melt because their r_s values are larger than that of magnesium.

Improving the oxidation resistance of magnesium alloys by way of strontium alloying is an example of an SAEE.^{46,84,126,127} Aydin *et al.*⁸⁴ found a progressive increase in T_i with increasing strontium concentration for magnesium–strontium alloys. Mg–6Sr exhibited the highest T_i of 854°C, which was 200°C higher than that of pure magnesium. Mg–6Sr could be melted directly in air without burning even after isothermal holding at 700°C for 12 h. Both X-ray diffraction and X-ray photoelectron spectroscopy detected a significant surface segregation of strontium oxide after oxidation, attributed to the SAEE of strontium in the magnesium melt. Hence, the improved oxidation resistance was attributed to the dense continuous strontium oxide-rich layer on the Mg–6Sr melt.^{46,84} Aydin *et al.*⁸⁴ considered that, despite the small R_{PB} value of strontium oxide/strontium of 0.66, any crack within the oxide layer was promptly healed through selective oxidation of strontium owing to the surface enrichment of strontium and its

Figure 7. Wigner–Seitz radius, r_s , of some elements. Elements including sodium, calcium, cerium, neodymium, tin and strontium have the potential to segregate to the surface of magnesium melt owing to their r_s values being larger than that of magnesium. Data retrieved from Aydin *et al.*⁸⁴ and Ren *et al.*¹²⁵

high affinity to oxygen. In comparison, alloying with strontium did not significantly increase the oxidation resistance of magnesium in the solid state.^{46,84} This was attributed to the insufficient surface accumulation of strontium through sluggish diffusion in the solid state.¹³

Many studies have reported^{52,53,87,92,118,128,129} that calcium improves the ignition resistance of magnesium alloys by forming a calcium oxide-rich oxide layer. However, as mentioned, calcium oxide/calcium exhibits a low R_{PB} value of 0.65, indicating a non-protective calcium oxide.²⁰ Hence, the protective capacity of calcium oxide is hard to reconcile with the R_{PB} model. In analogy with strontium and the high r_s value of calcium (~ 2.2 Å in Figure 7), the improved ignition resistance of calcium-containing magnesium alloys can be attributed to the SAEE of calcium. After melting of the alloy, surface accumulation of calcium is easily achieved due to the SAEE, promoting the formation of calcium oxide to heal any cracks within magnesium oxide.¹²⁹ Despite the low R_{PB} of calcium oxide/calcium, the formation of a continuous calcium oxide–magnesium oxide composite layer effectively suppresses magnesium vapourisation and thereby increases T_i . Unlike strontium, calcium also improves the oxidation resistance of magnesium alloys in the solid state.^{36,37,129} The authors’ recent study¹²⁹ further confirmed the formation of a continuous calcium oxide-rich oxide layer on AZ91 containing 1 wt.% calcium that significantly decreased the oxidation rate of the alloy at 400°C. Since the SAEE was marginal in the solid state, the outward diffusion of calcium ions (Ca^{2+}) through the magnesium oxide grain boundaries was the only channel enabling the formation of calcium oxide. The present authors consider that calcium oxide may segregate within the magnesium oxide grain boundaries, resulting in either a reinforcement effect to the magnesium oxide or the reactive element effect (REE) (more details are provided in section 4.3). Experimental evidence is required to check these hypotheses.

The protective oxide layer forming on strontium- and calcium-containing magnesium alloys indicated that the R_{PB} is not the only criterion for selecting proper alloying elements to improve the oxidation resistance of magnesium alloys. Due to the surface segregation of strontium and calcium in the magnesium melt, the formation of strontium oxide and calcium oxide is significantly facilitated, protecting the melt from oxidation despite their inappropriate R_{PB} values. Thus, alloying magnesium alloys with surface-active elements appears to be a promising approach for ignition-proof applications.

Figure 7 shows that sodium, cerium, neodymium and tin also tend to segregate to the magnesium melt surface because of the high r_s values. It would be fruitful to study the SAEE of these alloying elements in magnesium melts and therefore develop new ignition-resistant magnesium alloys.

4.3 Reactive element effect

The term ‘reactive element effect’ relates to the influence of minor alloying with a reactive element (X_{Re}) with high affinity to

oxygen (such as REs, zirconium, titanium and calcium) on enhancing the protective nature of the surface oxide.⁶⁰ This concept was first proposed by Pfeil¹³⁰ for a cerium-containing nickel–chromium (Cr) alloy, where alloying with cerium, a reactive element with a high affinity to oxygen, enhanced the protective nature of the surface nickel (II) oxide (NiO) layer. The REE of other elements such as yttrium and lanthanum has also been subsequently reported in nickel, chromium, and aluminium alloys.^{131–133} Czerwinski and Szpunar¹³⁴ and Czerwinski¹³⁵ confirmed the REE mechanism of cerium in nickel (II) oxide, wherein the segregation of cerium (IV) ions (Ce^{4+}) along the nickel (II) oxide grain boundaries effectively inhibited the diffusion of nickel (II) ions (Ni^{2+}) and therefore reduced the oxidation rate by two orders of magnitude.

