Production of Mg–Li alloys by aluminothermic vacuum reduction
Y.-W. Wang*,2, J. You, A.-G. Wang1,3, J.-P. Peng1, Y.-Z. Di1
1. School of Metallurgy, Northeastern University, Shenyang, Liaoning, China
2. Liaoning Institute of Science and Technology, Benxi, Liaoning, China
3. Shenyang Research Institute of Foundry Co., LTD, Shenyang, Liaoning, China
Corresponding author, email youjiyun_ok@163.com
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Abstract
Mg–Li alloys are the lightest metallic construction materials and one of the most representative light alloys. The process of producing Mg–Li alloys by vacuum aluminothermic reduction, using magnesite and lithium carbonate as raw materials, was studied. The influence of reduction parameters on the extents of reduction of MgO and Li2O was investigated. The results show that Mg–Li alloys can be produced by vacuum aluminothermic reduction using calcined magnesite and lithium carbonate. MgO was relatively easier to reduce by aluminum than Li2O. Almost all MgO was reduced to Mg and more than 96% of Li2O was reduced to Li. The main phase in the reduction slag was Li2O·5Al2O3. The reaction mechanism was discussed. Vacuum aluminothermic reduction can be considered as a highly efficient and environmentally friendly method for producing Mg–Li alloys.
Keywords: Mg-Li alloy, Vacuum aluminothermic reduction, Magnesite, lithium carbonate, Li2O·5Al2O3

1 Introduction
Magnesium–lithium alloys are the lightest metallic construction materials, having a specific gravity of 1.30–1.65 g/cm³, which is about 50% lighter than aluminum alloys and 10%–30% lighter than common magnesium alloys. They are therefore known as superlight alloys [1-3]. Because of their specific strength, rigidity, and good damping capacity, Mg–Li alloys have been widely explored in applications in the aircraft, electronics, and communication industries [4,5].

There are three main methods of producing Mg–Li alloys: mixing molten magnesium and lithium, electrochemical reduction and vacuum thermal reduction. Because Mg and Li are very active elements, their metals are prone to oxidize and burn during melting in air. Mg–Li alloys produced by mixing metallic magnesium and lithium are always conducted in a frequency induction furnace protected by argon, which demands strict operating procedures and leads to high production costs [6]. Preparation of Mg–Li alloys by electrochemical reduction uses liquid or solid magnesium as the cathode and carbon as the anode in a LiCl–KCl molten salt. This technique has the advantages of simplicity, low cost, and high product purity [7,8]. In the electrolysis process, lithium metal is generated at the cathode and reacts with
magnesium to form Mg–Li alloys, while chlorine is generated at the anode. Various multi-component Mg–Li alloys can also be produced by the addition of other metal chlorides in the molten salt [9-11]; however, the process parameters of molten salt electrolysis need to be strictly enforced to ensure suitability and stability of the reactions. Vacuum thermal reduction generally includes carbothermic [12] and silicothermic processes [13]: because of the high reduction temperature and reversible reaction of magnesium and CO gas, it is difficult to obtain pure Mg–Li alloys by vacuum carbothermic reduction. Preparation of Mg–Li alloys via vacuum silicothermic and aluminothermic reduction processes is considered as a promising approach.

Considering the demands for low energy consumption and environmental protection, a new method for producing Mg–Li alloys by vacuum aluminothermic reduction using magnesite and lithium carbonate as raw materials is proposed. The method is based on three steps: the first is calcination of magnesite and lithium carbonate, the second is reduction, and the third is a refining process. Figure 1 shows a flowchart of the vacuum aluminothermic reduction process.

This paper presents some important data on the production of Mg–Li alloy by vacuum aluminothermic reduction using magnesite and lithium carbonate as the raw materials.

2Reduction mechanisms

Magnesium and lithium metals can generally be produced by vacuum aluminothermic reduction [14,15]. The main raw materials for producing magnesium by thermal reduction are dolomite or magnesite, while that for producing lithium is lithium carbonate.

The main component of magnesite is MgCO₃ and the main phase of calcined magnesite is MgO. If magnesium is produced using calcined magnesite and aluminum
powder as the raw materials, the following reaction occurs:

$$4\text{MgO}(s) + 2\text{Al}(l) \rightarrow 3\text{Mg}(g) + \text{MgO} \cdot \text{Al}_2\text{O}_3(s) \quad \Delta G^o = 479600 - 296.81T$$

(1)

If aluminum is present in excess, MgO in the form of MgO·Al$_2$O$_3$ will be reduced to metallic magnesium [16]:

$$3\text{MgO} \cdot \text{Al}_2\text{O}_3(s) + 2\text{Al}(l) \rightarrow 3\text{Mg}(g) + 4\text{Al}_2\text{O}_3(s) \quad \Delta G^o = 622000 - 288.49T$$

