

A REVIEW OF WORKABILITY OF WROUGHT MAGNESIUM ALLOYS

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ABSTRACT

Despite being the lightest structural metal, magnesium alloys exhibited poor workability at low temperatures due to their hexagonal closed-packed crystal structure, consequently required them to be processed at elevated temperature. Their highly affinity to oxygen lead them to an easy oxidation. Moreover, they are poor corrosion resistance, poor creep resistance as well as fatigue failure but these can be improved by various techniques of surface treatments and alloying additions. Commercial wrought magnesium alloy grades, its mechanical properties as well as its workability at elevated temperatures are presented. Recent literatures showed that the workability of these alloys is increased at temperatures ranging from 100 to 350⁰C, 200 to 400 to 300 to 500⁰C and for AZ, ZK and WE alloy systems, respectively. The purpose of this paper is to review and reveal the issues in processing of wrought magnesium alloys.

KEYWORDS: Wrought magnesium alloys; mechanical properties; workability

INTRODUCTION

In recent years the interest in magnesium alloy has grown dramatically in research community to identify new manufacturing technology via near-net-shape manufacturing technology and extending the areas of their applications.

For its lightness and recyclability, many researches has push to the limit to explored the potential of magnesium and its alloys as replacement for plastics, aluminum and steel technology especially in highly demand in automotive sector (Gerald, 2003; Schumann and Freidrich, 2003; Alan, 2003; Tadakata and Masami, 2003). In natural resources magnesium is plentiful element on earth's crust and seawater in most countries makes this inherited material considerably inexhaustible and recyclable (Mordike and Ebert 2001). However, its application was limited mainly due to its poor workability at cold working temperatures, weak corrosion resistance, and poor thermal effects at elevated temperature, highly chemical reactivity and considerably high cost of material. The processing techniques of magnesium alloys is considerably challenging due to its low melting point, their atomic arrangements of hexagonal close-packed (HCP) crystal structure (William and David 2008) and their well known as natural corrosion behavior in air. Viewing the literatures published in the academic journals, it can be seen that the research on wrought magnesium alloys mainly focused on the plastic deformation behavior and the effects of deformation conditions on microstructure and its mechanical properties. This report is intent to discuss the issues of processing magnesium alloys in air at elevated temperatures. Subjects will includes its mechanical properties, the effect of temperature on its workability as well as thermal and corrosive aspects. In the present study, some of wrought magnesium alloys of AZ, ZK and WE alloy systems were presented in order to find out the issues relating to their workability on various deformation conditions.

MAGNESIUM AND ITS ALLOYS

Magnesium (Mg), its atomic number is 12, is the lightest among the metals for structural application. It has density 1.74 g/cm^3 , which is $2/3$ of that of aluminum and a quarter of that of steel. It also has considerably low melting temperature of 649°C , slightly lower than that of aluminum. Mg alloys, like other alloys with hexagonal closed-packed (HCP) crystal structures (William and David 2008), are much more workable at elevated temperatures than at room temperature. The advantages of Mg, among other, tougher than plastic, better damping capacity as compared to cast iron and aluminum, electromagnetic interference (EMI) shielding than that of plastic, heat dissipation much higher than that of plastics, absorb vibration energy effectively and recyclability (Mordike and Ebert 2001).

Their mechanical properties varies depends on alloys composition and its weight percentages constitute in the alloying system. Table 1 shows the mechanical properties for a selection of wrought Mg alloys at room temperature.

Table 1 Room temperature mechanical properties of selected wrought Mg alloys (Czerwinski 2008, Toros et. al. 2008, Yang et. al. 2008)

Alloy grade	Temper	Specific density, g/cm ³	UTS, MPa	Tensile YS, MPa	Compressive YS, MPa	Elongation %	Hardness HB
AM1A	rolled	1.77	240	180	76	7	48
ZM21	forged	1.80	200	124		9	
AZ31	extruded	1.77	250	180	97	15	49
AZ61	forged	1.80	300	220	125	12	55
AZ80	forged	1.80	330	230	170	12	
ZK21	rolled	1.80	260	195	135	4	
ZK40	extruded	1.83	275	250	140	4	
ZK60	extruded	1.83	340	260	230	11	80
WE43	extruded	1.85	270	195		15	
WE54	extruded	1.85	315	215		10	85

The selection of appropriate commercial alloy grade is significantly important for certain process being used because the chemical contents represent the process capabilities and final product microstructure. A selected alloys grades and key features of Mg alloys for wrought alloy were summarized by Czerwinski 2008 as exhibited in Table 2.

