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Processing and Nano-mechanical Characterization of Mg-Li-Al Based Alloys

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Abstract

Two novel Mg-Li-Al based alloys, namely Mg-9 wt% Li-7 wt% Al-1 wt% Sn (LAT971), and Mg-9 wt% Li- 5 wt% Al -3 wt% Sn- 1 wt% Zn (LATZ9531), were cast and hot rolled at 573K. Phase analysis revealed the presence of major Mg-rich (α) and Li-rich (β) phases along with precipitates. Nano-mechanical properties (via nanoindentation) of individual α and β-phases in Mg-Li rolled alloys elicited similar elastic modulus (between 57–60 GPa). However, variation in nanohardness (0.886–1.383 GPa) and plasticity index (0.86–0.93) were observed. Finally, wear mechanism has been proposed based on nano-scratch studies of Mg-Li-Al based alloys.

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1. Introduction

Mg-based lightweight materials (~1.74 g/cc) find applications in aerospace, electronics and automobile sectors [F.H. Froes et al. (1998), B.L. Mordike et al. (2001), Susan Housh et al. (1990), Zhen-hua CHEN et al. (2008)]. Mg alloys possess hexagonal close-packed (hcp) structure, which results in poor formability due to its limited slip systems inherent to an hcp structure. Limited formability thus inhibits wide applications of Mg alloys. To overcome this problem and synergistically reduce density, alloying with lightest metal lithium (Li) of density 0.54 g/cc, can fulfill both purposes [Tao Wang et al. (2008), Chung-Wei Yang et al. (2009), Bialobrzeski K. Saja et al. (2007), W.A. Counts et al. (2009)]. According to the equilibrium Mg–Li phase diagram, 5.5 –11 wt% Li content exhibits a two-phase structure, which consists of Mg-rich α-phase (hcp) and Li-rich β-phase (bcc) [W.A. Counts et
Owing to their ultra light density (<1.5g/cc) magnesium-lithium (Mg-Li) alloys, investigations on the alloy design and optimization of mechanical properties of Mg-Li alloys have been reported by many researchers [W.A. Counts et al. (2009), Yingwei Song et al. (2009), Yingwei Song et al. (2009), Xiaowei Yang et al. (2009), Fedor M. Elkin et.al. (2003)]. Li addition provides solid solution strengthening, but makes the alloys prone to enhanced corrosion rates [Fedor M. Elkin et.al. (2003), Yingwei Song et al. (2009)]. In this regard, addition of other elements may be beneficial to improve its tensile properties as well as enhanced corrosion resistance [B.L. Mordike et al. (2001), Susan Housh et al. (1990)]. Mg-Li alloys have also been tried and developed for better tensile properties and improved corrosion resistance [B.L. Mordike et al. (2001), W.A. Counts et al. (2009), Susan Housh et al. (1990), ]. Ultimate tensile strength up to 250 MPa with 12% elongation is reported in case of Mg-Li alloy [Fedor M. Elkin et al. (2003)]. Tao Wang et al. (2006) has reported the experimental data on the elastic properties of Mg-Li alloys. However, elastic properties of the individual phases constituting Mg-Li alloys remain uninvestigated. This paper aims at correlation of nano-mechanical and micro-wear properties with the evolved microstructures based on nano-scratch test of different phases of Mg-Li alloys.

2. Experimental Procedure

The materials used in this study are Mg-9 wt%Li-7 wt%Al-1 wt%Sn (LAT971), and Mg-9 wt%Li-5 wt%Al-3 wt%Sn-1 wt%Zn (LATZ9531) alloys. The charge is loaded and melted in capped stainless steel crucible due to low reactivity of Mg with stainless steel. The alloys were melted in an induction furnace under a protective atmosphere of mixture of argon and sulphur dioxide gas. Synthesis procedure of both alloys along with their phase and microstructure characterization have been reported somewhere else [Vinod Kumar et al. (2012), Vinod Kumar (2012)]. The final dimensions of the rolled sheet were ~ 100 x 100 x 2 mm$^3$. After hot rolling these Mg-Li alloys are denoted as LAT971R and LATZ9531R in the further discussion.

Microstructural characterization of as cast as well as rolled LAT971 and LATZ9531 were observed by SEM (model ZEISS,EVO50). To observe the phase contrast, back scattered mode was used in all the cases, whereas compositional analysis of the different phases was performed with an EDAX detector(Oxford Instruments model INCA Penta FET X3).