Although there is no experimental evidence confirming the REE during magnesium oxidation at present, this possible mechanism was proposed by Czerwinski³² in analogy with the REE in nickel (II) oxide, chromium (III) oxide (Cr_2O_3) and aluminium oxide. Figure 8 schematically portrays the REE mechanism on magnesium oxidation. During high-temperature oxidation, particles of the X_{Re} oxides ($X_{\text{Re}}\text{O}$) along the magnesium oxide grain boundaries decompose and populate the magnesium oxide grain boundaries with X_{Re}^{2+} through the following reaction³²

During the early oxidation stage, the growth of the magnesium oxide layer is dominated by the outward diffusion of magnesium cations, followed by reaction with superoxide anions (O_2^-) at the oxide/air interface.¹³⁶ The segregation of X_{Re}^{2+} cations along the magnesium oxide grain boundaries effectively hinders the grain boundary diffusion of magnesium cations,⁶⁰ as illustrated in Figure 8. As a consequence, at a sufficiently high X_{Re} concentration, the growth of the magnesium oxide is primarily governed by the inward diffusion of superoxide anions along the magnesium oxide grain boundaries, which is too slow to enable a substantial oxidation rate.³² Because the decrease in the ionic diffusion of magnesium ions requires a concentration of X_{Re}^{2+}

along the magnesium oxide grain boundaries, a higher X_{Re} concentration is expected to cause a lower oxidation rate.

In addition, the outward diffusion of magnesium cations leads to an inward vacancy flux, creating voids at the magnesium oxide/magnesium interface and thereby facilitating layer cracking.¹³ The present authors consider that the suppression of ionic diffusion of magnesium ion through the REE may also contribute to extending the protective incubation period. Further investigation is needed to test this hypothesis.

Based on this analogy, an REE tendency has been suggested for REs, calcium and beryllium in magnesium alloys.^{38,39,120} Wang *et al.*³⁹ reported a decreased oxidation rate of pure magnesium at both 400 and 500°C after yttrium implantation (yttrium ions of 90 keV with a dose of $5 \times 10^{17} \text{ cm}^{-2}$ for 1 h). The improved oxidation resistance was attributed to a dense compact surface oxide consisting of magnesium oxide and yttrium (III) oxide. In addition, there were scattered nodules with a high elemental oxygen (O) content on the surface of the implanted sample. Wang *et al.*³⁹ ascribed the oxide nodules to the segregation of yttrium ions along the grain boundaries of magnesium oxide, similar to the REE of cerium in nickel (II) oxide.¹³⁴ However, experimental evidence is required to check for the segregation of yttrium ions. A more recent study by Lee³⁸ reported an increase in the oxidation resistance and T_i of AZ31 after alloying with 0.3 wt.% calcium. Their transmission electron microscopy (TEM) indicated that the improved oxidation resistance resulted from the formation of a protective magnesium oxide layer which incorporated calcium cations. However, it was unclear whether the calcium ions segregated along the magnesium oxide grain boundaries and provided an REE or reacted with the element oxygen to form a calcium oxide barrier layer. Further investigation is required to clarify this mechanism. A similar result was found in a beryllium-containing AZ91 alloy by Czerwinski.¹²⁰ Microalloying with 10 ppm (wt) beryllium caused a noticeable decrease in the oxidation rate of AZ91 at 487°C by suppressing magnesium evaporation. Czerwinski¹²⁰ attributed the mechanism to the REE of beryllium. However, no experimental evidence was provided to support this hypothesis.

5. Evaluation of these models

The P–B ratio, R_{PB} , uses the volume ratio between the oxide and the corresponding metal to provide an indirect estimation of the surface oxide layer compactness and the stress within the oxide layer. However, this model is qualitative and is limited to the characterisation of the protectability of a continuous oxide such as an RE oxide layer on a magnesium alloy. This model does not explain how the alloying elements calcium, strontium and beryllium improve the oxidation resistance of magnesium alloys.