(2)

Li$_2$CO$_3$ is decomposed to Li$_2$O prior to producing lithium by vacuum thermal reduction. The melting point of Li$_2$CO$_3$ is lower than its decomposition temperature, so additives are required to depress the decomposition process. Al$_2$O$_3$ is the most common additive (Eq. (3)). The reduction reaction is given by Eq. (4):

$$\text{Li}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2 \quad \Delta G^o = 85570 - 134.39T$$

(3)

$$3\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 6\text{Li} \quad \Delta G^o = 1033150 - 645.28T$$

(4)

For preparing Mg-Li alloy, the mixture of calcined magnesite (MgO) and Li$_2$O·Al$_2$O$_3$ is used as the precursor. During vacuum aluminothermic reduction, the MgO and Li$_2$O·Al$_2$O$_3$ are firstly reduced by aluminum to form Mg vapor and Li vapor in reduction furnace. The two metal vapors will form alloys in the gaseous state and then co-crystallizes on the condenser. The overall reaction is reaction (5). The content of lithium in Mg-Li alloys can be adjusted by the addition of Li$_2$O·Al$_2$O$_3$.

$$\text{MgO} + \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Mg-Li}$$

(5)

3. Experimental

3.1 Materials

Mg–Li alloy was produced using magnesite and lithium carbonate as the raw materials and aluminum powder as the reductant. The main components of the raw materials are listed in Table 1. Aluminum powder was produced from pure aluminum and contained > 99.5% elemental aluminum.

Table 1 Chemical compositions of magnesite and lithium carbonate

<table>
<thead>
<tr>
<th>Compounds</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Li$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite [wt.%]</td>
<td>47.28</td>
<td>0.22</td>
<td>0.08</td>
<td>0.13</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>Lithium carbonate [wt.%]</td>
<td>&lt;0.1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
<td>&gt;98%</td>
</tr>
</tbody>
</table>

3.2 Experimental Method

Reduction experiments must be carried out in vacuum. The contributions of vacuum are mainly in two aspects. Firstly, the reduction temperature in vacuum could reduce by more than 200 °C and the reduction rate increases greatly. Secondly, since magnesium and lithium are readily oxidizable, vacuum can be prevented from oxidation of metal magnesium and lithium.

The reduction experiments were similar to those of the Pidgeon process. Firstly, magnesite and a mixture of lithium carbonate and alumina were separately calcined at 850 °C for 2 h. The two calcination products were ground into powder and then mixed well with aluminum powder. The mixture was pressed into pellets and the pellets were put into a horizontal pot which placed in reduction furnace (reduction equipment is
shown in Fig. 2). Reduction was carried out at the temperature of 900-1230 °C and the vacuum of 1-5 Pa. The magnesia and lithia in the pellets were reduced to metal magnesium and lithium by aluminum. Magnesium reacted with lithium to form alloys in the gaseous state and Mg–Li alloys crystallized on the condenser. The crystalline Mg–Li alloys was subsequently refined to get pure Mg–Li binary alloys. The reduction slag remained as briquettes. The reduction ratio of MgO (η_Mg) and Li_2O (η_Li) were calculated by Eqs. (6) and (7), respectively:

\[ \eta_{\text{Mg}} = \left(1 - \frac{\delta_{\text{Mg}} \cdot M_s}{\alpha_{\text{Mg}} \cdot M_0}\right) \times 100\% \]  \hfill (6)

\[ \eta_{\text{Li}} = \left(1 - \frac{\delta_{\text{Li}} \cdot M_s}{\alpha_{\text{Li}} \cdot M_0}\right) \times 100\% \]  \hfill (7)

where \( M_0 \) is the quantity of the raw materials and \( M_s \) is the quantity of reduction slag; \( \alpha_{\text{Mg}} \) and \( \alpha_{\text{Li}} \) are the mass percentages of MgO and Li_2O in the raw materials, respectively; \( \delta_{\text{Mg}} \) and \( \delta_{\text{Li}} \) are the mass percentages of MgO and Li_2O in the reduction slag, respectively.

![Figure 2 Schematic drawing of the vacuum thermal reduction equipment](image)

4 Results and discussions

In the process of producing Mg–Li alloys by vacuum aluminothermic reduction, the content of lithium in the alloy can be adjusted by changing the relative masses of Li_2O·Al_2O_3 and aluminum powder added. Therefore, various compositions of Mg–Li binary alloys can theoretically be produced. In this work, a Mg–Li alloy with 7% lithium content was prepared.

