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B. DUBOST, P. BOMPARD and I. ANSARA

Cegedur-Pechiney, Centre de Recherche et Développement, B.P. 27, F-38340 Voreppe, France
*Laboratoire de Thermodynamique et de Physico Chimie Métallurgiques, ENSEEI, B.P. 75, F-38402 Saint-Martin-d’Hères Cedex, France

ABSTRACT

A thorough study of the Al-Li-Mg equilibrium phase diagram in the Al-rich corner is described. An experimental approach of the constitution of this system by thermal analysis, metallography and microanalysis is combined to a thermodynamic calculation based on literature data, intermetallic compound recognition and a study of liquid-solid phase equilibria (monovariant and invariant reactions). Ternary or quasi-binary interactions involving the Al$_2$LiMg and (Mg, Li)$_{17}$Al$_{12}$ compounds are considered in addition to relevant results on the binary constitutive systems (Al-Li, Al-Mg). Using a relatively limited number of cast alloy samples, the ternary Al-Li-Mg equilibrium phase diagram is calculated over wide temperature and composition ranges (Li, Mg ≤ 50 at %; 300°C ≤ T ≤ 650°C) and compares satisfactorily with the literature and experimental results.

INTRODUCTION

The knowledge of equilibrium phase diagrams is a basic requirement for metallurgists working in the field of alloy design, process optimization and microstructural control of new alloy systems. The systematic experimental approach based on extensive metallographic evaluations and thermal analysis of numerous heat treated samples has been historically used for most of the binary alloys and several ternary alloys. However, this very costly and time consuming approach may appear as unrealistic or even hopeless when complex ternary and quaternary systems are involved especially when the time between the research evaluation of the alloy system and its industrial development is expected to be short, as it is the case for the light aluminium-lithium alloys currently developed for aerospace applications. The Al-Li-Mg system is likely to provide the lightest Al-rich alloys and has led to the development for number of industrial or experimental alloys in the last decades.

(1) Permanent address : Laboratoire de Métallurgie, Ecole Centrale des Arts et Manufactures, Grande Voie Vignes, P-92295 Châtenay-Malabry Cedex, France
On the other hand, materials scientists can now rely upon computer thermodynamic calculations of equilibrium phase diagrams using assessment and optimization programs, provided that thermodynamic data are available (1). However, except for most of the binary alloys, the latter condition is far from being met on more complex alloys, such as the new generation of aluminium-lithium-alloys, due to the lack of assessed data on most ternary or quaternary intermetallic compounds.

Previous studies of the Al-Li-Mg system concerned the following investigations:
1) In the Al-rich corner, besides intermetallic phase recognition, isothermal sections at 200°C, 430°C and 467°C have been compiled by Drits et al. (2) and Mondolfo (3), respectively.
2) In the Mg-rich corner (for very light cast alloys), extensive experimental studies have led to the establishment of isothermal sections of the Mg-Li system at 400°C, 300°C and 200°C by Levinson and Mac Pherson (4), Schurmann and Geißler (5) and Drits (2) in addition to the determination of several invariant equilibria.
3) In the Li-rich corner (for battery applications), a first thermodynamic calculation of the ternary phase diagram has been performed by Saboungi and Hsu (6) on the basis of data assessed only on the limiting binary systems, but without taking into account any ternary interaction.

In this study the results of the first determination of the ternary equilibrium phase diagram of the Al-Li-Mg system in the Al-rich corner by combination of both approaches (namely an experimental study consisting of metallography, microanalyses, thermal analysis and a thermodynamic calculation) will be presented.

EXPERIMENTAL

Metallurgical study
Small cylindrical ingots (Ø 18 X 60 mm) of high purity were cast from 720°C into graphite coated steel molds with a solidification time of approximately 1 minute, in order to simulate the solidification conditions of DC cast industrial products. The liquidus and other significant liquid-solid phase transformation temperatures were recorded by thermal analysis of the cast ingots; the latter also underwent differential scanning calorimetry (DSC) using a DU PONT DSC 910 analyzer in order to detect the eutectic temperatures and other invariant equilibrium temperatures. Metallographic studies of the alloys in as cast condition involved SIMS ion microscopy on a CAMECA IMS 3F ion microprobe for the visualization of lithium elemental distribution (7), as well as scanning electron microscopy (SEM) using backscattered electrons (8). X-Ray powder diffraction using the Seeman-Bohlin method (with CuKα radiation) was also used for intermetallic compound recognition. These techniques allowed to reveal the solidification path of the alloys, to determine the binary or ternary phase equilibria (including invariant reactions) and to sketch projections of the monovariant lines. DSC analyses and metallography were also performed on dilute alloys, following extended homogenization treatments in dry air, water quench and chemical analysis.