The SAEE indicates that a surface-active element, X_{Sa} , segregates to the magnesium melt surface to form $X_{\text{Sa}}\text{O}$ and thereby may form a more protective $X_{\text{Sa}}\text{O}$ –magnesium oxide composite oxide layer.⁸⁴ This model can explain the high efficiency of calcium and

Figure 8. Schematic diagram of the proposed REE mechanism on magnesium oxidation. The X_{Re}^{2+} in magnesium oxide grain boundaries block the diffusion of magnesium cations

strontium in improving the ignition resistance of magnesium alloys. However, this model is only qualitative. Validation of this model requires a quantitative relationship between the surface-active element and the protectability of the $X_{\text{Sa}}\text{O}$ –magnesium oxide layer, such as the layer integrity and strength.

The REE model is different from the prior two models. The REE model suggests that the X_{Re}^{2+} ions segregate along the grain boundaries of the native magnesium oxide and inhibit the ionic diffusion of the native metal (magnesium ion), instead of forming a separate barrier layer.⁶⁰ The key feature is that a minor or trace amount of alloying can decrease the oxidation rate significantly.⁶⁰ This model appears to be applicable for strontium and beryllium, which exhibit high efficiencies in improving the oxidation resistance of magnesium even at ppm concentration.^{119,120,126} However, validation of this model requires precise characterisation of the oxide and, in particular, the oxide grain boundary composition.

These existing models have been frequently used in the literature to rationalise the oxidation resistance of magnesium alloys. However, these models are only qualitative and do not correlate the improved oxidation resistance with the crack resistance of surface oxide layers.

A new approach is the realisation that the oxidation resistance of magnesium alloys is closely related to the mechanical properties of the surface oxide. A surface oxide with a higher mechanical strength is expected to be able to withstand a higher internal tensile stress without cracking, delaying the onset of non-protective oxidation. This new approach is presented in the next section.

6. Beryllium and the OR model

Previous research^{45,55,69,129} elucidated (a) the effect of trace beryllium additions on the high-temperature oxidation of cast magnesium alloys, (b) the microstructure of the surface oxide using TEM and (c) the mechanical properties of the oxide using nanoindentation results. The OR model was proposed for the oxidation resistance of magnesium alloys. Details of this research are reviewed in this section.

6.1 Oxidation behaviour of beryllium-containing AZ91

Prior research^{45,69,129} showed that trace alloying of beryllium (10–60 ppm (wt)) into AZ91 significantly decreases the oxidation rate at 400°C and increases the T_i of AZ91. The oxidation resistance increases with increasing beryllium content.

Figure 9 shows typical isothermal oxidation kinetics of AZ91 and AZ91Be60 (containing 60 wt. ppm beryllium) at 400°C for 300 min, determined by TGA.⁶⁹ AZ91 had an oxidation incubation period of 150 min at 400°C, after which there was accelerated oxidation with a rapid weight gain. In comparison, oxidation of AZ91Be60 followed parabolic kinetics for the entire testing period, indicating an incubation period of over 300 min. After oxidation at 400°C for 300 min, the overall specific weight gain of AZ91 was 0.118 mg/cm², but that for AZ91Be60 was only 0.016 mg/cm², a

Figure 9. The isothermal oxidation kinetics of AZ91 and AZ91Be60 at 400°C in air for 5 h. Reproduced from Tan *et al.*⁶⁹ with permission from Elsevier

decrease by ~7 times. This result indicates that microalloying with beryllium improves the oxidation resistance of AZ91 by effectively extending the protective incubation period.

Figure 10 shows macrographs of AZ91 and beryllium-containing AZ91 after long-term furnace oxidation (LTFO) at 400°C in air for 144 h and after removing the surface oxide.⁴⁵ AZ91 was massively destroyed after the test, attributed to the catastrophic oxidation, signifying a non-protective oxide layer on the specimen surface.²⁹ In comparison, all beryllium-containing alloys had much less oxidation. This indicates the formation of highly protective oxide layers on the beryllium-containing AZ91. Alloying AZ91 with 60 ppm (wt) beryllium also increased the T_i from 549 to 659°C.¹²⁹

6.2 (Mg,Be)O layer

The initial oxide is crack-free on both AZ91 and AZ91Be60, has a similar thickness of ~100 nm (Figures 11(a) and 11(e)) and consists of nanosized grains (Figures 11(b) and 11(f)).⁶⁹ The grain size of the oxide on AZ91Be60 is much smaller than that on AZ91, indicating grain refinement of the initially formed oxide layer through beryllium addition. The polycrystalline nature of the oxides is confirmed by the selected area diffraction (Saed) patterns (Figures 11(c) and 11(g)). Each oxide is composed of face-centred cubic magnesium oxide, and there is no beryllium oxide, as evidenced by indexing the diffraction patterns. The energy-dispersive spectroscopy (EDS) spectra (Figures 11(d) and 11(h)) show large magnesium and oxygen peaks within both oxide layers, confirming the formation of magnesium oxide. In addition, the oxide on AZ91Be60 contains beryllium, as evidenced by the noticeable beryllium peak in the EDS spectrum (Figure 11(h)) and the absence of such a beryllium peak for the AZ91 oxide (Figure 11(d)). In beryllium-containing magnesium alloys, beryllium is considered to mainly segregate along the grain boundaries of α -magnesium owing to limited solid solubility of