4.1 Effect of reduction temperature on reduction ratio of MgO and Li_2O

The reduction processes of MgO and Li_2O are endothermic; The higher reduction temperature is advantageous for reduction reaction. Usually, the high temperature will also enhance the reaction rate. Therefore, the higher the reduction temperature is, the better the reduction proceeds. However, the reduction temperature could not exceed 1250 °C in this work because of the working temperature limit of the industrial pot used. The effects of the reduction temperature on the extents of reduction of MgO and Li_2O are shown in Figure 2.
Figure 3 Effect of the reduction temperature on the reduction ratio of MgO and Li₂O (excess aluminum: 3%; reduction time: 2 h)

Figure 3 shows that the initial temperatures of the reductive reactions of MgO and Li₂O were both lower than 900 °C. The reduction ratio of MgO and Li₂O increased with the rise of reduction temperature; however, the reduction ratio of MgO was always 10% higher than that of Li₂O, indicating that MgO was relatively easier to reduce by aluminum. When the reduction temperature exceeded 1200 °C, the reduction of MgO was almost complete.

4.2 Effect of reduction time on reduction ratio of MgO and Li₂O

The time to completion of a reductive reaction depends on the reaction rate, which is mainly related to the reduction temperature, vacuum strength, and thermal conductivity of the materials. The extents of reduction of MgO and Li₂O after different reduction times are shown in Figure 4.

Figure 4 Effect of the reduction time on the reduction ratio of MgO and Li₂O (excess aluminum: 3%; reduction temperature: 1200 °C).

The extents of reduction of MgO and Li₂O increased very fast within the first 1.5 h, indicating that their reduction rates were very fast. When the reduction time exceeded 2 h, the aluminothermic reductions of MgO and Li₂O were close to completion at a reduction temperature of 1200 °C.

4.3 Effect of aluminum addition on reduction ratio of MgO and Li₂O

As the reducing agent, the additive amount of aluminum powder has a great
influence on the reduction ratio of MgO and Li₂O. In general, their reduction ratio will increase with an increase in aluminum addition, but excess addition will inevitably lower the utilization of AI. There is a balance between the cost of aluminum and the yields of lithium and magnesium. The effect of aluminum addition on the reduction ratio of MgO and Li₂O is shown in Figure 5, where zero excess aluminum refers to the stoichiometry quantity given by Eq. (5).

![Figure 5](image)

**Figure 5** Effect of excess Al on the reduction ratio of MgO and Li₂O  
(reduction time: 2 h; reduction temperature: 1200 °C).

The reduction ratio of Li₂O increased with increasing of aluminum addition, while that of MgO was unaffected. The reduction ratio of MgO was close to 100%, so addition of excess aluminum powder was mainly used for reducing Li₂O.

It is generally known that most magnesium metal is produced by vacuum silicothermic reduction. Lithium metal can also be produced by vacuum thermal reduction, but the low yield (mainly because of its lower melting point) limits industrial application of this technology. Lithium that reacts with magnesium to form Mg–Li alloy in the gaseous state will raise the alloy melting point and increase the yield, but if the reductions of MgO and Li₂O are not simultaneous during the reduction process, then the magnesium and lithium metals in the vapor state will crystallize separately in different areas of the crystallizer, which will decrease the yield of the alloy. The results shown in Figure 3 and 4 indicate that aluminothermic reduction of MgO and Li₂O occurred simultaneously, indicating that the lithium will deport to the Mg–Li alloy and improve its yield. These conclusions were proved by the lack of reactivity of the crystalline products with water, indicating that they did not contain elemental lithium.

### 4.4 Reaction mechanisms of producing Mg-Li alloys by vacuum aluminothermic reduction

Reduction slag and crystalline Mg–Li alloys were obtained after the reduction process; pure Mg–Li alloys can hence be obtained by remelting and refining the crystalline Mg–Li alloys. However, it is necessary to emphasize that the crystalline Mg–Li alloys produced by vacuum thermal reduction contain impurities, mainly oxide impurities and metal impurities. SiO₂, Al₂O₃, Fe₂O₃, CaO and Na₂O are the main impurities of raw materials. In reduction process, Fe₂O₃, CaO and Na₂O can be
reduced and some Na and Ca may be crystallized with Mg-Li alloy. The refining agent are mainly KCl, MgCl₂, LiCl and LiF. In refining process, the oxide impurities could be removed, and the main metal impurities, Ca and Na, will react with MgCl₂ and LiCl to produce CaCl₂ and NaCl. The other impurities are very few. The refined Mg–Li alloys can fully meet the standard. An X-ray diffraction (XRD) analysis of the crystalline Mg–Li alloy is presented in Figure 6.

Figure 6 X-ray diffraction analysis of crystalline Mg–Li alloy

As shown in Figure 4, the extent of reduction of MgO was always higher than that of Li₂O, which relates to the reaction mechanism of their aluminothermic reductions. XRD patterns of the reduction slag at temperatures between 900 °C and 1200 °C are displayed in Figure 7.

