ELSEVIER

Thermochimica Acta 344 (2000) 47–54

thermochimica acta

www.elsevier.com/locate/tca

# The Cu–Li–Mg system at room temperature

M.H. Braga[a,*], L.F. Malheiros[b], M. Hämäläinen[c]

[a]Instituto Superior de Engenharia do Porto, R. Dr. Roberto Frias, 4200 Porto, Portugal
[b]GMM-IMAT, DEMM, FEUP, Rua dos Bragas, 4099 Porto-Codex, Portugal
[c]Laboratory of Materials Processing and Powder Metallurgy, Helsinki University of Technology, PB 6200, FIN-02015, HUT, Espoo, Finland

Accepted 23 August 1999

## Abstract

The Cu–Li–Mg system still remains very unknown. Mel'nik et al. (Russ. Metall. 3 (1976) 152–156) studied it at 643 K. They considered the existence of a stoichiometric compound $Cu_8Li_2Mg_{15}$ with an orthorhombic structure.

In this work, the Cu–Li–Mg system was studied at room temperature by means of SEM (scanning electron microscopy) / EDS (energy dispersive spectroscopy) and X-ray diffraction. Results were compared with the ones from (Russ. Metall. 3 (1976) 152–156) and with the assessments for the binaries Cu–Li, Cu–Mg and Li–Mg present in the literature (COST-507, Thermochemical database for light metal alloys, in: I. Ansara (Ed.), Concerted Action on Materials Sciences, European Commission DGXII Publ., 1994, pp. 132–134; A.A. Nayeb-Hashemi, J.B. Clark, Phase Diagrams of Binary Magnesium Alloys, ASM International, 1988, pp. 184–194).

*Keywords:* SEM/EDS; XRD; Phase diagrams; Thermodynamic assessment

## 1. Introduction

The Cu–Li–Mg system was studied by Mel'nik et al. [1] at 643 K and the samples were examined by X-ray structural analysis. The only ternary compound they found in the system contains about 60 at.% Mg, 8 at.% Li and 32 at.% Cu (X-phase), and has an orthorhombic structure with $a = 5.24$ Å, $b = 8.99$ Å, and $c = 54.33$ Å. They also found that the compound $Cu_2Mg$ (Laves-C15) dissolves lithium approximately up to 13 at.%, that the solubility of Li in $CuMg_2$ is about 1 at.% and that there is no appreciable dissolution of Cu in hcp-A3 and in bcc-A2.

The aim of this study is to determine the configuration of the ternary phase diagram at room temperature.

## 2. Experimental

The alloys, for the present study, were prepared in Baikov Institute of Metallurgy from Cu 99.96%, Li 99.8% and Mg 99.96% pure elements. Melting of the alloys was performed in a resistance furnace in alumina crucibles under a flux, consisting of a salt mixture, 75% LiCl + 25% LiF, for preventing Li losses. The alloy melts were poured into a copper round mould with an inner cavity with 16 mm of diameter and cooled down. Afterwards, the ingots were hot squeezed at temperatures between 573 and 623 K to a 50% reduction of their initial thickness using a 160-tonne hydraulic press.

---

[*] Corresponding author.
*E-mail address*: lfmf@fe.up.pt (M.H. Braga).

0040-6031/00/$ – see front matter
PII: S0040-6031(99)00325-1

The composition of the samples was analysed in Baikov Institute of Metallurgy, Helsinki University of Technology, Minho University and Outokumpu Research Ltd. by atomic absorption spectroscopy with an accuracy of approximately 5%.

All samples were studied by SEM (scanning electron microscopy) / EDS (energy dispersive spectroscopy), in a JEOL JSM-35C; Li content was found by difference. For chemical control, by difference, it is critical to have good standards. In this system, special care must be taken with Mg standard because of its tendency to oxidise. If the standard of a certain element is oxidised, this will affect the composition of the sample in the sense that this element will present a higher content than the real one.

In this case, if Cu and Mg standards present some oxygen, the Li content of the sample will be lower than the real one.

On the other hand, if oxygen is present in the sample, the difference will include this oxygen and the result will be a higher Li content for the sample.

It should be also taken into account that standard and samples should be measured under the same conditions of the electron beam energy. In order to render this possible, a special sample support was used as a Faraday gage.

Samples were also analysed in Helsinki University of Technology, on a Philips X-ray diffractometer equipped with PC-APD software for Automated Powder Diffraction. The diffraction patterns were obtained at filtered Co K$\alpha$ and Cu K$\alpha$ radiation with a step-size of 0.02° for $2\theta$. The database for patterns matching was formed on the base of JCPDS-IDD with only one exception for the X-phase [1].

