ORIGINAL RESEARCH

Effect of Sr on microstructure and aging behavior of Mg–14Li alloys

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Abstract The as-cast and as-extruded Mg–14 wt\%Li–xSr (x=0.14, 0.19, 0.39 wt\%) alloys were, respectively, prepared through a simple alloying process and hot extrusion. The effects of Sr addition on microstructure and aging behavior of the Mg–14 wt\%Li–xSr alloys were studied. The results indicated that \(\beta\)(Li) and Mg\(\_\)Sr were the two primary phases in the microstructures of both as-cast and as-extruded Mg–14 wt\%Li–xSr alloys. Interestingly, with the increase of Sr content from 0.14 wt\% to 0.39 wt\%, the grain sizes of the as-cast and as-extruded Mg–14 wt\%Li–xSr alloys markedly decreased from 5000 \(\mu\)m and 38 \(\mu\)m to 330 \(\mu\)m and 22 \(\mu\)m respectively, while no obvious changes of the micro-hardness and microstructure of the as-extruded alloys were observed during the aging treatment.

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1. Introduction

Mg–Li alloys have the potential applications for the lightweight demand components in various industries, such as aviation, aerospace and electronics due to their good plasticity and low density [1,2]. It is worth noting that lithium content can definitely determine the microstructures and properties of Mg–Li alloys relying on different phase structures [3]. For an instance, Mg–14 wt\%Li alloy has body center cubic structure of the single \(\beta\)(Li) phase, which is a Mg–Li solid solution, and has a lower strength, impeding its wide applications [4].

In order to improve the strength of Mg–Li alloys, various novel approaches, such as, composite reinforcement [5,6] and rapid solidification [7] were developed. Considering that the composite reinforcement sacrifices the plasticity and the rapid solidification processing is costly for mass production, traditional minor...
alloying appears to be a simple and effective approach to strengthen the alloy through grain refinement without significant reduction of plasticity [8–10]. For example, Al and Zn are often selected as alloying elements of Mg–14 wt% Li alloy due to their obvious solid solution strengthening effects [2,11] and due to aging strengthening because of the formation of some intermetallic compounds like \( \text{Li}_2\text{MgAl} \) in Mg–14Li–1Al (LA141) or \( \text{Li}_2\text{MgZn} \) in Mg–14Li–1Zn (LZ141). However, \( \text{Li}_2\text{MgAl} \) or \( \text{Li}_2\text{MgZn} \) is metastable and will resolve at 66 °C or even at room temperature as LiMgAl2 or LiMgZn, respectively, and hence has no strengthening effect for \( \beta \)(Li) with the increase of aging time [12–16], resulting in over-aging of LA141 or LZ141 [12–17]. Therefore, ideal candidates need to be explored and developed, pursuing the advanced Mg–14Li alloys with fine microstructure and no over-aging. The results of many researches show that Sr has a good grain refinement effect on Al alloys [18,19], and also has an effective role in grain refinement of Mg alloys, and hence improve their properties. For example, the benefit of Sr addition in AZ91 [20,21], ZK60 [22], and Mg–Al–Ca alloys [23] were successfully realized.

In the present investigation, minor Sr addition was used to prepare the Mg–14Li–xSr alloys with body center cubic structure through a simple alloying process and hot extrusion. In the Mg–14Li–xSr alloys, Mg–Sr intermetallic compound preferentially formed during solidification since the difference in electro-negativity (\( \Delta:\text{EN} = 0.36 \)) between Mg and Sr is higher than that between Li and Sr (\( \Delta:\text{EN} = 0.33 \) [24]. Through the crystallography examination using the edge-to-edge matching model which has successfully predicted AlN [25], ZnO [26], Al2Y [27–29], TiB2 [30] compounds as an effective grain refiner for Mg–3Al–1Zn, Mg–10Y and Mg–5Li–3Al alloys, there is a crystallography matching relationship between Mg2Sr and Li. Mg2Sr can be considered as a potential grain refiner for the Mg–14Li–xSr alloys. Additionally, according to Mg–Sr and Li–Sr binary phase diagram [31], the Mg2Sr compound has higher melting point than Li–Sr compounds. Therefore, Mg2Sr has higher thermal stability and should not be decomposed during the aging treatment of the Mg–14Li–xSr alloys.