Micro hardness of both polished alloys, LAT971R and LATZ9531R, were tested using Bareiss Vickers micro-hardness tester at a load of 100 g load with a dwell time of 10 s as per ASTM specification E384, 2008ae1. An average of 10–12 indentations were performed on each sample and values are reported along with error bars. Indents were made on the defect free areas.

The elastic modulus and nano-hardness of both LAT971R and LATZ9531R were investigated using a Nano-indentation tester at CSM Instruments (Peseux, Switzerland). Nanoindentation tests were carried out using grid of Berkovich diamond three-sided pyramid indenter with a nominal angle of 65.27°. For calibrating the radius of curvature at the tip of the Berkovich indenter six indents were performed on a cleaned fused silica substrate. Within the grid (11 X 11)used for nanoindentation, each indent was separated by 8 µm, giving an overall area of 80 µm X 80 µm for analysis, which continuously measures force and displacement as an indentation is made. Area covered by indents contains both phases and precipitates as well. All samples were polished to very fine level to reduce any surface roughness affect. For each sample more than 20 indentations were made on both phases with a peak load of 5 mN by applying an increasing load with a rate of 10 mN / minute, followed by a 15 s dwell time at the peak load and then normal load is reduced until partial or complete relaxation occurs. The hardness and elastic modulus were calculated by the Oliver and Pharr method assuming the Poisson’s ration of Mg to be 0.30 [Horst E. Friedrich et al. (2006)]. Plasticity index (PI) based on nanoindentation data is defined as the ratio of residual depth to maximum depth achieved in during nanoindentation.

LAT971R and LATZ9531R were mounted using epoxy and ground up to 600 grit size emery paper followed by final metallographic 0.05 µm diamond polishing. Micro-scratch testing was carried out on the polished cross sections using a nanoscratch tester at CSM instruments (Peseux, Switzerland). It has a horizontal capacitive
transducer for applying normal load and two vertical capacitive transducers for measuring the lateral force experienced by the indenter during scratching. The transducers measuring the lateral force have a load resolution of 0.15 μN and a normal displacement resolution of 0.3 nm. The micro-scratch resistance of different phases in both alloys, in rolled condition, were measured at temperature 23°C and 40% humidity using nanoscratch tester at CSM instruments (Peseux, Switzerland). Sphero-conical 90° indenter with a tip-radius (r) of 5 μm used to scratch a total length (l) of 3 mm on each sample. The normal load applied was 10 mN and scratched at a speed of 6 mm/min. Three tests were carried out on each sample. After completion of the scratch test, each sample was observed in high resolution optical microscope to investigate the wear characteristic along the scratch path. The actual depth during scratching was obtained by subtracting the initial profile from the scratch depth measured during scratching. In order to measure the residual depth after scratch, the scratched surface was profiled and was subtracted from the surface profile before scratching. Wear volume per unit centimetre length (Wv) is defined as a section of spherical cylinder by nano-scratch by taking Δl (3.3μm) as step size along the scratch path:

\[
W_v = \frac{(0.571r + d_r)\Delta l \sqrt{2(r^2 - d_r^2)}}{l}
\]

Where \(r\) is indenter radius, \(d_r\) is residual depth.

Owing to the roughness associated with the polished surfaces, displacement is normalised by accounting for the asperities and valleys. For normalizing the roughness: the scratch depth is taken as residual depth; scratch is fragmented along its length and the normalized wear volume is determined for both alloys for total scratch length of 3 mm.

3. Results and Discussion

The microstructure of LAT971R and LATZ9531R alloys presents a multiphase microstructure, as shown in Fig. 1a and 1b respectively. The sizes of dendritic α-phase were observed to be 30-60 μm (see Fig. 1a). However, the structure of LATZ9531R alloy presents β matrix plus a distribution of α phase in lath form, as shown in Fig. 1b. Microstructure phase distribution revealed by image analyser in LAT971R confirmed 70.1±2.8% α phase, 27.2±2.1% β phase and 2.8±1.1% precipitates. The average size of α phase is 30-125 μm, whereas size of β-phase is ~10-80 μm dispersed as elongated pockets.