Samples were also measured in Pedro Nunes Institute, Coimbra, on a Philips X-ray diffractometer equipped with PC-APD software for Automated Powder Diffraction. The diffraction patterns were obtained at filtered Co K$\alpha$ radiation with a step-size of 0.02° for $2\theta$ between 10° and 130°. The interplanar distances and intensities obtained were compared with those from the database JCPDS-IDD except those corresponding to the X-phase.

Some samples analysed in the Helsinki University of Technology have been previously ground to fine powder; others were polished. All the samples studied in Pedro Nunes Institute, Coimbra, were polished.

The only way to identify the X-phase is to compare the obtained diffraction patterns from the different samples and search for unidentified peaks that appear all together, having into account the clear presence of the X-phase in the observations made by SEM and confirmed by EDS.

The results obtained, for the ternary at room temperature, both by SEM/EDS and X-ray diffraction are presented in Table 1, Figs. 1–3.

The microphotographs presented in Figs. 1–3 show the qualitative differences of the phases, in equilibrium, present in each sample.

## 3. Phase diagrams

In order to study the system further and compare the experimental results, at room temperature and at 643 K [1] for the ternary and the existing assessments of the binaries, an assessment of the system Cu–Li–Mg was made. This assessment was performed by using Thermo-Calc software [4] and the database of COST-507 [2], which contains the parameters for the Gibbs energies of the phases in equilibrium on the binaries.

The best assessment for the ternary, obtainable with the parameters for the binaries in COST-507 database [2], is presented in Fig. 2. An assessment was also made by changing the parameters of the system Li–Mg with those published by Nayeb-Hashemi and Clark [3]; the results were not better than the previous ones.

As it can be seen in Fig. 2 and Table 1, the samples corresponding to the photographs (a)–(c), (e) and (f) still evidence the existence of the three phases (white: $Cu_2Mg$; medium grey: $Cu_8Li_2Mg_{15}$; black: bcc-A2 (Li)), which means that all of them belong to the equilibrium region $Cu_2Mg + Cu_8Li_2Mg_{15} +$ bcc-A2. To reinforce the disagreement between the experimental results and the assessment presented in Fig. 2, it can also be noticed that the sample which corresponds to the photograph (b) in Fig. 1 only presents two phases in equilibrium at room temperature: $Cu_2Mg$ and bcc-A2 (see Table 1).

Due to the high disagreement between experimental results and the modelisation done, it was necessary to do a reassessment. It was not possible to reassess the ternary without reassessing the binary Li–Mg whose

Table 1
Comparison between the experimental results from SEM/EDS and X-ray diffraction for the phases present in equilibrium for samples at room temperature