Figure 10. The macrographs of AZ91 and beryllium-containing AZ91 alloys after oxidation at 400°C for 144 h. Reproduced from Tan *et al.*⁴⁵ with permission from Elsevier

almost zero in magnesium.^{45,55,103} Hence, during the high-temperature oxidation, the surface enrichment of beryllium is achieved through ionic diffusion of beryllium ions (Be^{2+}) along the grain boundary of α -magnesium, forming the beryllium-enriched magnesium oxide layer.⁶⁹

The lattice parameters a_{MgO} for the magnesium oxide and $a_{\text{Be-MgO}}$ for the beryllium-enriched magnesium oxide are 4.293 Å and 4.201 Å, respectively.⁶⁹ The beryllium enrichment leads to a decrease in the lattice parameter of the magnesium oxide by 2.14%, attributed to the formation of (Mg,Be)O substitutional solid solution, where the magnesium ion was partially substituted by beryllium ions, causing lattice distortion.^{69,121,137}

6.3 Reinforcement effect

The hardness H of both magnesium oxide and (Mg,Be)O layers was measured using nanoindentation and nanoscratch tests on the surfaces of AZ91 and AZ91Be60 after 2 h TGA oxidation at 400°C. The strength is expected to be related proportionally to the hardness.

Figure 12 presents fitting of the measured hardness values, H , to the hardness of the oxide and substrate through a power-law function as follows^{69,138}

$$10. \quad H = H_s \left(\frac{H_1}{H_s} \right)^{1/[1+A(h/d)B]}$$

where H_s and H_1 are the hardness of the substrate and the oxide layer, respectively; h represents the indenter penetration depth; d denotes the layer thickness, determined by the TEM; and A and

B are adjustable coefficients. The dashed line is the substrate hardness H_s . The best fits to Equation 10, as presented by the solid curves, yield $H_1 = 1.5$ GPa for magnesium oxide and $H_1 = 4.1$ GPa for (Mg,Be)O at the boundary condition of $h/d \rightarrow 0$. This indicates a significant reinforcement by beryllium on the initially formed (Mg,Be)O.

The significantly higher strength of (Mg,Be)O compared with that of magnesium oxide is confirmed by nanoscratch tests.⁶⁹ The critical scratch force causing cracking of the layer is 296 μN for magnesium oxide and 413 μN for (Mg,Be)O, confirming the higher resistance of the (Mg,Be)O layer against layer cracking.

The increased mechanical strength and hardness of (Mg,Be)O indicates significant reinforcement by beryllium on the initially formed magnesium oxide. The reinforcement is attributed to both solid solution strengthening and grain refinement strengthening in the (Mg,Be)O layer.⁶⁹ The lattice distortion within (Mg,Be)O owing to the substitution of magnesium ions with beryllium ions increases the energy barrier against dislocation movement, causing solid solution hardening.^{139–141} In addition, the (Mg,Be)O layer with refined oxide grains provided more grain boundaries that impede the movement of dislocations.^{46,142,143} As a result, the (Mg,Be)O layer exhibits a higher mechanical strength to resist layer cracking.

As mentioned before, the oxidation resistance of magnesium alloys is closely related to the oxidation incubation period, which is mainly governed by the protectiveness of the initially formed oxide layer. Layer cracking and debonding facilitate the evaporation of magnesium, causing catastrophic oxidation, ignition and burning of magnesium alloys.⁶⁹ The formation of the

Figure 11. Cross-sectional TEM bright-field images, high-resolution TEM images, Saed pattern, and compositional analysis by way of EDS of the oxide layers formed on (a–d) AZ91 and (e–h) AZ91Be60, respectively, after 2 h oxidation at 400°C in air. The values of the calculated interplanar distance (Cal. *d*) and the reference interplanar distance (Ref. *d*) for magnesium oxide (retrieved from Joint Committee on Powder Diffraction Standards card no. 4-0829) are included in (c) and (g). Reproduced from Tan *et al.*⁶⁹ with permission from Elsevier

fine-grained (Mg,Be)O solid solution provides higher mechanical strength and hardness of the oxide layer to withstand the internal tension stresses arising during oxidation. Therefore, layer cracking and the vapour phase transport of magnesium are effectively delayed, causing an extension in the oxidation incubation period of the AZ91Be60, as shown in Figure 9. As a result, the oxidation is mainly controlled by the outward diffusion of magnesium

cations through the (Mg,Be)O layer, which is too slow to allow a substantial oxidation rate.⁶⁹