<table>
<thead>
<tr>
<th>Designed composition</th>
<th>Measured composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–14Li–1Al</td>
<td>Mg–14.01Li–1.09Al</td>
</tr>
<tr>
<td>Mg–14Li–0.1Sr</td>
<td>Mg–13.63Li–0.14Sr</td>
</tr>
<tr>
<td>Mg–14Li–0.3Sr</td>
<td>Mg–14.10Li–0.19Sr</td>
</tr>
<tr>
<td>Mg–14Li–0.5Sr</td>
<td>Mg–14.27Li–0.39Sr</td>
</tr>
</tbody>
</table>

**Fig. 1** As-cast microstructures of LA141 alloy (a) and Mg–14Li alloys with different Sr contents (b) 0.14 wt%, (c) 0.19 wt%, and (d) 0.39 wt%.

**Fig. 2** Variation of grain size of the as-cast Mg–14 wt% Li alloys with various contents of Sr.
thus the over-aging in LA141 and LZ141 alloys can be restrained. The objective of this work is to prepare Mg–14Li–xSr alloys with fine grains and no over-aging by studying the effects of Sr addition on the microstructure and aging behavior of as-cast and as-extruded Mg–14Li–xSr alloys.

2. Experimental

The materials used in this experiment include commercial pure magnesium ingot, commercial pure lithium ingot and Mg–40 wt%Sr master alloy. In a typical procedure, small pure magnesium and pure lithium blocks (700 g) with different additions of the master alloy were placed in steel crucibles (90 mm in diameter, 250 mm in height). Then, the crucibles were placed into an induction furnace, followed by pumping the furnace chamber to vacuum state and inputting pure argon as a protective gas. Subsequently, the crucibles were heated at 700 °C until the alloy was completely melted and then the melted alloy was isothermally held for 10 min, followed by solidification and cooling of the melts with argon protection to minimize the oxidation. Finally, cast ingots (85 mm in diameter and 150 mm in height) were obtained. The compositions of as-cast alloys were measured with inductively coupled plasma atomic emission spectroscopy (ICP-AES). The designed compositions and measured results of all the alloys prepared in the experiment are shown in Table 1.

The extrusion was carried out at 250 °C and the extrusion ratio was 27. The mmMg–14 wt%Li–xSr (x=0.14, 0.19, 0.39 wt%) bars with the diameter of 16 mm were obtained. Meanwhile, to study the aging behavior of Mg–14 wt%Li–xSr (x=0.14, 0.19, 0.39 wt%), these bars were heat treated at 400 °C for 12 h for homogenization and quenched in water. The aging treatment was carried out at room temperature and at 100 °C. Here, LA141 alloy, as a reference sample, was prepared and extruded using the similar procedure.

The samples used for microstructure observation and aging treatment were cut from the same position. Microstructure was observed using optical microscopy and scanning electron microscopy (SEM, TESCAN VEGA). Before the observation, the specimens were polished and etched with an etchant of 4.0 vol% nital. The grain size was measured by the linear intercept method at the center of transverse sections. The phase in the alloys was identified by Rigaku D/Max 2500PC using Cu Kα radiation (λ=1.5418 Å) operating at 4°/min and 2θ (10–90°). The microhardness of the as-extruded alloys after
aging treatment was examined by HX-1000TM tester at a load of 0.25 N for 15 s.

3. Results and discussion

3.1. Grain sizes of the Mg–14Li–xSr alloys

The microstructures of the as-cast Mg–14 wt%Li–xSr (x = 0.14, 0.19, 0.39 wt%) and LA141 alloys are shown in Fig. 1. The coarse equiaxed grains are observed in the microstructures of as-cast LA141 and Mg–14 wt%Li–0.14 wt%Sr alloys, with the average grain sizes of more than 1 mm, as shown in Fig. 1(a) and (b). Fig. 2 indicates the change of the grain size with Sr content. With lower Sr content of below 0.19 wt%, the grain size is abruptly reduced from 500 μm to 389 μm (as-cast Mg–14 wt%Li–0.19 wt%Sr alloys), while the grain sizes present a gradual reduction with higher Sr content of above 0.19 wt%. Thus, the addition of Sr into Mg–14 wt%Li alloys has a significant grain refinement effect on the as-cast Mg–14 wt%Li alloys.

The microstructures of the as-extruded Mg–14 wt%Li–xSr (x = 0.14, 0.19, 0.39 wt%) and LA141 alloys are shown in Fig. 3. The as-extruded Mg–14 wt%Li alloys with different Sr contents have much finer microstructures than the as-extruded LA141 alloys. Fig. 4 indicates the transformation of the grain sizes of the as-extruded Mg–14 wt%Li alloys with different Sr contents. The grain sizes are reduced from 38.2 μm to 22.3 μm with the increase in content of Sr from 0.14 wt% to 0.39 wt%.