Thermodynamic calculation

The iterative calculation of the ternary diagram based on the Gibbs energy minimization of the system was performed after evaluation of the thermodynamic parameters of each phase. The latter were adjusted in order to obtain a good agreement between the
coordinates of the calculated invariant points and monovariant liquidus and solidus lines (composition, temperature) and the experimentally sketched ones. The excess Gibbs energy of mixing for substitutional solutions was derived by using the semi-empirical Redlich-Kister equation (9). A computation program developed at LTPCM and the optimization program of Lukas et al. (10) were used for this calculation. Isothermal sections and liquidus projections have also been obtained by use of the THERMOCALC program developed at the Royal Institute of Technology, Stockholm (11).

RESULTS

The chemical composition of 9 concentrated alloys and 6 dilute alloys with compositions close to the invariant points and the monovariant lines shown in figure 1.

Intermetallic compounds identification and melting characteristics

The following intermetallic phases have been found to be in equilibrium with the face centered cubic aluminium solid solution (α-Al) and/or with the liquid in ternary alloys with increasing Mg/Li ratio, in accordance with previous results (2, 3):

The binary compound δ-AlLi (20 wt % Li) presenting a cubic structure (a = 6.4 Å) is known to be congruently melting at 700°C (12). This highly reactive phase (in an ambient atmosphere) is the only equilibrium compound in the as cast alloy Al-4.3 wt % Li-2.0 wt% Mg.

The ternary compound usually designated by Al2LiMg, with a composition of 10.3 - 11 wt % Li and 27.1 - 24 wt % Mg (close to Al9Li4Mg4) and presenting a cubic structure (a = 20.2 - 20.5 Å) was reported by Levinson and McPherson (4). The alloy Al-12 wt % Li - 21.6 wt % Mg, with a composition very close to that of Al2LiMg and intermediate between those of Al2LiMg and AlLi, exhibits primary crystallization of δ-AlLi dendrites followed by secondary solidification of the Al2LiMg matrix (Fig.2 a). Hence the Al2LiMg compound is non congruently melting at a temperature lower than the liquidus temperature of this alloy (602°C). This phase is the major equilibrium compound in alloys Al-3-Li wt% Li - 5 wt% Mg, (a = 20.0 Å).

The cubic compound designated by γ-Mg17Al12 (55.7 wt%Mg) is known to have a cubic structure (a = 10.56 Å), a wide composition range (42-58 wt % Mg) and to melt congruently at 455°C in the binary Al-Mg system (3,13). In the ternary system the solidus temperature of this compound has been found to increase with its lithium solute content (e.g. T solidus = 473°C for a Al-1.2 wt % Li - 32.2 wt % Mg alloy). The composition range of this phase has been previously reported to extend towards that of the Al2LiMg compound by substitution of Mg with Li atoms up to a maximum composition corresponding to the formula Mg3Li2Al4 (14, 15).

In this study, a corresponding decrease of the lattice parameter to a = 9.97 Å has also been measured on an alloy Al-2.4 wt % Li - 8.8 wt % Mg, in which the (Mg,Li)17Al12 phase is the only compound in equilibrium with the α-Al matrix in as cast condition.

The binary compound designated by β-Al3Mg2 or Mg5Al8 (Mg = 34.8 - 37.1 wt %), has a cubic structure (a = 28.2 Å) and melt congruently at 451°C (13). It has only been detected in ternary alloys with very low lithium content (Li ≤ 1.2 %) cast in this study.
Phase equilibria

Besides the binary eutectic reactions previously existing in the Al-Li and Al-Mg systems (12, 13), two peritectic reactions and one eutectic reaction (Fig. 2 b-e) were identified in the Al-rich corner of the Al-Li-Mg system (Table I). The microstructures of cast ingots exhibiting ternary peritectic reactions are very often typical of non-equilibrium type reactions showing a border of the secondary phase forming around the primary phase (Fig 2 c - d - e). They are consistent with the successive reactions determined from the metallographic study of the solidification paths of the alloys, including the monovariant lines.

Table I: Invariant reactions in the Al-rich corner of the Al-Li-Mg system

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Phase equilibrium</th>
<th>Temperature (°C)</th>
<th>Liquid phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic (E₀)</td>
<td>Liq → α Al + δ -AILi</td>
<td>601</td>
<td>~ 8.3</td>
</tr>
<tr>
<td>Peritectic (P₁)</td>
<td>Liq + δ -AILi→α Al + &quot;AI₂LiMg&quot;</td>
<td>528</td>
<td>~ 5</td>
</tr>
<tr>
<td>Peritectic (P₂)</td>
<td>Liq + &quot;AI₂LiMg&quot; → Al +γ (Mg,Li)₁₇AI₁₂</td>
<td>485</td>
<td>~ 3.5</td>
</tr>
<tr>
<td>Eutectic (E₁)</td>
<td>Liq→α Al + γ(Mg,Li)₁₇AI₁₂ + β-Al3Mg2</td>
<td>447</td>
<td>~ 0.5</td>
</tr>
<tr>
<td>Eutectic (E₂)</td>
<td>Liq→α Al + β-Al3Mg2 (13)</td>
<td>450</td>
<td>~ 35.5</td>
</tr>
<tr>
<td>Eutectic (E₃)</td>
<td>Liq→βAl3Mg2 + γ-Mg₁₇Al₁₂ (13)</td>
<td>450</td>
<td>~ 39</td>
</tr>
</tbody>
</table>

