HT-XRD in the study of Cu-Li-Mg

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Abstract. In a previous study on Cu-Li-Mg system, the authors of the present paper concluded that the ternary phase in that system corresponds to $CuMg_{2-x}Li_x$ ($x \sim 0.11$), with a hexagonal structure, space group $P6_222$ (180), and lattice parameters a = b = 0.5260 nm, c = 1.3649 nm [1]. The structure was refined by the Rietveld method [2]. In order to characterize the thermal behaviour of the ternary compound and to assess the Cu-Li-Mg phase diagram [3], HT-XRD measurements were performed on samples whose compositions were close to the one corresponding to the ternary compound. SEM/EDS measurements of the phases' compositions in equilibrium, as well as DSC/DTA heating curves, contributed to the identification of the transition temperatures and the phases present in equilibrium. It was concluded that the ternary phase decomposes at $\sim 702 \pm 2K$.

Introduction

The Cu-Li-Mg system has not been, till now, the object of many studies although it is one of the ternaries of the Al-Cu-Li-Mg system which has been deeply studied, at least near the quasicrystalline T2 (Al_6Li_3Cu) phase, and which has many applications in the aeronautic industry.

Mel'nik *et al.* [4] referred to the existence of a ternary phase in the Cu-Li-Mg system: $Cu_8Li_2Mg_{15}$ with an orthorhombic structure (a = 0.524 nm, b = 0.899 nm, and c = 5.433 nm). Hämäläinen *et al.* [3] assessed the phase diagram of the system. Figure 1 presents two vertical sections for x(Li) = 0.04 and x(Li) = 0.07 from the Gibbs energy parameters obtained in [3]. In previous work, the present authors pointed out the existence of a phase with a stoichiometry close to that of $Cu_8Li_2Mg_{15}$ [5] and, in recent work, the latter phase was defined as being $CuMg_{2-x}Li_x$ ($x \sim 0.11$) [1]. Taking into account that there were no experimental data about the thermal behaviour of the ternary phase, nor the high temperature equilibria,

and that quenching seemed ineffective for such a narrow temperature range, some HT-XRD studies were developed.

On the other hand, an important feature for a successful assessment is the crystallographic data; thus the models used to describe the phases should be supported by the phase's crystal structure.

Experimental

DSC/DTA measurements

In the first part of this work, thirty samples were prepared in a resistance furnace and their compositions were analysed by AAS [5]. DSC/DTA experiments were performed on samples belonging to the vertical sections $x_{Mg} \sim 0.512$, $x_{Cu} \sim 0.097$, $x_{Cu} \sim 0.039$ and $x_{Li} \sim 0.050$ of the Cu-Li-Mg system under Ar atmosphere using quasi-hermetic stainless steel crucibles. Figure 1 presents some experimental data and figure 2 shows a DSC/DTA curve for a sample with x(Cu) = 0.088, x(Li) = 0.19, x(Mg) = 0.717.

In the second part of this work, samples were prepared in order to have compositions close to $Cu_8Li_2Mg_{15}$. Those samples were prepared and analysed in a similar way to the previous ones [1].
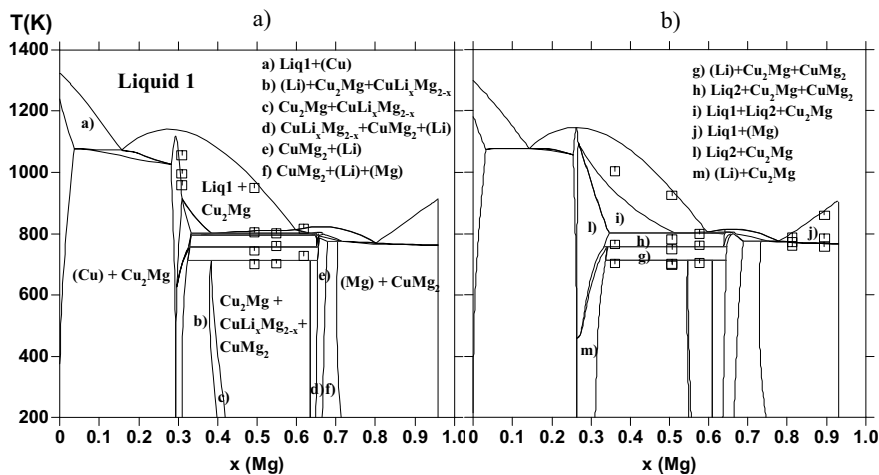

Figure 1. Assessed vertical sections of the ternary system Cu-Li-Mg [3]: a) x(Li) = 0.04 and b) x(Li) = 0.07. Some of the DSC/DTA experimental data are represented by squares.