The volume fraction of each phase, in case of rolled LATZ9531, by image analysis is about 59.5±2.8% α, 30.0±2.4% β, and 10.5±3.2% precipitates, as shown in Table 1. The α phase appears as lath, with a width of ~20 μm and a length of ~200 μm, in case of LATZ9531R. Elemental distribution in α and β phase by energy dispersive spectroscopy (EDS) analysis shows the presence of 5.64 ± 0.99 wt. % of Al in α-phase and 3.12 ± 1.03 wt.% of Al in β-phase of LAT971R confirming that α phase has higher solid solubility of Al than β phase. Similar trend was also observed in case of LATZ9531R, but other additional alloying elements like Zn (~0.7-0.8 wt %) and Sn (~0.3 - 0.4 wt %) were also present in both phases.

The variations of microhardness of different phases are shown in Table 1. It is observed that the microhardness of α phase is higher than β phase. For LAT971R, this difference is hefty, although in case of LATZ9531R it is marginal. The increase in microhardness of α phase in case of LAT971R is due to the solid solution strengthening. This effect is in agreement with the EDS results of both regions in LAT971R, which shows that 5.64 ± 0.99 wt. % of Al in α-phase and 3.12 ± 1.03 wt. % of Al in β-phase. The nano-hardness results of the different phases in specimens LAT971R and LATZ9531R are shown in Table 1.
For LAT971R, the nanohardness (H) value of α phase was $1.383 \pm 0.080$ GPa and $0.886 \pm 0.088$ GPa was observed in case of β phase. For LATZ9531R, the nanohardness (H) value of α phase was $1.372 \pm 0.112$ GPa whereas $1.040 \pm 0.113$ GPa was observed in case of β phase. It is clear that α has higher nanohardness in comparison to β phase, which is attributed to solid solution strengthening of α phase due to high Al concentration. It was observed that nanohardness value of α phase in case of LAT971R and LATZ9531R is almost same, but there was significant difference in nanohardness values of β phase. On the basis of EDS analysis, it is clear that slightly high amount of Zn (< 0.8 wt %) and Sn (< 0.9 wt %) present in β phase in case of LATZ9531R, provide solid solution strengthening, whereas these elements were not detected in LAT971R resulting higher hardness in LATZ9531R than that of LAT971R.

Table 1: Micro- and nanohardness of α and β phases in LAT971R and LATZ9531R

| Material   | Phase | E [GPa] | Micro-hardness [HV] | H [GPa] | M₀ [nm] | R₀ [nm] | R₀/M₀ | E/H |
|------------|-------|---------|---------------------|---------|---------|---------|--------|-----|
| LAT971R    | α     | 58.5±3.0| 88.0±6.9            | 1.383±0.08 | 407±28  | 351±32  | 0.86   | 42.30 |
|            | β     | 56.9±5.5| 65.0±6.5            | 0.886±0.09 | 528±35  | 490±31  | 0.93   | 64.22 |
| LATZ9531R  | α     | 59.3±3.5| 79.6±7.2            | 1.372±0.11 | 411±14  | 352±14  | 0.86   | 43.22 |
|            | β     | 60.0±4.8| 73.7±3.1            | 1.040±0.11 | 429±31  | 389±34  | 0.91   | 57.69 |

Fig.2 (a) and 2 (b) show plot of load (P) versus penetration depth (h) of LAT971R and LATZ9531R respectively. This shows several discontinuities in the curve, named as ‘pop-in’ effect [W. Wang et al. (2003), Vinod Kumar et al. (2013)]. The pop-ins are much more clear in case of α phase of LAT971R and LATZ9531R, which is attributed to the alloying addition and twinning (because of its hcp crystal structure ) associated with above discontinuities in the indentation load-displacement curves[S.W. Youn et al. (2006)], whereas load-displacement curves of β phase is smoother due to its bcc crystal structure. It is interesting to note that elastic modulus value of both Mg-Li alloys is around 57-60 GPa, which is approximately 33% higher than pure magnesium i.e. 45 GPa [W.A. Counts et al. (2009), Vinod Kumar, et al. (2013), Vinod Kumar (2012)], this beneficial effect is due to combined effect of alloying of magnesium with lithium [W.A. Counts et al. (2009)] and minimization of different defects like porosity, cracks, second phase segregation, etc. at the place of indentation.
The plasticity index (PI = ratio of residual depth to maximum depth) of α phase and β phase in case of LAT971R was about 0.86 and 0.93 respectively. In case of LATZ9531R, PI of α phase and β phase was 0.86 and 0.91 respectively. Higher PI of the β phase is due to its bcc crystal structure in comparison to relatively lower PI value for α arising due to its limited slip systems in an hcp structure. In particular, marginally lower PI value for the β phase in LATZ9531R (0.91) than LAT971R (0.93) is attributed to the presence of slightly high amount of Zn (< 0.8 wt %) and Sn (< 0.9 wt %) in β-phase.