Thermodynamic calculations

The optimization of the thermodynamic parameters relative to the ternary phases required a critical assessment and an evaluation of the Gibbs energies of formation of the various phases existing in the limiting binary systems. Both δ and γ compounds were assumed to be stoichiometric and equatomic. In addition it was assumed that Li would substitute to Mg in the γ compounds according to the formula Al₀.5(Li₀.5Mg₁₀.5)₀.5. Moreover, the formula of the ternary compound "AI₂LiMg", was assumed to be AI₅Li₃Mg₂. These minor modifications are consistent with the observation of Levinson and Mc Pherson on the γ-δ equilibria (4), and with the peritectic decomposition of "AI₂LiMg" mentioned by Shamray (14).

With these assumptions, the phase diagram of the ternary Al-Li-Mg system was calculated in the Al-rich corner (Li ≤ 20 wt %, Mg ≤ 50 wt %) by adjusting the ternary interaction coefficients of the f.c.c. and liquid phases as well as the Gibbs energy of formation of the Al₅Li₃Mg₂ and Al₀.5(Li₀.5Mg₁₀.5)₀.5, using the experimental data of 9 concentrated and 3 dilute ternary alloys.

The calculated monovariant lines relative to the equilibria involving the liquid phase are shown in figure 1. The calculated compositions and temperatures of the invariant points are in excellent agreement with the experimental values listed in table I. Furthermore isothermal sections calculated for selected temperatures (550, 475, 400°C and 350°C), shown on figures 3 a-d are in good agreement with those previously published (2-5). These results illustrate the usefulness of such an approach for the quantitative study of phase transformations in this system.
MONOVARIANT LINES

1: Liquid - (AD - AlLi
2: Liquid - (AD - Al2LiMg
3: Liquid - AlLi - Al2LiMg
4: Liquid - Al2LiMg - Al12(Li,Mg)17
5: Liquid - (AD - Al12(Li,Mg)17

wt% Li

wt% Mg

Fig. 1: Projections of calculated liquid alloy compositions for ternary phase equilibria (* = cast alloys)

a) Al-12 % Li - 21,6 % Mg
   Primary Al2LiMg dendrites in Al LiMg matrix

b) Al-6,1 % Li - 17,2 % Mg
   AlLi-cored Al Mg dendrites in (Mg,Li)17Al12 (grey)
   and Al (white) matrix near P1 point

c) Al-5 % Li - 17,2 % Mg
   Primary Al2LiMg dendrites (dark grey), often with
   AlLi core in (Mg,Li)17Al12 (grey) and aAl (white)
   matrix

d) Al-6 % - Li - 21 % Mg
   Primary Al2LiMg(polyhedral, dark grey) surrounded
   by (Mg,Li)17Al12 matrix (grey) and aAl (white)

e) Al-1,2 % Li - 32,2 % Mg
   Primary (Mg,Li)17Al12 phase (grey) surrounded
   by a Al (white) + Mg2 Al3 (light grey) +
   (Mg,Li)17Al12eutectic

f) Al-3,3 % Li - 8,2 % Mg
   Primary a Al dendrites with interdendritic
   (Mg,Li)17Al12 (grey) and
core in border of Al2LiMg phase (black)

Fig. 2 a-f : Backscattered electron micrographs of as-cast Al-Li-Mg alloys
Fig. 3a-d: Calculated isothermal sections of the Al-Li-Mg equilibrium phase diagram.
CONCLUSION

With an iterative procedure combining an experimental study and an optimized thermodynamic computation, the ternary Al-Li-Mg equilibrium phase diagram has been determined over a wide composition domain (Li ≤ 20 wt% ; Mg ≤ 50 wt %) and a large temperature range (350 - 650°C), by using a relatively small number of cast alloys. The computed phase diagram, as obtained mainly on the basis of the knowledge of all binary and ternary phase equilibria (invariant and monovariant reactions), appears to be in excellent quantitative agreement with the available literature data and with the results of the metallographic and thermal analyses performed on experimental ingots. However, due to the occurrence of ternary intermetallic compounds as in most of the aluminium alloys with high specific strength, the achievement of such a feasible phase diagram for metallurgical alloy optimization implies an important research work on the experimental side in order to study all the ternary interactions involved. This powerful and attractive approach will prove its usefulness for complex alloy systems with potential aerospace applications.

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