Figure 7 X-ray diffraction analysis of reduction slag
(reduction time: 2 h; excess aluminum: 3%; reduction temperature: 1200 °C)

According to the XRD analysis of the reduction slag, MgO and Li₂O·Al₂O₃(LiAlO₂) were first reduced to Mg and Li by aluminum at a low temperature to form MgO·Al₂O₃ (as shown in Eqs. (1) and (8)). Li₂O in form of Li₂O·Al₂O₃ and MgO in form of MgO·Al₂O₃ were then further reduced and formed Li₂O·5Al₂O₃ (as shown in Eqs. (9) and (10)). Li₂O·5Al₂O₃ is more stable than MgO·Al₂O₃, so the reduction of MgO in the form MgO·Al₂O₃ was relatively easier than that of Li₂O in the form of Li₂O·5Al₂O₃. Li₂O in the form of Li₂O·5Al₂O₃ can be reduced further (Eq. (11)), but this requires additional aluminum, which would significantly reduce its utilization ratio and therefore undoubtedly increase the cost of the reduction process.

\[ \text{MgO} + 4(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3) + 2\text{Al} \rightarrow 4\text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{Mg} + 8\text{Li} \]  
(8)

\[ 4(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3) + 2\text{Al} \rightarrow \text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 + 6\text{Li} \]  
(9)

\[ 3\text{MgO} \cdot \text{Al}_2\text{O}_3 + 2(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3) + 3\text{Al} \rightarrow \text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 + 3\text{Mg} + 3\text{Li} \]  
(10)

\[ 3(\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3) + 2\text{Al} \rightarrow 16\text{Al}_2\text{O}_3 + 6\text{Li} \]  
(11)

4.5 Effect of Li₂O·Al₂O₃ addition in raw materials on reduction process

Theoretically, a wide range of Mg–Li binary alloys can be produced by adjusting the proportion of Li₂O·Al₂O₃ added to the raw material mixture. However, the lithium content of Mg–Li binary alloys cannot be too high because a higher lithium content correlates with a lower melting point of the alloy, which would decrease its yield. According to the Mg–Li binary alloy phase diagram, the lithium content should not exceed 40% to avoid affecting the yield. The effect of Li₂O·Al₂O₃ addition (i.e., the content of lithium in Mg–Li alloys) on the extents of reduction of MgO and Li₂O is shown in Figure 8; the XRD patterns of the respective slags are shown in Figure 9.

![Figure 8](image_url)

**Figure 8** Effect of Li₂O·Al₂O₃ addition on the reduction ratio of MgO and Li₂O
(reduction time: 2 h; excess aluminum: 3%; reduction temperature: 1200 °C).

As shown in Figure 8 and 9, the main phases of the reduction slags were similar, but the reduction ratio of Li₂O increased when the Li₂O·Al₂O₃ addition increased. The highest extent of reduction exceeded 96%. Increasing the proportion of Li₂O·Al₂O₃ added decreased the relative proportion of MgO, and hence the amount of alumina produced from the reduction of MgO by aluminum, which further reduced the amount of Li₂O in the form of Li₂O·5Al₂O₃. This is the primary reason for the increase in the extent of reduction. Another reason is the increase in contact area between Li₂O and aluminum.

The reduction slag contains mainly Li₂O (about 0.5%–0.8%) and Al₂O₃, so it can be reused as an additive to the calcination process, as shown by the reduction reaction given as Eq. (12):

$$\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 + 4\text{Li}_2\text{CO}_3 \rightarrow 5(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3) + 4\text{CO}_2$$ (12)

5Conclusions

(1) A method of producing Mg–Li alloys by vacuum aluminothermic reduction using magnesite and lithium carbonate as the raw materials was proposed. In the reduction process, the extent of reduction of MgO was always higher than that of Li₂O, indicating that MgO was relatively easier to reduce by aluminum. The reduction ratio of MgO was almost 100% and that of Li₂O exceeded 96%. The main phase of the reduction slag was Li₂O·5Al₂O₃. Li₂O in the form of Li₂O·5Al₂O₃ is difficult to reduce, which is the main reason for the lower reduction ratio of Li₂O.

(2) Compared with other vacuum thermal reduction process, the aluminothermic reduction process can achieve simultaneous reduction of MgO and Li₂O and zero discharge of waste residues. Therefore, it can be regarded as a highly efficient and environmental friendly method with low energy consumption and low emissions of 

Figure 9 X-ray diffraction analysis of reduction slags produced by varying Li₂O·Al₂O₃ addition to the raw material
waste residues.

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Reference