The OR model is supported by the experimental findings (a) that beryllium is incorporated into the magnesium oxide solid solution to form (Mg,Be)O and (b) that (Mg,Be)O has a higher hardness. This means that the OR model can explain the better oxidation

Figure 12. The hardness values of each oxide as a function of the relative indentation depth h/d . The substrate hardness is represented by the dashed line. The solid curves were best fits of Equation 10. The actual hardness value of each oxide is derived from the curves at $h/d \rightarrow 0$. Reproduced from Tan *et al.*⁶⁹ with permission from Elsevier

resistance of beryllium-containing magnesium alloys. In addition, the incorporation of beryllium into (Mg,Be)O does mean that there is beryllium potentially available at the oxide grain boundaries to inhibit grain boundary diffusion of magnesium ion in the oxide.

6.4 Generalisation of the OR model

In order to generalise the OR model, 60 ppm (wt) beryllium was microalloyed into magnesium alloys: Mg–2Zn, Mg–2Sn, Mg–2Y, AS21, AM60, ZK20 and ZC63.⁵⁵ TGA, LTFO and continuous heating tests indicated that microalloying with 60 ppm (wt) beryllium effectively lowered the oxidation rates at 500°C and increased the T_i of Mg–2Zn, Mg–2Sn, AS21 and ZC63. Mg–2Zn–Be, Mg–2Sn–Be and AS21Be exhibited incubation periods over 300 min at 500°C and T_i values either close to or slightly above their respective liquidus temperatures, demonstrating the high ignition resistance of these alloys through microalloying with beryllium.^{55,103,144} Similarly, Mg–2Y exhibited a slow oxidation rate at 500°C and a high T_i of 647°C, similar to the oxidation behaviour of Mg–2Y–Be (containing 60 ppm (wt) Be).⁵⁵ All of these alloys had high hardness values of their initially formed oxide layers (Figure 13).⁵⁵ Microalloying with 60 ppm (wt) significantly reinforced the oxide on Mg–2Zn–Be, Mg–2Sn–Be, AS21Be and ZC63Be by increasing the hardness values by over two times. Similarly, the oxide layer on Mg–2Y exhibited the highest hardness value of 10.2 GPa among these alloys, and there was still a high hardness after alloying with beryllium of 8.1 GPa for Mg–2Y–Be.

In comparison, beryllium alloying provided a small influence on the oxidation resistance of ZK20 and AM60. ZK20Be and

Figure 13. The hardness values of the initially formed oxide layers on Mg–2Zn, Mg–2Y, Mg–2Sn, AS21, AM60, ZK20 and ZC63 with and without beryllium, measured by nanoindentation tests. Data retrieved from Tan *et al.*⁵⁵ with permission from Elsevier

AM60Be exhibited relatively short incubation periods of 60 and 20 min at 500°C, respectively. Their T_i values were marginally increased by less than 10°C compared with those of the counterpart alloys without beryllium. In agreement with the OR model, Figure 13 shows that the reinforcement effect was relatively small in ZK20Be and AM60Be.

These results confirmed that the oxidation resistance of magnesium alloys is closely related to the hardness of the initially formed oxide layer.⁵⁵ The high oxidation resistance of Mg–2Zn–Be, Mg–2Sn–Be, Mg–2Y, Mg–2Y–Be, AS21Be and ZC63Be is attributed to their surface oxide layers with high hardness values, which provided sufficient strength to delay layer cracking and therefore extended the protective incubation period. In contrast, there were insufficient reinforcement in the initially formed oxide layers on AM60Be and ZK20Be, so that both alloys exhibited low oxidation resistance.

In analogy with AZ91Be60, the reinforcement effect on Mg–2Zn–Be, Mg–2Sn–Be, AS21Be and ZC63Be was ascribed to the (Mg,Be)O solid solution.⁵⁵ This is consistent with the fact that each of these alloys exhibited a significantly extended incubation period and an increased T_i higher than its liquidus temperature. The TEM results shown in Figure 11 indicated that the surface accumulation of beryllium is the necessary condition to form (Mg,Be)O during oxidation. Inductively coupled plasma emission spectroscopy and field emission scanning electron microscopy (FESEM) showed that the zirconium and manganese solutes in ZK20Be and AM60Be chemically reacted with the alloyed beryllium, forming thermally stable beryllium-containing intermetallic compounds that arrested beryllium to diffuse outwards.⁵⁵ Therefore, the reinforcement effect was dramatically weakened. This suggested the incompatibility of beryllium with zirconium and manganese in improving the oxidation resistance of magnesium alloys.