| No. | Composition (mole fraction) | | | Phases in equilibrium (results from SEM/EDS) | Phases in equilibrium (results from X-ray diffraction) |
|---|---|---|---|---|---|
| | Cu | Li | Mg | | |
| 1 | 0.649 | 0.042 | 0.309 | bcc-A2, $Cu_2Mg$ | fcc-A1?, $Cu_2Mg$ |
| 2 | 0.578 | 0.061 | 0.361 | bcc-A2, $Cu_2Mg$ | bcc-A2, $Cu_2Mg$ |
| 3 | 0.424 | 0.070 | 0.506 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 4 | 0.477 | 0.030 | 0.493 | $Cu_2Mg$, X | $Cu_2Mg$, X |
| 5 | 0.435 | 0.093 | 0.472 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 6 | 0.360 | 0.134 | 0.506 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 7 | 0.321 | 0.162 | 0.517 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 8 | 0.255 | 0.219 | 0.526 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 9 | 0.206 | 0.290 | 0.504 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 10 | 0.164 | 0.320 | 0.516 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 11 | 0.089 | 0.383 | 0.528 | bcc-A2, $Cu_2Mg$, X | bcc-A2, $Cu_2Mg$, X |
| 12 | 0.035 | 0.439 | 0.526 | bcc-A2, $Cu_2Mg$ | bcc-A2, $Cu_2Mg$ |
| 13 | 0.087 | 0.655 | 0.258 | bcc-A2, $Cu_2Mg$ | – |
| 14 | 0.110 | 0.531 | 0.359 | bcc-A2, $Cu_2Mg$ | – |
| 15 | 0.090 | 0.422 | 0.488 | bcc-A2, $Cu_2Mg$ | bcc-A2, $Cu_2Mg$, X? |
| 16 | 0.126 | 0.292 | 0.582 | bcc-A2, X | bcc-A2, X |
| 17 | 0.088 | 0.195 | 0.717 | bcc-A2 (or hcp-A3), $CuMg_2$ | hcp-A3, $CuMg_2$ |
| 18 | 0.091 | 0.118 | 0.791 | bcc-A2 (or hcp-A3), $CuMg_2$ | bcc-A2?, hcp-A3, $CuMg_2$ |
| 19 | 0.050 | 0.055 | 0.895 | hcp-A3, $CuMg_2$ | hcp-A3, $CuMg_2$ |
| 20 | 0.031 | 0.152 | 0.817 | bcc-A2 (or hcp-A3), $CuMg_2$ | bcc-A2?, hcp-A3, $CuMg_2$ |
| 21 | 0.036 | 0.239 | 0.725 | bcc-A2 (or hcp-A3), $CuMg_2$ | bcc-A2, hcp-A3?, $CuMg_2$ |
| 22 | 0.027 | 0.344 | 0.629 | bcc-A2, X | bcc-A2, X? |
| 23 | 0.048 | 0.440 | 0.512 | bcc-A2, $Cu_2Mg$ | bcc-A2, $Cu_2Mg$, X? |
| 24 | 0.044 | 0.495 | 0.461 | bcc-A2, $Cu_2Mg$ | bcc-A2, $Cu_2Mg$, X? |
| 25 | 0.363 | 0.060 | 0.577 | – | $Cu_2Mg$, X, $CuMg_2$ |
| 26 | 0.347 | 0.034 | 0.619 | – | $Cu_2Mg$, X, $CuMg_2$ |
| 27 | 0 | 0.202 | 0.798 | bcc-A2, hcp-A3 | – |
| 28 | 0.589 | 0 | 0.411 | – | $Cu_2Mg$, $CuMg_2$ |
| 28 | 0.589 | 0 | 0.411 | – | $Cu_2Mg$, $CuMg_2$ |

parameters were not in agreement with the experimental results for the system Cu–Li–Mg. The calculation of the system Li–Mg was also performed with Thermo-Calc software [4]; the Gibbs energies parameters are presented in Table 2.

Fig. 4 shows the phase diagram of the system Li–Mg present in COST-507 database [2] and Fig. 5 the phase diagram of the same system resulting from the present work; both were compared with the experimental points from the literature.

Fig. 3 shows the final ternary, at room temperature, after the reassessment of the binary Li–Mg. The correspondent parameters are shown in Table 2.

Finally, Fig. 6 is an isothermal section, at 643 K, of the system Cu–Li–Mg [1] and Fig. 7 is an isothermal section at 643 K, of the ternary which allows the comparison between the final ternary and the experimental section presented in [1].

## 4. Optimisation

The Gibbs energy of the pure element, *i*, in a given structure is represented by the following equation:

$$\begin{aligned}\mathrm{GHSER}_i &= {}^0G_i(T) - {}^0H_i^{\mathrm{SER}}\ (298.15\,\mathrm{K}) \\ &= a + bT + cT\ln(T) + dT^2 + e/T + \\ &\quad + fT^3 + gT^7 + hT^{-9},\end{aligned}$$

as defined by Dinsdale [5].

