# Deformability and strengthening of superlight Mg-Li alloys

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#### Abstract

Deformability of Mg-Li alloys at room temperature and heat treatment characteristics of superlight Mg-8~30mass%Li alloys containing aluminum will be reviewed. Li addition enhances the deformability of magnesium. Particularly, the deformability of magnesium increases remarkably by the addition of lithium of more than 6mass%, which crystallizes lithium solid solution (β phase with bcc lattice). Al, Zn or Ag addition to Mg-Li alloys leads to quenching hardenability due to solutionizing to β phase, and age hardening by spinodal decomposition into the additives+Li rich and poor phases from supersaturated solid solution. Alloying elements are solutionized to some extent and the growth of recrystallized grains is restricted by shortening the holding time at 300°C or 350°C. Consequently, high strength and reasonable elongation can be obtained by such a heat treatment.

#### Riassunto

Verranno esaminate sia la deformabilità a temperatura ambiente delle leghe Mg-Li sia le caratteristiche di trattamento termico delle leghe superleggere Mg-8~30 mass%Li contenenti Al. L'aggiunta del Li aumenta la deformabilità del Mg, soprattutto con l'aggiunta del Li di più del 6mass%, il quale cristallizza la soluzione solida di Li (fase ß con reticolo bcc). L'aggiunta alle leghe Mg-Li dell'Al, dello Zn o dell'Ag porta all'aumento della durezza dovuto alla conversione in soluzione alla fase ß, nonché all'aumento con l'invecchiamento per la decomposizione spinodale negli additivi con fasi ricche ed povere di +Li dalla soluzione solida supersatura. Gli elementi alliganti vengono in una certa misura convertiti in soluzione e la crescita dei grani ricristallizati viene limitata abbreviando il tempo di permanenza ai 300° o ai 350°C. Di conseguenza un tale trattamento termico è in grado di conferire l'alta resistenza ed un allungamento ragionevole.

## INTRODUCTION

Recently, requirements for lighter structural metallic materials have been enhanced from the viewpoint of saving energy and environmental protection on the earth. Mg-Li based alloys are very attractive for such applications because of their potential for reducing the weight of various components. In general, both density and strength of Mg-Li binary alloy decreases with an increase in Li content [1,2].

In this paper, the deformability of Mg-Li alloys at room temperature, and heat treatment characteristics of superlight Mg8~30mass%Li alloys containing aluminum will be focused. Deformability significantly depends on constituent phases, particularly matrix phases [1-3]. Since the matrix phases of Mg-Li alloys are classified into three types, We will consider the corresponding deformation mechanisms. Furthermore, quenching hardenability, spinodal decomposition and strengthening methods for Mg-Li alloys by the metastable precipitates reported up to date will be reviewed.

# EFFECT OF LITHIUM ADDITION ON THE DEFORMABILITY

### (a) Pure Magnesium

Main deformation mechanism in pure magnesium crystal has been reported to be the  $(1000) < 11\overline{2}0$ > basal slip, the  $\{10\overline{1}0\} < 11\overline{2}0$ > prismatic slip, the  $\{10\overline{1}1\} < 11\overline{2}0$ > pyramidal slip and the  $\{10\overline{1}2\} < 10\overline{1}1$ > twining [4].

Fig. 1 shows shear stress-shear strain curves for the basal and non-basal slip systems in pure magnesium crystal [5]. The basal slip has a wide easy glide region more than 100% in shear strain, whereas the non-basal slip has no plastic region corresponding to this easy glide and rapid work hardening occurs at the early stage of deformation. Below 100°C, this rapid hardening continues up to fracture and the elongation to fracture is limited to only several percent. At above 200°C, however, the work hardening rate becomes practically zero during further deformation beyond a certain strain. With rising temperature, this critical strain decreases and the ductility is remarkably enhanced.

# (b) Mg-Li alloys

By an addition of lithium to magnesium, as shown in Fig. 2

[6], critical resolved shear stress for basal slip increases linearly with lithium concentration by solid solution hardening. The critical resolved shear stress for pure magnesium is almost independent of the test temperature above room temperature, while the stresses for Mg-Li alloys begin to decrease with an increase in temperature above about 200°C. This decrease with temperature is more remarkable, as the lithium concentration is higher.