The samples were polished and cleaned in pure ethanol in order to remove the oxide layer and to ensure a flat surface for a better thermal contact between sample and crucible. Experiments took place in a DSC of continuous flux (indeed a DTA) *Shimadzu 50* that operates between room temperature and 1003 K, using stainless steel crucibles especially conceived for this propose. Crucibles were quasi-hermetic and the volume of the samples and the inner

volume of the crucibles were very close. For each composition, at least four cycles of heating /cooling were made, always with four different samples. The heating/cooling rates used were 5, 10 and 20 K/min. Transformation temperatures in figure 1 correspond to a "0 K/min." heating rate.

SEM/EDS measurements

SEM/EDS analyses were also performed on each sample, at room temperature and after being annealed for 60 min. at 773 K followed by quenching into liquid N_2. The Li content was found by difference [5]; high quality standards of Cu and Mg were used as patterns. A JEOL, JSM - 35C or JFM 6301 F was used. Figure 2 shows one of the photomicrographs of the samples studied which reveals the presence of a eutectic constituent. In Table 1 it can be seen the obtained EDS results for three of the system's component phases.
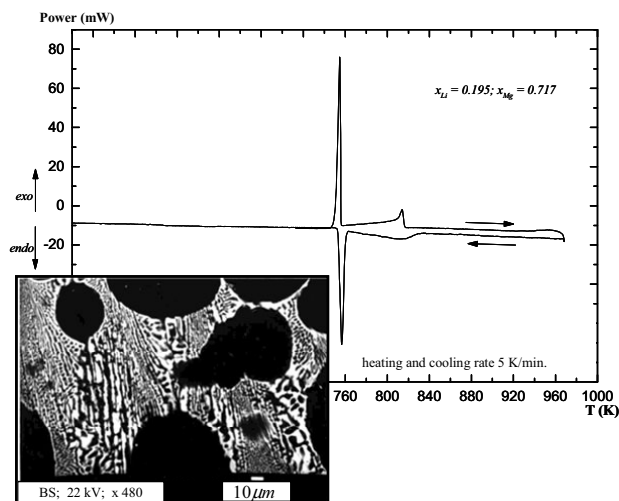

Figure 2. A DSC/DTA heating/cooling curve for a sample with x(Cu) = 0.088, x(Li) = 0.19, x(Mg) = 0.717, for a heating/cooling rate of 5 K/min. SEM backscatter photomicrograph (x 480) of the same sample after being annealed at 773 K for 60 min. followed by quenching into liquid N_2. Two phases can be distinguished: (Mg) and/or (Li) in black and CuMg$_2$ in white. Li content was obtained by difference [5].

Table 1. SEM/EDS results. Average contents were obtained from more than twenty measurements. The error associated with the Li content cannot be precisely determined because Li was found by difference.

Phase	x(Cu) ± 0.005	x(Li)	x(Mg) ± 0.005	Phase	x(Cu) ± 0.006	x(Mg) ± 0.006	Phase	x(Cu) ± 0.005	x(Mg) ± 0.005
CuLi$_x$Mg$_{2-x}$	0.334	0.040	0.626	CuMg$_2$	0.674	0.326	Cu$_2$Mg	0.669	0.332