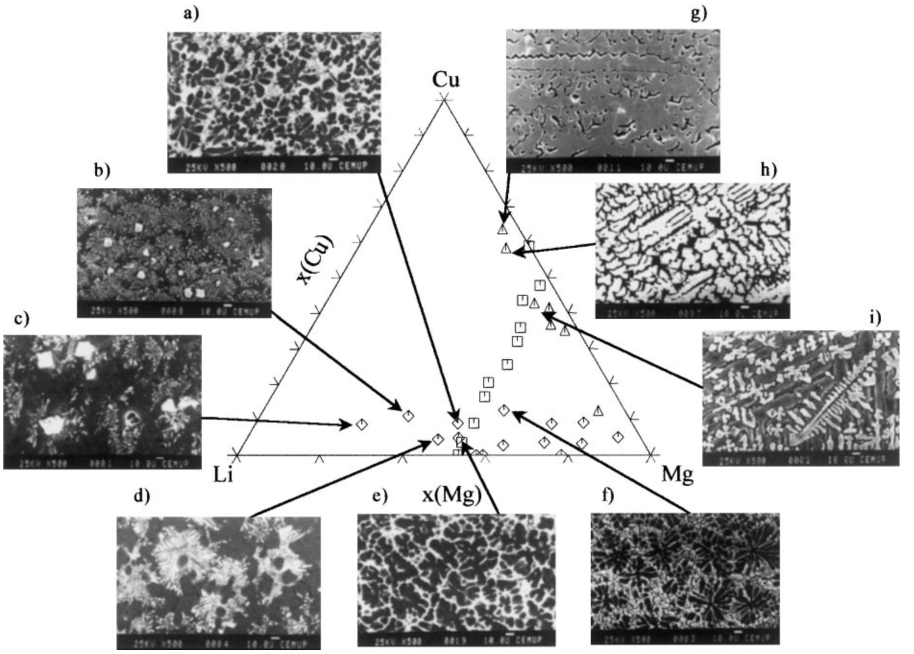

Fig. 1. Isothermal section at room temperature of the system Cu–Li–Mg. Microphotographs of the samples (magnification × 500): (a) 15; (b) 14; (c) 13; (d) 24; (e) 23; (f) 16; (g) 1; (h) 2; (i) 3 (see Table 1).

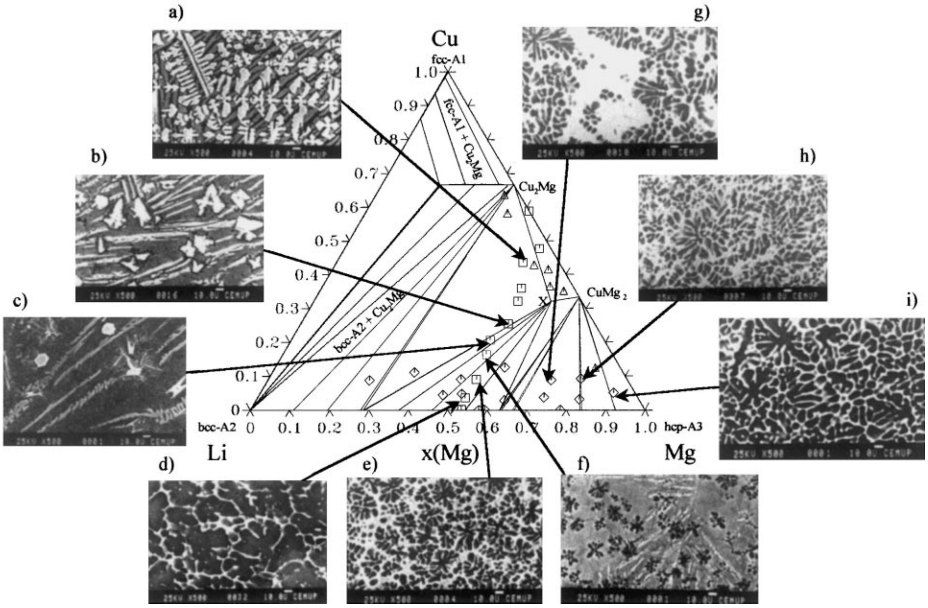

Fig. 2. Isothermal section, at room temperature, of the system Cu–Li–Mg. Ternary calculated with the best obtainable parameters deducted from those available in the literature for the binary Li–Mg. Microphotographs of the samples (magnification × 500): (a) 5; (b) 8; (c) 9; (d) 12; (e) 11; (f) 10; (g) 17; (h) 18; (i) 19 (see Table 1).

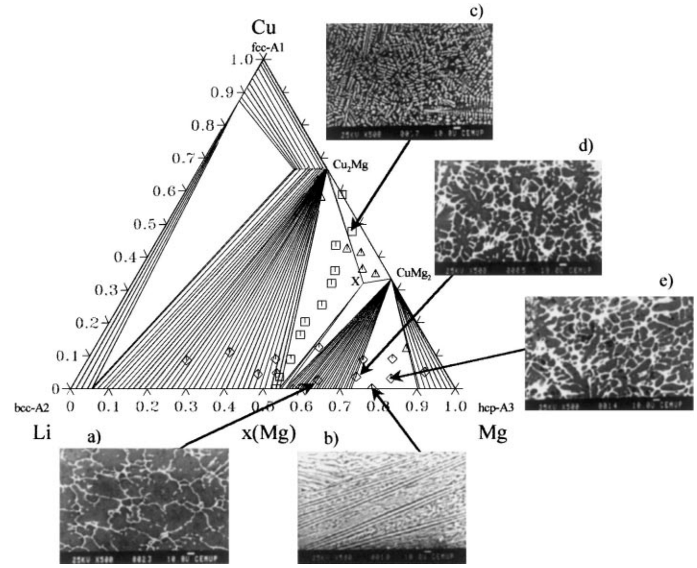

Fig. 3. Isothermal section, at room temperature, of the system Cu–Li–Mg. Ternary calculated with the parameters from the reassessment of the binary Li–Mg. Microphotographs of the samples (magnification × 500): (a) 22; (b) 27; (c) 4; (d) 21; (e) 20 (see Table 1).