3.2. The intermetallic compounds in the Mg–14Li–xSr alloys

The intermetallic compounds exist in the β(Li) phase, the matrix of the as-cast and as-extruded Mg–14 wt%Li–xSr alloys, shown as the darker parts in Figs. 1 and 3. SEM images of the as-cast Mg–14 wt%Li–xSr alloys in Fig. 5 show that some intermetallic compounds are distributed along the grain boundaries and some inside the grains. Electron energy disperse spectroscopy confirmed that these intermetallic compounds contain Mg and Sr, as shown in Table 2. They are identified as Mg2Sr through XRD examination of the as-cast Mg–14.10 wt%Li–0.19 wt%Sr alloy (Fig. 6). The volume fraction of the Mg2Sr compound in the as-cast Mg–14 wt%Li–xSr alloys is analyzed (Table 3). The volume fraction of the Mg2Sr compound along the grain boundaries is much more and increases with the enhancement of the Sr content. Its morphology evolves from granular to small block, further to near net-like when the content of Sr reaches to 0.39 wt%, because the melt point of Mg2Sr is 680 °C [31], close to the casting temperature of 700 °C, and the near net-like Mg2Sr compound forms easily during casting and solidification.

The intermetallic compounds in the as-extruded Mg–14 wt%–xSr (0.14, 0.19, 0.39 wt%) alloys are shown in Fig. 7 as fine particles and their electron energy dispersive spectroscopy results are listed in Table 4. The fine particles are identified as Mg2Sr phase (Fig. 8). Compared to the as-cast Mg–14 wt%–xSr alloys, the structures and compositions of the phases of the as-extruded alloys have no change. Mg2Sr particles are mainly distributed inside the β(Li) grains, different from the as-cast alloys, and their morphology changes from net-like or blocky to fine granular (about 5 μm) due to the extrusion stress and dynamic recrystallization, which is advantageous to the grain refinement of the as-extruded alloys.

3.3. The mechanism of grain refinement of Mg–14Li–xSr alloys

The grain refinement of the as-cast Mg–14 wt%Li–xSr alloys may be caused by the growth restriction of the β(Li) grains, deriving from the segregation power of Sr in β(Li) during solidification and/or by the second phase. According to the calculation method of the growth restriction parameter of solute in alloys [32–35] and Li–Sr binary phase diagram [31], the growth restriction parameter of Sr in Li is 0.74, much less than that of Sr in Mg which is about 3.51 [32]. Thus, Sr has almost no grain growth restriction effect on β(Li) during solidification. Additionally, Mg2Sr in Mg–14 wt%Li–xSr (x = 0.14, 0.19, 0.39 wt%) alloys could be the primary cause

<table>
<thead>
<tr>
<th>Table 2</th>
<th>EDS results of the as-cast Mg–14 wt%Li–xSr at different positions in Fig. 5.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>Mg (at%)</td>
</tr>
<tr>
<td>A</td>
<td>39.04</td>
</tr>
<tr>
<td>B</td>
<td>33.73</td>
</tr>
<tr>
<td>C</td>
<td>7.02</td>
</tr>
<tr>
<td>D</td>
<td>72.66</td>
</tr>
<tr>
<td>E</td>
<td>30.11</td>
</tr>
<tr>
<td>F</td>
<td>36.54</td>
</tr>
</tbody>
</table>

Note: The content of O in the alloys is high because this type of alloy can be easily oxidized during the sample preparation, which has no effect on the ratio value of Mg to Sr basically.
Fig. 6  XRD result of the as-cast Mg–14.10 wt%Li–0.19 wt%Sr alloy. LiOH·H₂O was observed in the XRD result, because Li has high chemical activity and is easy to react with H₂O during the sample preparation, basically, its existence do not disturb the observation of Mg₂Sr and β(Li).

Table 3  The volume fraction of the intermetallic compounds in the as-cast Mg–14 wt%Li alloys with various contents of Sr.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Total vol%</th>
<th>vol% Inside grain</th>
<th>Morpohology Inside grain</th>
<th>vol% At the boundary</th>
<th>Morpohology At the boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–13.63Li–0.14Sr</td>
<td>0.55</td>
<td>0.22</td>
<td>Granular</td>
<td>0.33</td>
<td>Granular</td>
</tr>
<tr>
<td>Mg–14.10Li–0.19Sr</td>
<td>0.83</td>
<td>0.24</td>
<td>Granular</td>
<td>0.59</td>
<td>Small block</td>
</tr>
<tr>
<td>Mg–14.27Li–0.39Sr</td>
<td>0.92</td>
<td>0.26</td>
<td>Granular</td>
<td>0.66</td>
<td>Near net-like</td>
</tr>
</tbody>
</table>