In contrast, as shown in Fig. 3 [6], the critical shear stress for non-basal slip is found presumably to decrease at temperature below 200°C by alloying with lithium. Yoshinaga [6] has reported that the abnormal behavior observed in nonbasal slip might be quantitatively interpreted by cross glide mechanism.

Fig. 4 shows changes in lattice parameters of magnesium solid solution with an addition of various elements [7]. Lithium decreases both **a** and **c** spacing in comparison with other elements. Particularly, **c** spacings is remarkably reduced by lithium addition. Consequently, as shown in Fig. 5, the axis ratio is significantly decreased with an increase in lithium content compared with other elements. This may result in the easy cross glide of non-basal slip.

Fig. 6 shows stress-strain curves of Mg-Li alloys with compositional ranges from 0 to 12.5mass%Li [8]. From these curves it can be seen that for pure magnesium and the



Figure 1: Shear stress-strain curves for the non-basal and basal slip systems in pure magnesium [5]



Figure 2: Temperature dependence of the critical resolved shear stress for basal slip in Mg-Li alloys [6]



Figure 3: Effect of Li addition on the critical resolved shear stress for nonbasal slip in magnesium [6]

1.2mass%Li alloy the effect of adding a small amount of lithium to magnesium gives the expected increases in yield strength and rate of strain hardening which are known to accompany solid solution alloying. However, as more lithium is added to reach 4.2mass% the yield strength is apparently reduced and the rate of strain hardening is also lowered, the stress-strain curve being below that for pure magnesium. This is in agreement with the work of other researchers. They found that increasing the lithium content led to the introduction of prismatic slip in addition to the basal slip that occurs in pure magnesium. The presence of lithium reduces the critical resolved shear stress for prismatic slip and this in turn reduces the yield strength by allowing larger amounts of plastic strain to occur at lower stresses. The change in microstructure from hcp to bcc, as lithium content increases from 8.4mass% to 12.5mass%, is accompanied by an increase in ductility.

Similar tendency can be seen in cold rolling of more than 8mass%Li containing Mg alloys, as shown in Fig. 7 [1]. Hardness and rate of work hardening during cold rolling are the highest in the 8mass%Li alloy with  $\alpha$ + $\beta$  matrix phase, which results in the edge cracks. Such a behavior is due to the presence of  $\alpha$  phase. In the alloys containing  $\beta$  phase as a matrix phase, hardness and rate of work hardening of Mg-



Figure 4: Lattice parameters in magnesium solid solution containing various solutes[7]



Figure 5: Axis ratio (c/a) in magnesium solid solution containing various solutes

Li alloys increases as the magnesium content increases because of solid solution hardening of  $\beta$  phase occurring by a magnesium addition. This means that the addition of more lithium to magnesium leads to no work hardening such as in Mg-38mass%Li alloy [9].

Above-mentioned contents about the deformability of Mg-Li alloys are summarized as follows: Deformability of Mg alloy is remarkably improved by Li addition. In the addition of Li less than 6mass%Li, both yield stress and rate of strain hardening are lowered with an increase in lithium content. This is because the presence of lithium reduces the critical resolved shear stress for non-basal slip. Consequently, increasing the lithium content leads to the introduction of nonbasal slip in addition to the basal slip occurring in pure magnesium and, therefore, enhances the deformability of Mg-Li alloy. The change in constituent phases from hcp to bcc as Li content increases from 8 to 12mass% is accompanied by an increase in ductility. In that case as lesser magnesium, that is, as more lithium is contained in  $\beta$  phase, deformability of Mg-Li alloys improves owing to the decrease of solid solution hardening in  $\beta$  phase by magnesium.



Figure 6: Stress-strain curves for Mg-Li alloys [8]. The strain to failure for Mg-8.4mass%Li was 33% and for Mg-12.5mass%Li was 45%

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Figure 7: Relationships between Vickers hardness number and reduction in thickness for Mg-Li alloys during cold rolling [1]

# STRENGTHENING METHODS FOR MG-LI ALLOYS

#### (a) Conventional Strengthening Methods

Many researchers have confirmed that Al, Zn and Ag additions lead to a remarkable age hardening [10-16]. The precipitate contributing to age hardening is called  $\theta$  phase, which has chemical formula of MgLi<sub>2</sub>X and crystal structure of FCC of NaTl type [10-12]. Here X represents an alloying element such as Al, Zn, Ag.