Table 2
The Gibbs energies parameters for the different phases of Li–Mg and Cu–Li–Mg systems[a]

| Phase | Parameters |
|---|---|
| *Li–Mg* | |
| Liquid | ${}^{0}L_{\mathrm{Li,\,Mg}} = -48322 + 59.25T$<br>${}^{1}L_{\mathrm{Li,Mg}} = -784-1.6129766T$<br>${}^{2}L_{\mathrm{Li,Mg}} = 3905.8-5.2579T$ |
| bcc-A2 | ${}^{0}L_{\mathrm{Li,Mg:Va}} = -59707.36 + 67.316T$<br>${}^{1}L_{\mathrm{Li,Mg:Va}} = 773.7 + 6.127T$<br>${}^{2}L_{\mathrm{Li,Mg:Va}} = 8498.4-0.84851T$ |
| hcp-A3 | ${}^{0}L_{\mathrm{Li,Mg:Va}} = -35764.97 + 38.946T$<br>${}^{1}L_{\mathrm{Li,Mg:Va}} = 1445.66-13.10915T$<br>${}^{2}L_{\mathrm{Li,Mg:Va}} = -6116.61-0.75T$ |
| *Cu–Li–Mg*[b] | |
| Liquid | ${}^{0}L_{\mathrm{Cu,\,Li,\,Mg}} = 7944.25 + 29.51T$<br>${}^{1}L_{\mathrm{Cu,\,Li,\,Mg}} = -3062.89 + 76.38T$<br>${}^{2}L_{\mathrm{Cu,\,Li,\,Mg}} = -1.20089 + 0.9116T$ |
| Laves-C15 ($Cu_2Mg$) | ${}^{0}G_{\mathrm{Li:Cu}}-H_{\mathrm{Cu}}^{0,\,\mathrm{fcc\text{-}A1}}$ (298.15 K)$-2\,H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K)$= -2585.038 + 30000 + \mathrm{GHSER}_{\mathrm{Cu}} + 2\ \mathrm{GHSER}_{\mathrm{Li}}$<br>${}^{0}G_{\mathrm{Cu:Li}}-2\,H_{\mathrm{Cu}}^{0,\,\mathrm{fcc\text{-}A1}}$ (298.15 K)$-H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K)$= 2585.038 + 2\ \mathrm{GHSER}_{\mathrm{Cu}} + \mathrm{GHSER}_{\mathrm{Li}}$<br>${}^{0}G_{\mathrm{Li:Li}}-3\,H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K) $= 15000 + 3\ \mathrm{GHSER}_{\mathrm{Li}}$<br>${}^{0}G_{\mathrm{Mg:Li}}-H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K)$-2\,H_{\mathrm{Mg}}^{0,\,\mathrm{hcp\text{-}A3}}$ (298.15 K)$= -3902.278 + \mathrm{GHSER}_{\mathrm{Li}} + 2\ \mathrm{GHSER}_{\mathrm{Mg}}$<br>${}^{0}G_{\mathrm{Li:Mg}}-2\,H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K)$-H_{\mathrm{Mg}}^{0,\,\mathrm{hcp\text{-}A3}}$ (298.15 K)$= 3902.278 + 30000 + 2\ \mathrm{GHSER}_{\mathrm{Li}} + \mathrm{GHSER}_{\mathrm{Mg}}$ |
| $Cu_8Li_2Mg_{15}$ (X) | $G(T)-8\,H_{\mathrm{Cu}}^{0,\,\mathrm{fcc\text{-}A1}}$ (298.15 K)$-2\,H_{\mathrm{Li}}^{0,\,\mathrm{bcc\text{-}A2}}$ (298.15 K)$-15\,H_{\mathrm{Mg}}^{0,\,\mathrm{hcp\text{-}A3}}$ (298.15 K) $=$<br>$= -9995.299 + 0.4988T + 8\ \mathrm{GHSER}_{\mathrm{Cu}} + 2\ \mathrm{GHSER}_{\mathrm{Li}} + 15\ \mathrm{GHSER}_{\mathrm{Mg}}$ |

---

[a] Note: The Gibbs energies of formation at the temperature, $T$, are relative to the enthalpy of the pure elements in their reference phase (HSER) at 298.15 K. Values are in J/mol where mole is the g-formula mass.