Figure 2: Typical load-depth curves for α and β phases in (a) LAT971R and (b) LATZ9531R.

The nano-scratch tester measures the instantaneous depth penetrated by the indenter as it moves along the surface. A typical scratch recording correspond to LAT971R and LATZ9531R, including the normal force, penetration depth, residual depth and its actual length, is shown in Fig. 3a and 3b respectively. Scratch results of LAT971R and LATZ9531R are shown in Fig. 3a and 3b. The overall value of average residual depth is approximately the same (~ 302-314 nm) for both alloys. In case of LAT971R, it was observed that the average scratch width was 4.82 μm and 4.68 μm for α and β phase respectively. Scratch width 4.97 μm for α phase and 4.25 μm for β phase were observed in case of LATZ9531R. The significant difference of scratch width ~0.43 μm among β phase of both alloys occurs because of higher amount of precipitates present and higher content of Zn and Sn in LATZ9531R. The micro-wear volume per unit length (per cm), determined based on Eq.1, of LAT971R was slightly higher (6.04 X 10⁻¹¹ cm²) than that of LATZ9531R (5.88 X 10⁻¹¹ cm²). This shows that scratch resistance of both alloys is not only different, but also possess different tribological characteristics. As it was discussed that amount of precipitates is high (~10%) in case of LATZ9531R, which provide obstacle during scratching in comparison to that of LAT971R (~3%), which inducts lower micro-wear volume observed in LATZ9531R.

The schematic of wear mechanism during scratch testing of LAT971R and LATZ9531R is shown in Fig. 3c. α and β phases have different nano-hardness values, as shown in Table 1, so they also provide different amount of resistance during scratching. The α phase is harder than β phase, so it is predicted that phases with higher nano-hardness will have larger resistance and vice versa, but scratch mechanism of Mg-Li alloys will be complex when high amount of precipitates (3-10 vol. %) are also present in β phase.

On the basis of present study, we propose that precipitates contribute mainly in three ways. First depending on chemical composition and physical properties of the precipitates, i.e. precipitates possessing high hardness reduces the wear losses. Second is based on their sizes, i.e. the size variations of precipitates also play an important role during scratching.
Figure 3: (a) Normal force, penetration depth and residual depth profile of LAT971R, (b) Normal force, penetration depth and residual depth profile of LATZ9531R, and (c) Schematic showing wear mechanism during nano-scratching of Mg-Li alloys.

Fine precipitates provide obstacles at more frequent sites when compared to coarse precipitates for a similar volume fraction. Third is due to the precipitate distribution i.e. uniformly distributed precipitates will cause uniform wear loss across the surfaces. In our study, since the indent size (5 μm) is bigger than most of the precipitates (< 1-4 μm) present in lithium rich β-phase of LATZ9531R, so enhanced volume fraction more number of precipitates coming across the scratch path finally ends up with lower wear volume in case of LATZ9531R.

4. Conclusions

Two Mg-Li alloys, namely LAT971 and LATZ9531 were processed by casting and hot rolling. Both Mg-Li alloy presents multiphase microstructure (α and β) along with two types of precipitates. The α-phase has higher nano-hardness value (1.37-1.38 GPa) as compared to β-phase (0.89-1.04 GPa). Elastic modulus value of both Mg-Li alloys (57-60 GPa) is higher than pure magnesium (45 GPa). The enhancement in the modulus of Mg-alloy occurs due to the combined effect of alloying of magnesium with lithium and minimization of defects like porosity, cracks and
presence of second phase precipitates. Higher degree of precipitate (~10 vol. %) in LATZ9531R is responsible for comparatively lower micro-wear volume in comparison to that of LAT971R.

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