In general, Mg-Li alloys are superlight and have high specific strength. Furthermore, an appearance of Li solid solution with bcc structure by addition of more than 6 mass% enhances workability at room temperature. A large amount of the Li addition, however, reduces the strength. Needless to say, aluminum is well known to be a strengthening element for Mg-Li alloys. Thus, in this study, 7.5~12.5mass% Al as a third alloying element is added to Mg-17.5~22.5mass%Li alloy, in order to improve strength, and their quenching hardenability, aging characteristics and tensile properties are investigated.

#### (b) Experimental Procedure

The alloys used in this study were prepared by melting in vacuum high frequency induction furnace as shown in Fig. 8 in argon atmosphere [9]. Table 1 shows the nominal composition and density of Mg-Li-Al alloys prepared for the present study [17, 18]. The amount of aluminum addition was close to the solubility limit in the Mg-Li-Al ternary alloy phase diagram [19]. The specific gravity is in the ranges of 1.20 to 1.34 and is lighter than that of commercial Mg-Li alloys. Rolling was performed with a reduction ratio of about 10% per pass at 150°C.

Heat treatment was conducted employing the hot-rolled specimens in order to investigate both quenching hardenability and age-hardening characteristics at room temperature and 50°C. Isothermal holding temperature and time

dependencies of quenching hardenability were evaluated. The quenching hardenability was evaluated in the range from 100 to 350°C with increasing steps of 50°C. The specimens were kept at given temperatures for 1h or at 300°C for given times and followed by rapid cooling by immersing the sample into oil. The hardness was measured within 15min after quenching to prevent age hardening at room temperature. Furthermore, aging characteristics at room temperature and 50°C were also investigated. The microstructural analyses and lattice parameter measurement were conducted using X-ray diffraction technique.

Tensile test specimens of 2mm thickness×4mm width×20mm gauge length were machined from the hot-rolled specimens. The tensile testing was carried out using an Instron type tensile tester at room temperature. Tensile testing was performed within 16h after quenching because the hardness of the quenched specimen decreases after16h. The fracture surfaces were observed using scanning electron microscope (SEM).

#### TABLE 1 - Nominal composition and specific gravity of investigated Mg-Li-Al ternary alloys

Nominal composition (mass%)	Specific gravity Theoretical Measured	
Mg-17.5%Li-7.5%Al	1.28	1.31
Mg-17.5%Li-10.0%Al	1.29	1.33
Mg-17.5%Li-12.5%Al	1.29	1.34
Mg-20.0%Li-7.5%Al	1.24	1.26
Mg-20.0%Li-10.0%Al	1.25	1.28
Mg-20.0%Li-12.5%Al	1.24	1.28
Mg-22.5%Li-7.5%Al	1.20	1.20
Mg-22.5%Li-10.0%Al	1.21	1.21
Mg-22.5%Li-12.5%Al	1.20	1.23
		100



Figure 8: Melting and casting method for Mg-Li-Al alloys [9] Vol. 16 (1-2) (1998)

# (c) Quenching Hardenability

Fig. 9 shows the effect of quenching temperature on the hardness of specimens [17,18]. Specimens were quenched after isothermal holding at the respective temperatures for 1h. The hardness of specimens rises in the case where the specimens are quenched from temperatures higher than 200°C. In particular, specimens quenched from over 300°C show a remarkable hardening. Hardness increases with an increase in Al content.

Fig. 10 shows the dependence of the hardness of specimens on holding time [17,18]. Specimens were quenched after isothermal holding at 300°C for the respective time. The hardness of all investigated specimens is proportional to the holding time in the range between 5 to 30s, but remains constant for longer holding times. The time to reach maximum hardness becomes shorter as the aluminum content decreases. Similar quenching hardenability has been confirmed in Mg-30mass%Li alloys containing large amounts of Al or Zn [20] and Mg-8 and 13mass%Li alloys containing large amounts of Al or Ag [15].