Table 2 Classification of selected wrought Mg alloys (Czerwinski 2008)

Alloy group	Alloy grade	Al	Mn	Zr	Zn	Other	Solid to liquid, °C	Key features
Mg–Mn–Al–Zn	AZ10	1.2	0.2		0.4		630–645	Low cost extrusion alloy with moderate strength and high elongation
	AZ21	2.0	0.15		1.2		Liquid 645	Extrusions
	AZ31	3.0	0.3		1.0		605–630	General purpose alloy with moderate strength
	AZ61	6.5	0.3		1.0		525–620	General purpose extrusions with good properties and moderate cost
	AZ80	8.5	0.12		0.5		490–610	Extruded products and press forgings, heat treatable
Mg–Zn–Zr	ZK21			0.45	2.3		626–642	Moderate strength extrusion alloy with good weldability
	ZK40			0.45	4.0			High yield extrusion alloy, lower strength than ZK60
	ZK60			0.45	5.5		520–635	Extruded products and press forgings with high strength and good ductility
Mg–Y–RE	WE43			0.7		4.0Y, 3.4RE	540–640	High temperature creep resistance up to 300°C, long term exposure up to 200°C
	WE54			0.7		5.2Y, 3.0RE	545–640	High strength, fully heat treatable, application to 300°C

THE EFFECTS OF WORKING TEMPERATURES AND STRAIN RATES

The principle in processing Mg alloys is temperature (ASM Handbook 1993). In order to achieve favourable mechanical properties, one must really understand the Mg alloys behaviour at different deformation conditions namely temperature and strain rate. It also extremely important for researcher able to correlate the effect of changing these deformation conditions on the resulting microstructure and its mechanical properties. Zhang et. al. (2006) studied the formability of AZ31 Mg alloy sheets on mechanical properties during hot-rolling process. They observed that the mechanical properties of the rolled AZ31 Mg alloy changed with temperature, as temperature increased, tensile strength decreased while elongation increased. The relationship was illustrated in Figure 1, showing the mechanical properties of AZ31 Mg alloy changed as a function of temperature at a constant strain rate. On the other hand, the elongation decreased with the increased of strain rates at constant temperature. These properties also demonstrated that the AZ31 Mg alloys was softening and enhanced its ductility with temperatures.

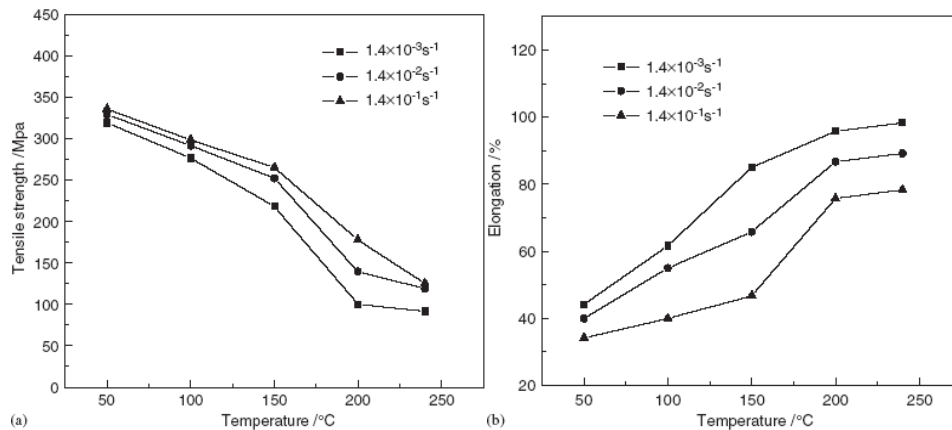


Figure 1 Influence of strain rate on tensile strength (a) and elongation (b) of AZ31 Mg alloy. (Zhang et al. 2006)

The effects of working temperatures and strain rate on workability of selected wrought Mg alloy systems were illustrated in Table 3-5. From the literatures reviewed, most investigation of AZ alloy system processing at temperatures higher than 100°C but below 350°C. Cold working temperature is limited to prevent cracking while creep failure occurred during hot working. The workability of drawing process is slightly lower than 200°C. Iwanaga et. al. (2004) has reported that AZ31 Mg alloy can achieved good deep drawability at temperature as low as 175°C by applying M_0S_2 lubricant. While, Xia et. al.