RT and HT - powder XRD

At room temperature, some powder samples were measured on a Philips X´Pert Pro MPD using CuKα_1 radiation (λ = 0.15406 nm) primary monochromated by a symmetric Ge (111) crystal [1]. When those samples were studied at high temperatures, instead of the primary monochromated radiation CuKα_1 and CuKα_2 (λ = 0.15443nm) were used, because the inten-

sity of the incident/diffracted beam was already attenuated by the protective graphite foil of the heating chamber. Intensity can become crucial when a sample is being heated because the counting time cannot be very high owing to the sample's reactivity. The heating chamber was an Anton Parr that operates from room temperature to 1473 K. The diffraction pattern in figure 3 was obtained under the same conditions as those for high temperature. Patterns were collected from 5 to 120º (2θ) with steps of 0.01º and a counting time of 10 s.
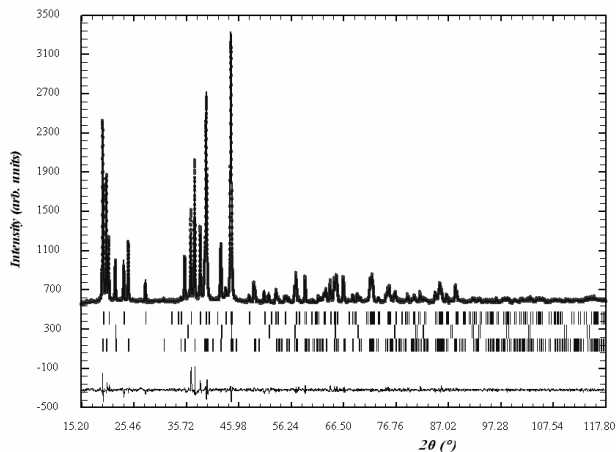

Figure 3. XRD diffraction pattern of $CuLi_xMg_{2-x}$ (x ~ 0.11) + Cu_2Mg + $CuMg_2$, at 300 K, after Rietveld refinement, of a sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578. (1) observed – points, and calculated - continuous line, (2) Bragg positions for Cu-Li_xMg_{2-x} (x ~ 0.11), Cu_2Mg and $CuMg_2$, respectively, (3) difference between observed and calculated patterns.

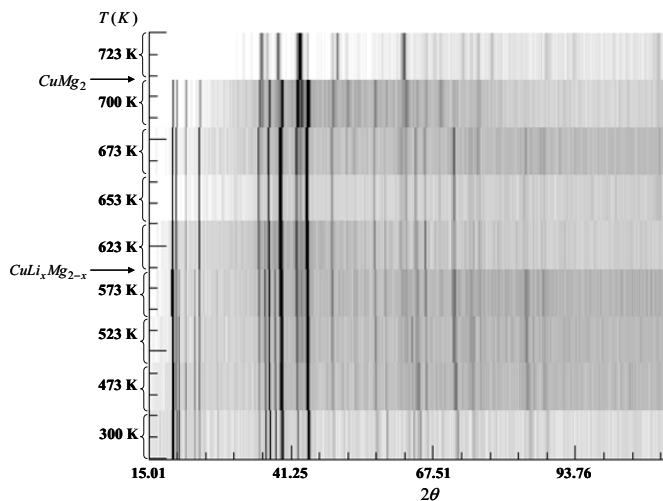Figure 4. 2D film diffractogram of a sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578. Above 573 K $CuLi_xMg_{2-x}$ (x ~ 0.11) cannot be distinguished, and above 700 K $CuMg_2$ cannot be distinguished.

Discussion

DSC/DTA results denote the existence of at least three invariant transitions at T = 702 ± 2 K, T = 757 ± 2 K and T = 804 ± 2 K (see figures 1 and 2). It seems that $CuLi_xMg_{2-x}$ (x ~ 0.11) decomposes at T = 702 ± 2 K, although its peaks couldn't be distinguished at temperatures above 623 K in the HT-XRD pattern (see figures 4 and 5). SEM/EDS results assisted us to conclude about the nature of the transitions (see figure 2) and to identify the phases in equilibrium. It was very difficult to determine the Li content due to the difficulties pointed out in [5].
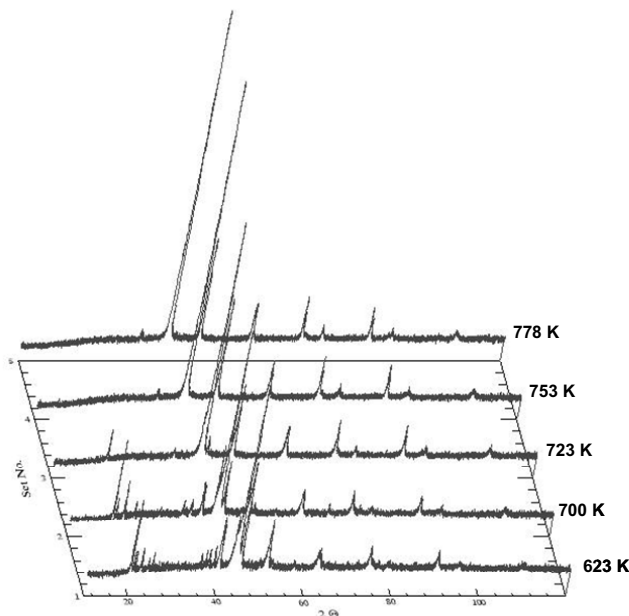