Fig. 11 shows the results of X-ray diffraction analyses for as-rolled and as-quenched Mg-20mass%Li-12.5mass%A1 alloy [17,18]. As-quenched specimen exhibits diffraction peaks of AlLi, Al<sub>2</sub>Li<sub>3</sub> and Al<sub>4</sub>Li<sub>6</sub> in addition to those of Li solid solution. These additional peaks are lowered by quenching after isothermal holding at a temperature higher than 250°C as shown in (b) and (c). In particular, the specimen has only peaks of Li solid solution without those of the other compounds by quenching after isothermal holding at 350°C for 1 h as shown in (c). From these results the obtained quenching hardenability may be caused by an increase of soluble Al and Mg in Li solid solution. Furthermore, as shown in the diffraction peak from (211) plane, it is clearly found that the peaks of Li solid solution shift to a higher angle by quenching after isothermal holding. A similar phenomenon is also confirmed in the case where the specimens are quenched after isothermal holding for a long time at 300°C. This means that lattice parameter of Li solid solution becomes small because Al with smaller atomic radius than that of Mg and Li is largely solutionized.



Figure 9: Effect of quenching temperatures on Vickers hardness of asquenched specimens [17,18]. Specimens were held at quenching temperatures for 1h and then oil-quenched



Figure 10: Effect of isothermal holding times on Vickers hardness of asquenched specimens [17,18]. Specimens were held at 300°C for the given times and then oil-quenched

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Figure 11: Results of X-ray analyses of Mg-20mass%Li-12.5mass%Al alloys. Specimens were oil-quenched after the isothermal holding at the given temperatures for 1h [17,18]

Fig. 12 shows the dependence of the lattice parameters of Li solid solution on the quenching temperature and holding time [17,18]. The lattice parameters are calculated employing diffraction peaks from (211) planes of lithium solid solution. The lattice parameters rapidly decrease with a rise of the holding temperatures in the range above 200°C. Also, in the case of isothermal holding at 300°C the lattice parameters of all investigated alloys significantly decrease with an increase of the holding time up to 15s, and then slowly decrease for a longer holding time. The decrease of the lattice parameter corresponds well to the increase of hardness. The theoretical lattice parameter is in the range of 0.3491~0.3495nm on assumption that all of aluminum at-



Figure 12: Dependencies of lattice parameter of lithium solid solution on (a) quenching temperatures and (b) isothermal holding times [17, 18]. Specimens were held (a) at given temperatures for 1h or (b) 300°C for given times, and then oil-quenched. Lattice parameters were calculated using a diffraction peak from (211) plane [17, 18].

oms are perfectly solutionized and substitutes for magnesium. The experimental lattice parameters of specimens quenched after isothermal holding at the temperature above 200°C for a longer period of time are smaller than theoretical ones. This implies that the bonding force between atoms increases by conducting such a heat treatment and may consequently contribute to increase in both strength and Young's modulus.

# (d) Aging Characteristics

Fig. 13 shows the aging curves of all examined alloys quenched after isothermal holding at 350°C for 1h [17,18]. The specimens except for Mg-22.5mass%Li-7.5mass%Al alloys exhibit age hardening at room temperature and reach peak hardness for aging times from 256 to 1024h. The time to reach the peak hardness is decreased by aging at 50°C and is from 16 to 32h in most of the investigated alloys. Mg-17.5mass%Li-10mass%Al or 12.5mass%Al alloys exhibit a peak hardness of over HV130, but their hardness rapidly decreases during over-aging. Similar age hardening has been confirmed in Mg-30mass%Li alloys containing large amounts of Al or Zn [20] and Mg-8 and 13mass%Li alloys containing large amounts of Al or Ag [15].

Fig. 14 shows the changes in X-ray diffraction profiles for Mg-20mass%Li-12.5mass%Al alloy during aging [17,18]. Two peaks like the side bands at both sides of the diffraction peak of Li solid solution appear in specimens aged for 64h and 256h. The appearance of the side bands may be caused by spinodal decomposition, which causes the age hardening. Peaks at low angles among side bands are located at the same angle as that of Li solid solution in asrolled Mg-20mass%Li-12.5mass%Al alloy and is, therefore, considered to be the diffraction peak from Al+Li-poor phase. Equilibrium phase such as AlLi, Al<sub>2</sub>Li<sub>3</sub> and Al<sub>4</sub>Li<sub>9</sub> compounds reappear in a specimen aged for 2048h as shown in Fig. (e). Consequently, the hardness of over-aged specimen deteriorates.