(2005) reported AZ31 Mg alloy can be processed smoothly as low as 100⁰C owing to the ultra fine grain size of 0.2~0.5 μ m. For ZK alloy system, the workability deformation temperatures in the range of 200 to 400⁰C while WE alloy system in the range of 300 to 500⁰C. In comparison, AZ and ZK alloy systems are softer than that of WE alloy system. Moreover, WE alloy system exhibits the better creep resistance than that of AZ and ZK alloy system.

Table 3 Summary of workabilty of AZ alloying systems on different routes

References	Processed	Temp., ⁰ C	Strain Rate, s ⁻¹	Remarks
AZ31 Mg alloy				
Vespa et. al. (2008)	as-hot rolled	400	0.1 to 10 ⁻³	Dynamic recrystallization (DRX) at lower strain rates
Zhang et. al. 2006)	extruded	350	5	DRX grain grows up rapidly as temp. elevates to 350 ⁰ C
Spigarelli et. al. 2007)	as-extruded	300	5 and 0.05	Fully recrystallized structure when grain size is fine
Zhang et. al. (2006)	hot-rolling	240	1.4x10 ⁻²	
Zhang et. al. (2006)	Drawing	200	1.4x10 ⁻³	Drawing ratio, DR2.6
Iwanaga et al. (2004)	Drawing	175	2.8x10 ⁻³	M ₀ S ₂ lubricant
Yoshihara et al. (2003)	Drawing	400		DR5.0. Demonstrate AZ31 softening with temp.
Chen and Huang (2003)	Drawing	300		elongation of 58% at 400 ⁰ C
Watanabe et al. (2007)	Drawing	200		Elongation of 5 %
Yang et. al. (2009)	hot compression	250 to 400	0.01 and 10	
Zhang et. al. (2008)	Extrusion	350		Enhanced ductility but decreased tensile strength
Liang et. al. (2008)	Cold-extrusion	RT	1x10 ⁻³	2 μ m. Improved strength but doesn't improve elongation
Xia et. al. (2005)	ECAP	100	1x10 ⁻³	Using back pressure and UFG of 0.2~0.5 μ m
Kang et. al. (2008)	ECAP	200 to 350	10 ⁻⁴ to 10 ⁻¹	3 μ m. Improved the fracture elongation but decreased strength
Zuberova et. al. (2007)	hot-rolled+ ECAP	400, 200	10 ⁻³	improvement in mechanical properties
Mallick et. al. (2009)	Cold-compaction + tensile	RT, 250	4x10 ⁻⁴	PM-AZ31, sintered 450 ⁰ C in an argon
AZ61 Mg alloy				
Niu et. al. (2007)	Warm compression	200 to 400	0.01 to 10	DRX at higher temp., plasticity increased
Skubisz et. al. (2006)	forged	350		Showing cracks formation at lower temperature
Yamin et al. (2007)	Extrusion	350		Good plasticity with colorless lubricant.
Chandrasekaran and John (2004)	Forward extrusion	200, 300		AZ31 at 200 ⁰ C while AZ61 and ZK60 at 300 ⁰ C
Valle et. al. (2003)	Hot rolling	375		85% thickness reduction

Valle et. al. (2005)	accumulative roll bonding	300		50% thickness reduction
Doege and Droder (2001)	Drawing	200 (AZ31), 250 (AZ61)		AZ31 have better ductile behavior than AZ61.
Huang et al. (2009)	Rolled	250		Exhibits a superior stretch formability
AZ80 Mg alloy				
Haroush et. al. (2008)	Extrusion	350		Exhibits cracks due to corrosion attacks at 300 and 350 ⁰ C.
Shahzad and Wagner (2009)	Extrusion	175 to 350		Lower extrusion ratio exhibits superior in strength
Huang et. al. (2009)	Rolling	430		Exhibited high strength of 329 MPa and improved 25% ductility

Table 4 Summary of workability of ZK alloy systems on different routes

References	Processed	Temp., ⁰ C	Strain Rate, s ⁻¹	Remarks
Wang et. al. (2007)	squeeze cast	375	0.001	smooth cast
Yang et. al. (2009)	deformation	200 and 400	10 and 0.01	without fractured
Chandrase-karan and John (2004)	Forward extrusion	300		Smooth extruded