Both Mg–2Y and Mg–2Y–Be exhibit high oxidation resistance and high oxide hardness values, indicating the same OR mechanism for the yttrium-containing magnesium alloys. The authors attributed such a significant OR effect to the formation of the yttrium (III) oxide layer ($R_{PB} = 1.13$).^{48,55,85} The somewhat decreased oxide hardness on Mg–2Y–Be was attributed to the influence of redundant aluminium introduced by the aluminium–5 wt.% beryllium master alloy during the alloy production.⁵⁵ FESEM showed the existence of thermostable Al_2Y within Mg–2Y–Be, which consumed yttrium and resulted in less yttrium (III) oxide on the alloy surface.¹⁴⁵ Hence, despite the formation of (Mg,Be)O, the reinforcement effect of yttrium was weakened, resulting in the decrease in the oxide hardness on Mg–2Y–Be. This also suggests that alloying with 2 wt.% yttrium provided greater reinforcement of the oxide on magnesium alloy compared with 60 ppm (wt) beryllium.

6.5 Evaluation of the OR model

The OR model differs from the previous models and quantifies the protective capacity of an oxide using the mechanical strength/hardness determined by nanoindentation and nanoscratch techniques. It has been shown that the oxidation resistance of magnesium alloys is closely related to the strength/hardness of the initially formed oxide layer. The formation of an oxide layer with higher mechanical strength and hardness is accompanied by a higher resistance to layer cracking and therefore an extended incubation period of the alloy.

The improved oxidation resistance of beryllium-containing magnesium alloys has been well explained by the reinforcement effect of beryllium on the initially formed magnesium oxide layer. TEM, nanoindentation and nanoscratch analyses provided evidence confirming the surface accumulation of beryllium and the formation of a fine-grained (Mg,Be)O solid solution with improved mechanical strength and hardness during the incubation period. Thus, the (Mg,Be)O layer exhibits a high protective capacity against cracking during oxidation, resulting in high oxidation resistance. However, the (Mg,Be)O structure has not been fully understood yet. Further investigation on the (Mg,Be)O structure at the atomic level – that is, the distribution of beryllium within the oxide layer – is needed to achieve an in-depth understanding of the reinforcement mechanism of beryllium-containing magnesium oxide layer.

The nanoindentation and nanoscratch techniques provide new approaches to understanding the oxidation resistance of magnesium alloys and to quantifying the protectability of the surface oxide. Based on the OR effect of beryllium and yttrium, it would be reasonable to expect that the OR effect would be valid for other elements such as calcium, strontium and REs in improving the oxidation resistance of magnesium alloys. Thus, further investigations are needed in this area to generalise the OR model in other magnesium alloy systems. Such studies will provide significant breakthroughs in developing alloys particularly for applications at elevated temperatures.

7. Synergistic effect of beryllium and calcium

Considering the cost and toxic nature of beryllium, the usage of beryllium has long been expected to be minimised in magnesium alloys.^{23,37,146,147} The authors' recent work¹²⁹ investigated the combined effect of beryllium and calcium on improving the oxidation resistance of magnesium alloys, trying to replace beryllium partially with calcium in oxidation-resistant magnesium alloys. Beryllium- and calcium-containing AZ91 alloys were produced by alloying beryllium (10, 20 and 60 ppm (wt)) and calcium (0.5 and 1.0 wt.%) into alloy melts. Both TGA and LTFO tests, and the determined T_i , evidenced that the combined addition of beryllium and calcium provided better protection to AZ91 than single addition of either beryllium or calcium.

Figure 14 shows the macroscopic surface appearances of the alloys after the LTFO at 400°C in air for 144 h.¹²⁹ Similar to the result presented in Figure 10, AZ91 was massively consumed by the catastrophic oxidation during the LTFO test, attributed to the non-protective nature of the magnesium oxide layer. Compared with AZ91, alloying with either calcium or beryllium resulted in less oxidation for AZX910 (0.5 wt.% calcium), AZX911 (1.0 wt.% calcium) and in particular AZ91Be60 (60 ppm (wt) beryllium) after the LTFO test, indicating an increase in oxidation resistance. However, the formation of black scales on AZX910 and AZX911 and oxide nodules on AZ91Be60 indicated insufficient protections of their surface oxide layer against long-term oxidation at high temperatures.^{13,58,62} In comparison, AZX910Be20 (0.5 wt.% calcium and 20 ppm (wt) beryllium), AZX911Be10 (1.0 wt.% calcium and 10 ppm (wt) beryllium), AZX911Be20 (1.0 wt.% calcium and 20 ppm (wt) beryllium), AZX910Be60 (0.5 wt.% calcium and 60 ppm (wt) beryllium) and AZX911Be60 (1.0 wt.% calcium and 60 ppm (wt) beryllium) showed no noticeable oxidation after the LTFO test, signifying the high oxidation resistance of these alloys. This result demonstrated that combined alloying with beryllium and calcium achieves better oxidation resistance of AZ91 compared with single alloying with either beryllium or calcium.