[b] The parameters of the binaries Cu–Mg and Cu–Li are those published in [2].

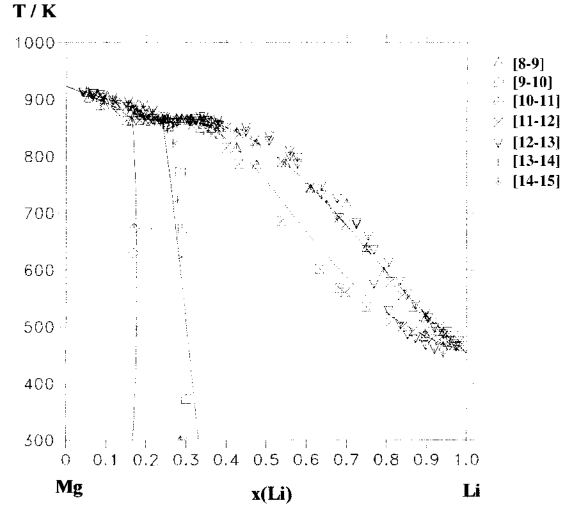

Fig. 4. Phase diagram of the binary system Li–Mg as published in [2]. Comparison with the available experimental data [8–15].

For the compounds, the corresponding Gibbs energy is represented as follows:

$$G_{\mathrm{c}}^{T} = {}^{0}G_{\mathrm{c}}^{T} - \sum_{i=1}^{2} x_i H_i^{298.15\,\mathrm{K}}$$
$$= A + BT + \sum_{i=1}^{2} x_i \mathrm{GHSER}_i.$$

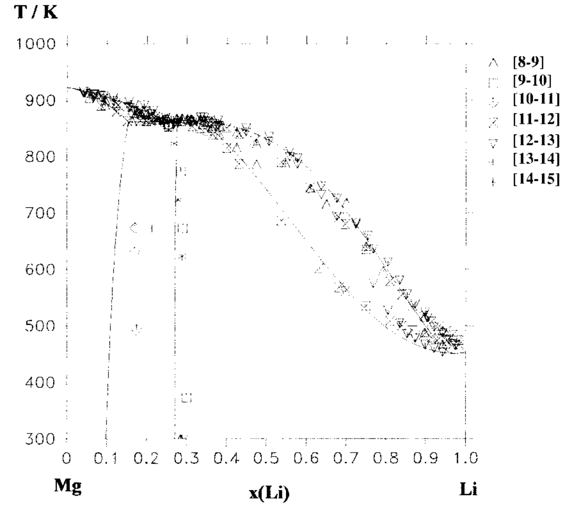

Fig. 5. Reassessed phase diagram of the binary system Li–Mg. Comparison with the available experimental data [8–15].

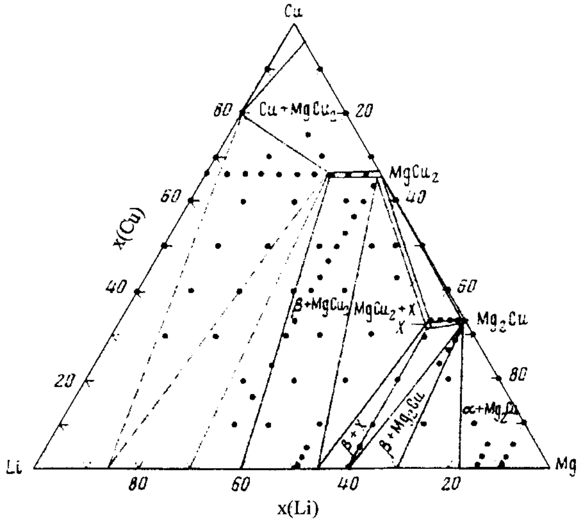

Fig. 6. Isothermal section, at 643 K, of the system Cu–Li–Mg [1].