Fig. 7  SEM images of the as-extruded Mg–14 wt%Li alloys with various contents of Sr. (a) 0.14 wt%, (b) 0.19 wt%, and (c) 0.39 wt%.
of the grain refinement. It may act as nucleation sites and/or restrain the growth of the β(Li) grains to refine microstructure. However, since Mg₂Sr cannot stably exist in the alloy melt at 700 °C during casting (its melting point is 680 °C), it is impossible to act as heterogeneous nucleation sites during solidification. Therefore, during solidification, Mg₂Sr at the grain boundary could restrain the growth of the β(Li) grains at some degree by impeding the atomic diffusion and the movement of grain boundaries.

During extrusion, the Mg₂Sr compounds in the as-cast Mg–14 wt%Li–xSr alloys were broken up into the uniform fine granular (Fig. 7) due to the extrusion stress and dynamic recrystallization. Hence, these Mg₂Sr particles can play the grain refinement role as following aspects [36]: (1) restrain growth of the grains as the grain boundaries are in touch with these particles, and (2) conduce to the refinement of the β(Li) grains because the particle deformation zone formed near the Mg₂Sr particles is an ideal site for a dynamic recrystallization nucleus. As for the second aspect, it is necessary that there exists a crystallography matching relationship between Mg₂Sr and β(Li). This matching relationship can be identified using the edge-to-edge matching model [37,38]. According to this model, Mg₂Sr particle can be the grain refiner for the β(Li) grains if at least one mismatch of the interplanar spacing of the close or near close packed planes of Mg₂Sr and Li is less than 10% and meanwhile in the matched planes exist at least one pair of close or nearly close packed directions in which the misfit of the interatomic spacing is less than 10%. Mg₂Sr has hexagonal crystal structure with lattice parameters of \(a=0.6439 \text{ nm}\) and \(c=1.0494 \text{ nm}\) and Li has cubic crystal structure with lattice parameter of \(a=0.3510 \text{ nm}\) [39]. Through the XRD study, three close packed planes of Li are defined as \{110\}, \{211\}, and \{200\} planes, those of Mg₂Sr as \{10\1\0\}, \{11\2\2\}, and \{11\2\0\} planes [39,40]. Thus, there are nine pairs of potential matching planes for Li and Mg₂Sr. As for the mismatches of the potential matching planes, defined by

<table>
<thead>
<tr>
<th>Table 4</th>
<th>EDS results of the as-extruded Mg–14 wt%Li–xSr alloys at different positions in Fig. 7.</th>
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</thead>
<tbody>
<tr>
<td>Position</td>
<td>Mg (at%)</td>
</tr>
<tr>
<td>A</td>
<td>41.67</td>
</tr>
<tr>
<td>B</td>
<td>85.88</td>
</tr>
<tr>
<td>C</td>
<td>23.94</td>
</tr>
<tr>
<td>D</td>
<td>56.78</td>
</tr>
<tr>
<td>E</td>
<td>43.96</td>
</tr>
<tr>
<td>F</td>
<td>33.60</td>
</tr>
</tbody>
</table>

*Note: The content of O in the alloys is high because this type of alloy can be easily oxidized during the sample preparation, which has no effect on the ratio value of Mg to Sr basically.*

![Fig. 8](image_url) XRD result of as-extruded Mg–14.10 wt%Li–0.19 wt%Sr alloy. LiOH·H₂O was observed in the XRD result, because Li has high chemical activity and is easy to react with H₂O during the sample preparation, basically, its existence do not disturb the observation of Mg₂Sr and β(Li).