The synergistic effect of beryllium and calcium was also manifested in the ignition resistance of AZ91.¹²⁹ AZ91 had a T_i of 549°C. Alloying with either 60 ppm (wt) beryllium or 1.0 wt.% calcium significantly increased the T_i by ~110 to ~660°C. In comparison, with the combined addition of 20 ppm (wt) beryllium and 0.5 wt.% calcium, AZX910Be20 exhibited a higher T_i of 677°C. This result indicated that 0.5 wt.% calcium addition enabled a remarkable reduction in the beryllium usage in AZ91 by over 60% owing to the synergistic effect of beryllium and calcium. Further addition of either calcium or beryllium resulted in higher T_i . AZX911Be60, containing 60 ppm (wt) beryllium and 1.0 wt.% calcium, exhibited the highest T_i of 697°C among all studied alloys.

The FESEM results indicated that the synergistic effect of beryllium and calcium enabled the formation of a compact duplex oxide layer on AZX911Be60, which was composed of the outer reinforced magnesium oxide layer and the inner calcium

Figure 14. The macrographs of studied alloys after the LTFO test in air at 400°C for 144 h. Compared with AZ91, AZX910, AZX911 and AZ91Be60 showed less oxidation. However, the oxide nodules and black scales on these alloys indicated insufficient protection of their surface oxide layers. AZX910Be20, AZX911Be10, AZX911Be20, AZX910Be60 and AZX911Be60 were completely protected, indicating the achievement of high oxidation resistance of these alloys through combined addition of beryllium and calcium. Reproduced from Tan *et al.*¹²⁹ with permission from Elsevier

oxide-enriched magnesium oxide layer.¹²⁹ This duplex layer acted as a more protective barrier to suppress both the outward diffusion of magnesium vapour and the inward penetration of oxygen compared to the reinforced magnesium oxide monolayer and the calcium oxide-enriched magnesium oxide monolayer. Based on the OR model in beryllium-containing magnesium alloys, the reinforced magnesium oxide is expected to be the beryllium-enriched (Mg,Be)O solid solution, which formed through fast outward diffusion of beryllium ions and substitution of magnesium ions with beryllium ions within magnesium oxide.^{55,69,129,148} The reinforced calcium oxide–(Mg,Be)O duplex oxide layer provided higher mechanical strength/hardness to delay layer cracking during oxidation and therefore to extend effectively the oxidation incubation period. Both TEM characterisation and nanoindentation tests are needed to test this hypothesis.

8. Concluding discussion

Published studies indicated that the oxidation resistance of magnesium alloys is mainly governed by the incubation period, which is closely related to the crack resistance of the initially formed surface oxide layer. Layer cracking and the subsequent vigorous magnesium evaporation are major causes of catastrophic oxidation and eventual burning of magnesium alloys. Due to the incompact nature of the magnesium oxide layer ($R_{PB} = 0.81$), layer cracking is easily caused by the internal tensile stresses rising during oxidation. There is a critical temperature for the non-protective oxidation of magnesium alloys, which ranges from 400 to 450°C, depending on the alloy composition.

It has also been found that the geometrical factors, such as the surface roughness and section thickness of the sample, significantly influence the initial oxidation rate and the

flammability of magnesium alloys. A more rapid initial oxidation rate and a higher burning tendency are caused by a higher surface roughness and a thinner section thickness of the sample, respectively. Further investigations are needed to clarify the effects of geometrical factors and therefore to standardise the testing method of the oxidation behaviours of magnesium alloys.