Table 5 Summary of workability of WE alloy systems on different routes

References	Processed	Temp., ⁰ C	Strain Rate, s ⁻¹	Remarks
Gao et. al. (2008)	hot compression	340-460 ⁰ C	0.01-1	Dynamic recrystallization during softening
Sanchez et al. (1996)	extrusion	300	3.5x10 ⁻⁵ to 7x10 ⁻³	WE43 and WE54 exhibited better creep resistance

This studies has eventually reveals that AZ alloys are ductile material than ZK and WE Mg alloys. Currently, Mg-RE-Zr alloys are said to be the best mechanical properties both at ambient and elevated temperature. From the literatures reviewed, WE alloy is recommended for use up to 300⁰C. Moreover, the effect of rare earth elements such as gadolinium, dysprosium and yttrium on the microstructure and mechanical properties have been found to give increased yield strength and creep resistance (Yang et. al. 2008).

In case of superplasticity behavior, Yin et. al. (2005) reported that apart from temperature and grain size, strain rate is also play an important role influencing superplasticity in AZ31 Mg alloy. Their studies showed that maximum elongation of about 360% is achieved at 400°C under lower strain rate of $0.7 \times 10^{-3} \text{s}^{-1}$. Watanabe and Fukusumi (2008) found that high temperature deformation of 500°C with lower strain rate $1 \times 10^{-5} \text{s}^{-1}$ exhibited higher ductility and lower strength. Yang et. al. (2008) reported that the key of getting superplasticity in an Mg alloy is to obtain uniform fined grained microstructure. Therefore, from the literatures, to behave in a superplasticity manner, Mg alloys should be processed at high deformation temperatures, lower strain rates range and relatively coarse grain size. However, superplasticity can be achieved at high strain rates with ultra fine grain size (Lin et. al. 2005). To get pictorial explanation of plasticity behavior of AZ Mg alloy, the influence of strain rate as function of temperature on elongation is illustrated in Figure 2.

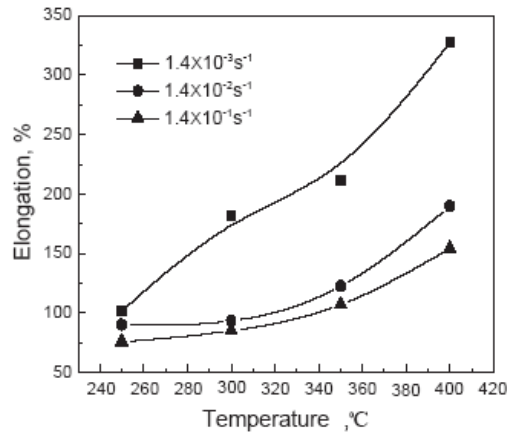


Figure 2 Influence of temperature on elongation at various strain rates (Yin et. al. 2005)

The effects of elevated temperatures and strain rates on superplasticity for selected wrought Mg alloys were illustrated in Table 6. Viewing from these literatures, it has eventually reveals that AZ and ZK alloy systems are ductile material than that of WE alloy systems. For WE alloy systems to have ductile behavior, they required higher temperature as low as 400°C.

Table 6 Summarized of superplasticity characteristic for selected wrought Mg alloys

References	Alloy Grade	Processed	Grain size, μm	Deformation Temp., $^{\circ}\text{C}$	Strain Rate, s^{-1}	Elongation, %
Lin et. al. (2005)	AZ31	EX + ECAP	0.7	300, 200	1.0×10^{-4}	460
Watanabe and Fukusumi (2008)	AZ31	EX	40	500	1×10^{-5}	596
Yin et. al. (2005)	AZ31	EX	4.5	400	0.7×10^{-3}	360
Valle et. al. (2003)	AZ61	Hot rolling	15.2	250		>T
Miyahara et. al. (2006)	AZ61	EX + ECAP		200	3.3×10^{-4}	1320
Watanabe et. al. (1999)	AZ61		20	375	3×10^{-5}	460
Huang et. al. (2009)	AZ80	rolled	7	300		25
Yakubtsov et. al. 2008	AZ80	HT		420	1.5×10^{-4}	>T
Figueiredo and Langdon (2006)	ZK60	ECAP	0.8	200	2.0×10^{-4}	1310
Lapovok et. al. (2005)	ZK60	ECAE	1	220	3×10^{-4}	2040
Watanabe et. al. (2003)	ZK60	EX+E CAE	1.4	200	1×10^{-5}	1083
Bussiba et. al. (2001)	AZ31, ZK60	EX	15, 2+25	450	10^{-5} to 10^{-1}	ZK60>AZ31
Watanabe et al. (1999)	ZK60	PM	0.05	200	1×10^{-5}	283
Nieh and Wadsworth (1995)	ZK60/SiC/17p	PM	0.3	450	1.3	360
Liu et. al. (2008)	PM-WE54	EX+E CAE	4.4	400	1×10^{-3}	600
Garces et. al. (2006)	PM-WE54	EX	0.65	400	10^{-1}	450
Nakashima et. al. (2000)	PM-WE54	EX	0.5	500	1.7×10^{-1}	346

OXIDATION, CREEP AND FATIGUE FAILURE.