Figure 5. 3D plot diffractogram of sample with x(Cu) = 0.290, x(Li) = 0.096 and x(Mg) = 0.614. Above 623 K it cannot be distinguished $CuLi_xMg_{2-x}$ (x ~ 0.11), and above 700 K it cannot be distinguished $CuMg_2$.

FullProf - WinPLOTR software [6] was used to make a Rietveld refinements of the phase $CuLi_xMg_{2-x}$ (x ~ 0.11) for the sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578 at 300 K, 473 K, 523 K, 573 K and 623 K. At 300 K (see figure 3) the lattice parameters obtained were a = b = 0.5262(1) nm and c = 1.3644(1) nm and x ~ 0.08 in $CuLi_xMg_{2-x}$ for an R_p = 13.4% and R_{wp} = 9.71% (conventional Rietveld R-factors), χ^2 = 0.212 and R_B = 5.36% and R_f = 3.91%. These results are in close agreement with those obtained in [1]. However, although the sample has the same composition as that analysed in [1], an extra phase ($CuMg_2$) was detected. A potential explanation for the presence of a third phase in equilibrium relies on the proximity of the sample's composition to the border of the two and three phase domains. The results of the lattice parameters obtained at high temperatures are shown in figure 6. For the other phases in equilibrium, a Le Bail fit was performed.

Even if there is not a straight forward correspondence between the transition' temperatures obtained by DSC/DTA and by HT-XRD, HT-XRD allowed us to know what were the phases

present at different temperatures. The linear thermal expansion parameters were calculated following the obtained lattice parameters (see figure 6) and were found to be, at 300 K, $\alpha_{a=b}$ = 2.89x10^{-5} K^{-1} and α_c = 3.13x10^{-5} K^{-1}. As expected, these results are in good agreement with each other.
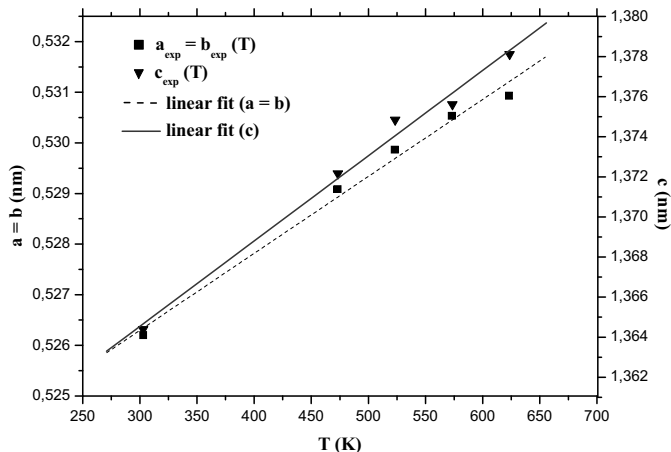

Figure 6. Lattice parameters of the phase CuLi$_x$Mg$_{2-x}$ (x ~ 0.11) obtained by Rietveld refinement of the diffraction patterns of the sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578 at different temperatures.

Concluding remarks

The Cu-Li-Mg system was studied by DSC/DTA, SEM/EDS and XRD at room and high temperatures. Results are in good agreement and the techniques complemented each other. The crystal structure and the thermal behaviour of CuLi$_x$Mg$_{2-x}$ (x ~ 0.11) was studied by HT-XRD which seems to be essential for the phase diagram's assessment.

References

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