![Fig. 9](image_url) Atomic configurations in the close packed plane \{11\2\2\} containing close packed direction as indicated by the bold solid lines.
the edge-to-edge matching model [37,38], it is concluded that there is one matching plane pair (\{110\}/\{11\bar{2}\}) of Li and Mg2Sr with about 10% mismatch. Fig. 9 shows the atom configuration in \{11\bar{2}\} plane of Mg2Sr. A close packed direction in \{11\bar{2}\} plane of Mg2Sr is determined as [4\bar{2}\bar{3}] atom row that is a near direct atom row and its interatomic spacing is 0.3220 nm. The close packed direction in \{110\} plane of Li can be obtained as [\bar{1}1\bar{1}] atom row [41] and its interatomic spacing is 0.3039 nm. Hence, there exists a pair of close packed directions ([\bar{1}11]_{\text{Li}}/[4\bar{2}\bar{3}]_{\text{Mg2Sr}}) in \{110\}_{\text{Li}}/\{11\bar{2}\}_{\text{Mg2Sr}} plane pair of Mg2Sr and \beta(Li) with the interatomic spacing misfit of 6.0%. Consequently, a crystallography matching relationship exists between \beta(Li) and Mg2Sr, identified as [\bar{1}1\bar{1}]_{\text{Li}}/[4\bar{2}\bar{3}]_{\text{Mg2Sr}}, \{110\}_{\text{Li}}/\{11\bar{2}\}_{\text{Mg2Sr}}, although \{11\bar{2}\}_{\text{Mg2Sr}} needs to be rotated an angle against the [4\bar{2}\bar{3}]_{\text{Mg2Sr}} direction and the crystallography orientation relationship is still being confirmed using transmission electron microscopy.

Fig. 10  Microhardness versus aging time for quenched samples (Mg–14.10 wt%Li–0.19 wt%Sr) aging at room temperature and at 100 °C.

Fig. 11  Microstructures of the as-extruded Mg–14.10 wt%–0.19wt% alloy (a) without aging treatment, with aging treated (b) at room temperature for 384 h, (c) at 100 °C for 384 h.

Fig. 12  SEM images of the as-extruded Mg–14.10 wt%–0.19wt% alloy (a) without aging treatment, with aging treated (b) at room temperature for 384 h, (c) at 100 °C for 384 h.
The microhardness of the as-extruded Mg-14.10 wt%Li-0.19 wt%Sr alloy during the aging treatment, shown in Fig. 10, is different from the reference LA141 alloy [13,15–17]. Interestingly, its microhardness changes a little without sharp decrease at the initial stage of aging treatment, and then becomes stable with the increase of aging time at room temperature and at 100 °C. According to the Mg-Sr binary phase diagram in ASM handbook [31], this observation can be attributed to MgSr as a stable compound and effective strengthening phase for β(Li) due to the crystallography matching relationship. To further clarify the aging behavior of the as-extruded Mg-14.10 wt%Li-0.19 wt%Sr alloy, the microstructures of this alloy after different aging treatments were examined through optical microscopy and scanning electron microscopy, as indicated in Figs. 11 and 12. It is noted that the grain size of the alloy aging treated at room temperature and at 100 °C for 384 h almost kept unchanged, compared to the alloy without aging treatment (~260 μm). Table 5 presents the electron energy dispersive spectroscopy result of the compounds in Fig. 12 of the as-extruded Mg-14.10 wt%Li-0.19 wt%Sr alloy with different aging treatments. It shows that the composition has little change before and after the aging treatment. Both MgSr and β(Li) in the as-extruded Mg-14.10 wt%Li-0.19 wt%Sr alloy are stable during the aging treatment. Therefore, the as-extruded Mg-14.10 wt%Li-0.19 wt%Sr alloy has no over-aging during aging treatment.

### 4. Conclusions

From the observation of their microstructures, it is found that the grain size of both as-cast and as-extruded Mg-14Li alloys decreased with the increase of Sr content. β(Li) and MgSr were identified as the two primary phases in the alloys, the volume fraction of MgSr increases with the enhancement of Sr content. The morphology of MgSr in the as-cast Mg-14 wt%Li-xSr alloys evolved from granular to small block and further to near net-like with the increase of Sr content. After extrusion, MgSr compound became fine granular and can act as the nucleation site for dynamic recrystallization during extrusion due to the crystallography matching relationship. Additionally, after Mg-14 wt%Li-0.19 wt%Sr alloy is aging treated at room temperature and at 100 °C for 384 h, no over-aging appears as the microhardness of this alloy keeps stable and both β(Li) and MgSr have little change during aging treatment.

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### References


### Table 5 EDS results of the as-extruded Mg–14.10 wt%–0.19 wt% at different positions in Fig. 12.

<table>
<thead>
<tr>
<th>Position</th>
<th>Mg (at%)</th>
<th>Sr (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49.38</td>
<td>6.50</td>
<td>44.11</td>
</tr>
<tr>
<td>B</td>
<td>67.49</td>
<td>9.34</td>
<td>27.58</td>
</tr>
<tr>
<td>C</td>
<td>43.46</td>
<td>6.40</td>
<td>50.14</td>
</tr>
</tbody>
</table>

*Note:* The content of O in the alloys is high because this type of alloy can be easily oxidized during the sample preparation, which has no effect on the ratio value of Mg to Sr basically.