Another major obstacle in processing magnesium is their high affinity of magnesium to oxygen makes them easy to oxidation. The oxidation spontaneously formed a thin layer on the surface of magnesium and its alloys upon exposed in air. Commonly processing stages such as casting, injection molding, powder metallurgy and etc. were directly associated with elevated temperatures exposed them to oxidation. This may refers to feedstock preparation, service temperatures, molding pressures, heat treatment, sintering and etc. Norbert and Martin 2008 reported oxidation is one of the major obstacle in processing magnesium in

powder injection molding. They found that the lower volume of magnesium oxide compared to the base material created blisters and crack easily. Moreover, the thin oxide layer formed on the surface of Mg will act as retention to the smooth process of densification during sintering. Besides air, contact with water vapor leads also to an oxide growth, but the rate of reaction is much slower because the oxide layer contains large amounts of hydroxide species (Czerwinski 2002). Their poor corrosion resistance materials, however, can be improved by coating and surface modification techniques. One of the most effective ways, or maybe the simplest, to prevent corrosion is to coat the Mg alloys from contact with environment. The types of corrosion in magnesium alloys were reviewed and discussed in detailed by Zeng et. al. 2006. The corrosion types are galvanic corrosion, pitting corrosion, intergranular corrosion, fillform corrosion, crevice corrosion, stress corrosion cracking and corrosion fatigue. Gray and Luan 2002 reviewed comprehensively the typical type of coating and surface modification techniques. The review discussed, among others, such as anodizing, electrochemical plating, physical evaporation, cladding and organic coatings. Wu et. al. (2008) reported that a loose oxide film was spontaneously formed on the surface of as-polished AZ31 Mg alloy. To overcome this problem, they applied aluminium PVD-coating on a mechanically polished AZ31 Mg alloy as the barrier to corrosion resistance. The studies, however, does not fully react as corrosion resistance as the aluminium coating still suffered from severe corrosion. Yue et. al. (1997) reported that surface treatment on PM-ZK60/SiC composite by using KrF excimer laser as well as the refinement of the surface microstructure can significantly improved the corrosion resistance.

Reviewing from the literatures, most of the processing techniques of Mg alloy were exceeded $0.4T_m$, whereby T_m is melting tempertaure, creep occurance is unavoidable. In forming, creep failure is the clear factor for cracking defects. However, thanks to the development of highly creep resistant Mg alloys of rare earth additions such as yttrium, gadolinium and dysprosium, the operation at temperatures above 250°C is feasible (Yang et. al. 2008). Mordike (2001) has developed highly creep resistant Mg alloys that operated at temperatures of 300°C . He suggested the additions Sc, Gd, Mn, Ca and Ce in WE alloy systems have influences to creep resistance. Apart from poor corrosion resistance and poor creep resistance, Mg alloys were also has low fatigue resistance (Lin et. al. 2008, Zeng et. al. 2009). However, the low fatigue strength can be improved by mechanical surface treatments (Zhang and Lindermann 2005) and by an addition of appropriate ratio of manganese contents (Sabrina et al. 2006).

CONCLUSION

In this paper, the workability issues in wrought Mg alloys were reviewed. The principle of processing wrought Mg alloys is temperature. The workability at elevated temperature, strain rate and grain size on mechanical properties were investigated and they were dependent variables. Summarizing the literatures published in the academic journals, the workability deformation temperature for wrought Mg alloys were justified. The requirements for wrought Mg alloy to become superplastic includes a fine grain size, typically below 10 μ m, low strain rate as well as maintain the fine grain structure at the high temperature. Their corrosion resistance can be improved by various surface modification techniques. Their creep failure can be reduced and/or eliminated by using highly creep resistance Mg alloys. Their fatigue strength can be improved by an appropriate addition of manganese contents. The finding of this paper is very useful for the selection of wrought Mg alloy and their feasible for potential near-net-shape manufacturing technology.

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