Microstructural modification of the magnesium oxide layer into a more protective barrier layer has long been considered as the basic concept for improving the oxidation resistance of magnesium alloys. Alloying with elements such as calcium, beryllium, strontium and REs has been confirmed as an effective method for improving the oxidation resistance of magnesium alloys. Theoretical models such as R_{PB} , SAEE and REE have been widely used throughout the literature to rationalise the mechanism of the improved oxidation resistance. All these models only provide qualitative characterisations of the protectability of the oxide layer but cannot quantify the crack resistance of the surface oxide. In fact, high-temperature oxidation of magnesium alloys is a complex process that involves chemical reactions, ionic diffusion and phase transformation. Multiple mechanisms may work simultaneously to improve the crack resistance of the surface oxide layer. For example, the reported scattered yttrium-containing nodules and the continuous yttrium (III) oxide layer on yttrium-containing magnesium alloys indicate that both REE and R_{PB} mechanisms might synergistically contribute to the improved protective capacity of the surface oxide.^{21,39,149}

The recently proposed O_R model evidenced the correlation between the oxidation resistance of magnesium alloys with the crack resistance of their surface oxide layers, which is quantified by their mechanical strength/hardness. Experiment results confirmed that the improved oxidation resistance of beryllium-containing magnesium alloys was attributed to the formation of a fine-grained (Mg,Be)O layer with high crack resistance. This model provides a new concept in developing oxidation-resistant magnesium alloys. Techniques that can strengthen the oxide layers can improve the oxidation resistance of magnesium alloys.

Based on the current proposed models, the following criteria are formulated to select a potential alloying element X to improve the oxidation resistance of magnesium alloys.

- The element X should exhibit a high chemical activity.
- Surface accumulation of the element X can be obtained through ionic diffusion during oxidation. The compatibility of X and other solutes in the alloy should be taken into consideration to avoid the formation of X -containing thermostable intermetallic compounds.
- The surface oxide layer can be reinforced by the accumulated X on the alloy surface by either (a) forming a continuous oxide layer with high mechanical strength/hardness or (b) strengthening the initially formed magnesium oxide – for example, the formation of (Mg, X)O solid solution.

- Surface activity, solute solubility in magnesium and the REE of the element X are important factors that should also be considered during the alloy design.

At present, magnesium alloys with high ignition resistance are associated with high concentrations of calcium, strontium, yttrium, strontium, gadolinium, neodymium and dysprosium, which not only increases the alloy cost but also introduces high embrittlement susceptibilities, particularly in magnesium–aluminium-based alloys. Based on the proposed synergistic effect of beryllium and calcium, combined alloying magnesium with these alloying elements appears to be an effective method to attain the synergistic elemental effect, thereby reducing their usage in ignition-proof magnesium alloys. Further research is needed to validate their synergistic effect.

Research is also needed into the influence of alloying on the strength of the initially formed (Mg, X)O layer.

9. Conclusions

- The magnesium oxide layer, with an R_{PB} of 0.81, exhibits an incompact structure with internal tension stresses. The thin magnesium oxide layer provides some protection for the substrate at relatively low temperatures. However, at temperatures above 400–450°C, there is a non-protective oxidation stage with linear or power-law kinetics after the incubation period.
- The oxidation resistance of magnesium alloys is closely related to the protective incubation period, which is controlled by the crack resistance of the surface oxide layer. Within the incubation period, the oxidation rate is mainly governed by the ionic diffusion of magnesium ions, which is a slow process.
- The non-protective oxidation is associated with the fast, outward diffusion of magnesium vapour after surface oxide layer cracking. The nodular growth of oxide represents the end of the protective incubation period and the onset of non-protective oxidation. Continuing oxidation or further increasing the temperature results in catastrophic oxidation and subsequent burning of magnesium alloys.
- Alloying elements (including calcium, beryllium, strontium and REs) decrease the oxidation rate and increase the T_i of magnesium alloys by forming a more protective oxide layer on the alloy surface to suppress magnesium vapourisation and oxygen penetration.
- The R_{PB} , SAEE and REE models provide qualitative descriptions of the protective capacities of the surface oxide layer on magnesium alloys. These models provide some indications of the underlying mechanism of how the alloying elements affect the oxidation resistance of magnesium alloys.
- The O_R model establishes the relation between the oxidation resistance of magnesium alloys with the mechanical strength of their surface oxide layers. A surface oxide layer with a higher mechanical strength provides a higher resistance to layer cracking during oxidation, extending the incubation period as a consequence.

- Trace addition of beryllium, even at ppm concentrations, provides significant reinforcement to the initially formed magnesium oxide layer by forming a fine-grained (Mg,Be)O solid solution. The oxide strengthening effect of beryllium effectively extends the protective incubation period of magnesium alloys.
- Combined alloying of magnesium alloys with calcium and beryllium achieves a synergistic elemental effect that significantly reduces the usage of the expensive and poisonous beryllium.
- Research is needed into the influence of alloying on the strength of the initially formed (Mg,X)O layer.

Acknowledgement

The authors are very grateful to the University of Queensland Collaboration and Industry Engagement Fund grant for funding support (number 2014003109).

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