The Gibbs energy of mixture of the liquid, hcp-A3 and bcc-A2 phases, in the binary Li–Mg, is given by

$$G_{\mathrm{m}} = {}^{\mathrm{ref}}G + {}^{\mathrm{id}}G + {}^{\mathrm{ex}}G,$$
$${}^{\mathrm{ref}}G = \sum_{i=\mathrm{Li,Mg}} x_i\, {}^{0}G_i, \quad {}^{\mathrm{id}}G = RT \sum_{i=\mathrm{Li,Mg}} x_i \ln(x_i).$$

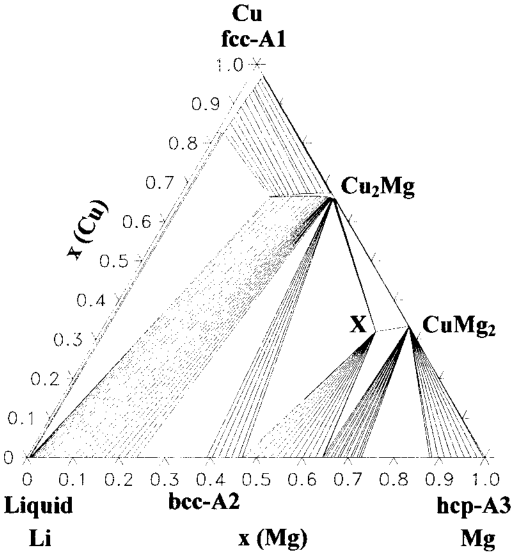

Fig. 7. Isothermal section, at 643 K, of the system Cu–Li–Mg. Ternary calculated with the parameters from the reassessment of the binary Li–Mg.

The Redlich–Kister equation [6] used to represent the excess Gibbs energy of mixing, ${}^{\mathrm{ex}}G$, is expressed as follows:

$$
\begin{aligned}
{}^{\mathrm{ex}}G &= x_{\mathrm{Li}} x_{\mathrm{Mg}} \sum_{\nu=0}^{n} L_{\nu} (x_{\mathrm{Li}} - x_{\mathrm{Mg}})^{\nu}, \\
L_{\nu} &= a + bT.
\end{aligned}
$$

The Thermo-Calc software [4] was used to obtain the optimal parameter sets for the parameter $L_{\nu}$, $A$ and $B$.

For the Laves-C15 phase ($Cu_2Mg$), a sublattice model with two sublattices was used: $(\mathrm{Cu, Li, Mg})_p(\mathrm{Mg, Li, Cu})_q$, described by the Wagner–Schottky [7] formalism:

$$G_{\mathrm{m}} = {}^{\mathrm{ref}}G + {}^{\mathrm{id}}G + {}^{\mathrm{f}}G \ (+{}^{\mathrm{ex}}G),$$

where:

$$
\begin{aligned}
{}^{\mathrm{id}}G = RT[&p(y'_{\mathrm{Cu}} \ln(y'_{\mathrm{Cu}}) + y'_{\mathrm{Li}} \ln(y'_{\mathrm{Li}}) + \\
&+ y'_{\mathrm{Mg}} \ln(y'_{\mathrm{Mg}})) + q(y''_{\mathrm{Mg}} \ln(y''_{\mathrm{Mg}}) + \\
&+ y''_{\mathrm{Li}} \ln(y''_{\mathrm{Li}}) + y''_{\mathrm{Cu}} \ln(y''_{\mathrm{Cu}}))]/(p+q)
\end{aligned}
$$

and

$$
\begin{aligned}
{}^{\mathrm{f}}G = [&G(\mathrm{Cu}_p:\mathrm{Cu}_q) y'_{\mathrm{Cu}} y''_{\mathrm{Cu}} + G(\mathrm{Cu}_p:\mathrm{Li}_q) y'_{\mathrm{Cu}} y''_{\mathrm{Li}} \\
&+ G(\mathrm{Cu}_p:\mathrm{Mg}_q) y'_{\mathrm{Cu}} y''_{\mathrm{Mg}} + \\
&+ G(\mathrm{Li}_p:\mathrm{Cu}_q) y'_{\mathrm{Li}} y''_{\mathrm{Cu}} + G(\mathrm{Li}_p:\mathrm{Li}_q) y'_{\mathrm{Li}} y''_{\mathrm{Li}} + \\
&+ G(\mathrm{Li}_p:\mathrm{Mg}_q) y'_{\mathrm{Li}} y''_{\mathrm{Mg}} + \\
&+ G(\mathrm{Mg}_p:\mathrm{Cu}_q) y'_{\mathrm{Mg}} y''_{\mathrm{Cu}} + \\
&+ G(\mathrm{Mg}_p:\mathrm{Li}_q) y'_{\mathrm{Mg}} y''_{\mathrm{Li}} + \\
&+ G(\mathrm{Mg}_p:\mathrm{Mg}_q) y'_{\mathrm{Mg}} y''_{\mathrm{Mg}}]/(p+q)
\end{aligned}
$$