Figure 13: Aging curves of Mg-Li-Al alloys quenched after the isothermal holding at 350°C for 1h [17,18]



Figure 14: Results of X-ray analyses of Mg-20mass%Li-12.5mass%Al alloys oil-quenched after the isothermal holding at 350°C for 1h [17,18]

From these results, by shortening the holding time at 300°C or 350°C alloying elements are solutionized to some extent and the growth of recrystallized grains is restricted. Consequently, high strength and reasonable elongation can be obtained by such a heat treatment.

# CONCLUSIONS

(1) Li addition enhances the deformability of magnesium. Particularly, the deformability of magnesium increases remarkably by the addition of lithium of more than 6mass%, which crystallizes lithium solid solution ( $\beta$  phase with BCC lattice).

(2) Al, Zn or Ag addition to Mg-Li alloys leads to quenching hardenability due to solutionizing into  $\beta$  phase, and age hardening by spinodal decomposition into the additives+Li rich and poor phases from supersaturated solid solution.

(3) Alloying elements are solutionized to some extent and the growth of recrystallized grains is restricted by shortening the holding time at 300°C or 350C. Consequently, high strength and reasonable elongation can be obtained by such a heat treatment.



Figure 17: Scanning electron micrographs of tensile fracture surfaces of Mg-17.5mass%Li-7.5mass%Al alloy oil-quenched after the isothermal holding at 300°C for the time shown above the micrographs [17, 18]. Tensile elongation is also indicated in parenthesis

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Based on the results of X-ray diffraction analyses, the precipitation sequence of investigated Mg-Li-Al alloys is summarized as follows: Firstly, spinodal decomposition occurs from supersaturated solid solution and then modulated structure with Al+Li-poor and –rich phases is formed. Maximum hardness is obtained at this stage. After that, the respective phases transform into  $\beta$  phase and Al-Li compounds, which leads to overaging.

## (e) Tensile Properties

Figs. 15 and 16 show the dependencies of tensile strength and elongation on the holding time at 300°C, respectively [17,18]. Specimens quenched from 300°C have a higher tensile strength than as-rolled ones except for Mg-20mass% Li-5mass%Al alloy. Also, tensile strength of as-quenched specimens increases as the holding time prolongs in the range from 5 to 30s. Mg-17.5mass%Li-10mass%Al alloy held for 30s indicates maximum tensile strength of 270MPa which is the highest value among the investigated specimens. The enhancement of tensile strength may be caused mainly by the increase of soluble Al in Li solid solution. Tensile strength decreases with long period of holding. However, it also decreases for shorter holding times in specimens with smaller Al content and with larger Li content. As-quenched specimens exhibit extremely lower elongation than as-rolled specimens. Also, elongation of as-quenched specimens decreases with an increase in the holding time in the range from 5 to 30s. As-quenched specimens held for longer time than 30s become very brittle and exhibit small elongation.

Fig. 17 shows scanning electron micrographs of the tensile fractured surfaces for Mg-17.5mass%Li-7.5mass%Al alloys [17,18]. As-rolled specimens indicate a dimple pattern, which characterizes a ductile fracture corresponding to the large elongation. As-quenched specimens after the isothermal holding at 300°C in the range from 5 to 30s have fractured surfaces with lamellar cracking parallel to the rolling direction. On the other hand, specimens held for over 30s show a brittle intergranular fracture. Also, isothermal holding at 300°C for a long time causes recrystallization and subsequent grain growth. These microstructural changes may result in the degradations both of elongation and strength.



Figure 15: Dependence of tensile strength of as-quenched specimens on the isothermal holding times [17,18]. Specimens were held at 300°C for given time and then oil-quenched



Figure 16: Dependence of elongation of as-quenched specimens on the isothermal holding times [17,18]. Specimens were held at 300°C for given times and then oil-quenched