as used in Thermo-Calc software [4]; where $y_i'$, $y_i''$ are site fraction of species $i$ on sublattice $'$ or $''$; $G$(I:J) is the Gibbs energy of formation of ideal compounds and "fictious" compounds. Note that if $n_{ij}$ is the number of moles of the species $j$ on sublattice $i$ in one mole of atoms of the phase, then $n_{1j} = y_j' p/(p+q)$ and $n_{2j} = y_j'' q/(p+q)$. ${}^{\mathrm{ex}}G$ was neglected in the description of the Laves-C15 phase.

## 5. Conclusions

1. The experimental results for both techniques, SEM/EDS and X-ray diffraction, for each sample, are almost in quite good agreement.
2. It was found the compound reported in [1] is $Cu_8Li_2Mg_{15}$ (X). The SEM/EDS experiments reveal the existence of a phase with a ratio Cu/Mg very similar to that of the compound, but due to the fact that the lithium content is found by difference, we cannot be sure of its stoichiometry by only relaying on this method. As none of the samples were composed simply by $Cu_8Li_2Mg_{15}$ (X), all the diffraction patterns contained peaks, at least, from two phases. So the peaks corresponding to the compound were always found by difference. A deeper study is being performed to confirm the structure and the parameters of the unitary cell and to add the information of the sites occupied by the different atoms in the unitary cell.
3. The assessed Li–Mg is in agreement with the experimental points for compositions $x(\mathrm{Li}) \geq 0.3$. The *solvus* line in Mg rich side is not in agreement with the results from [8–10]. It was not possible to confirm if the assessed line allows a better agreement with the results from the ternary. Nevertheless it is sure that these parameters for the Gibbs energies of the Li–Mg system permit the tie lines, corresponding to the equilibrium region $Cu_2Mg$ + bcc-A2, to be in good agreement with the experimental data.
4. The assessed ternary is in good agreement both with the experimental results at room temperature as well as with the published isothermal section at 643 K [1]. This diagram is still not to be used at higher temperatures. For a reliable assessment, more data has to be obtained for different temperatures.

## Acknowledgements

The authors would like to thank Eng. César Correia from Instituto Pedro Nunes, Eng. Carlos Sá and Mr. Ricardo Guedes from CEMUP for their contributions to this work. The contribution of Mr. José Soares from CINFU in the metallographic preparation of the samples is also acknowledged.

## References

[1] E.V. Mel'nik, M.F. Mitrofanova, P.I. Kripyakevich, M.Yu, Teslyuk, A.N. Malinkovich (L'vov), Russ. Metall. 3 (1976) 152–156.

[2] COST-507, Thermochemical database for light metal alloys, in: I. Ansara (Ed.), Concerted Action on Materials Sciences, European Commission DGXII Publ., 1994, pp. 132–134.

[3] A.A. Nayeb-Hashemi, J.B. Clark, Phase Diagrams of Binary Magnesium Alloys, ASM International, 1988, pp. 184–194.

[4] B. Sundman, B. Jasson, J.O. Andersson, Calphad 9(2) (1985) 153–190.

[5] A.T. Dinsdale, Calphad 15(4) (1991) 317–425.

[6] O. Redlich, A. Kister, Ind. Eng. Chem. 40 (1948) 345–348.

[7] C. Wagner, Thermodynamics of Alloys, Addison-Wesley, Cambridge, MA, 1952.

[8] W. Hume-Rothery, G.V. Raynor, E. Butcher, J. Inst. Met. 71 (1945) 589–601.

[9] W. Hume-Rothery, G.V. Raynor, E. Butcher, J. Inst. Met. 72 (1946) 538–542.

[10] M.-L. Saboungi, C.C. Hsu, Calphad 1(3) (1977) 237–251.

[11] G. Grube, H.V. Zeppelin, H. Bumm, Z. Electrochem. 40(3) (1934) 160–164.

[12] W.E. Freeth, G.V. Raynor, J. Inst. Met. 82 (1953/1954) 575–580.

[13] O.H. Henry, H.V. Cordiano, Trans. Metall. Soc. AIME 111 (1934) 319–332.

[14] P. Saldau, F. Schamray, Z. Anorg. Chem. 224 (1935) 388–398.

[15] J.A. Catterall, Nature 162 (1952) 336.