Thermodynamic investigations in the solid state of the lanthanum–magnesium–zinc system

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A B S T R A C T

The La–Mg–Zn phase diagram is experimentally investigated at 595 K, $x_{La} > 4\%$ and the corresponding isothermal section is partially determined. This section includes 5 substitutional solid solutions based on the binary compounds (LaMg, LaZn, LaMg$_3$, LaMg$_{10.3}$ and La$_2$Zn$_{17}$) and three ternary phase (La$_8$(Mg,Zn)$_{92}$, La$_3$(Mg,Zn)$_{11}$ and La$_{4.27}$Mg$_{2.89}$Zn$_{30}$). The enthalpies of mixing in the ternary solid solutions are calculated at 298 K on the basis of tin solution calorimetry experiments.

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1. Introduction

As structural materials, magnesium alloys have obvious advantages such as lowest density of all metallic materials associated with relatively high specific strength [1]. Therefore these alloys are playing an increasing role in automotive and aircraft industries [1,2]. For optimizing the effects of Rare Earth (RE) additions on the mechanical properties of Mg–Zn–Zr alloys like the ZK61, a more precise knowledge of the corresponding phase diagrams represents a valuable tool [3].

The Mg–Zn–RE systems were previously investigated, however their phase diagrams have only been scarcely and incompletely studied.

The present work is the first part of a La–Mg–Zn system investigation. A complete description of the three constitutive binary phase diagrams (La–Mg, La–Zn and Mg–Zn) on the basis of a critical review of the relevant literature data and additional experimental work has been given in previous papers [4–11].

Eight binary intermediate compounds are evidenced at room temperature in the La–Mg system (LaMg, LaMg$_3$, La$_2$Mg$_{17}$, and LaMg$_{12}$) and in the Mg–Zn system (Mg$_{21}$Zn$_{25}$, Mg$_4$Zn$_7$, MgZn$_2$, and Mg$_2$Zn$_{11}$). The La–Zn system contains nine intermediate compounds: LaZn, LaZn$_2$, LaZn$_4$, LaZn$_5$, LaZn$_7$, La$_3$Zn$_{22}$, La$_2$Zn$_{17}$, LaZn$_{11}$, and LaZn$_{13}$.

Recently, De Negri et al. [12] have shown that La$_2$Mg$_{17}$ is in fact a disordered LaMg$_{10.3}$ structure.

To improve the description of solid phase equilibria in the ternary La–Mg–Zn system, an isothermal section is investigated at 595 K and the mixing enthalpies in the ternary solid solutions are measured by calorimetric method.

2. Literature data

2.1. Experimental results

A La$_2$Mg$_3$Zn$_3$ ternary phase with a cubic crystal structure was identified by Melnik et al. [13], quoted by Pavlyuk et al. [14].

From metallographic observations and X-ray diffraction measurements, Dobatkina et al. [15,16] show on the 573 K isothermal section the existence of three ternary solid solutions with Mg/Zn substitution (La(Mg,Zn), La(Mg,Zn)$_3$ and La$_2$(Mg,Zn)$_{17}$) and one ternary compound named V-phase containing 5 at.% La, 42 at.% Mg and 53 at.% Zn. Magnesium and zinc exhibit complete mixing in the La(Mg,Zn) and La$_2$(Mg,Zn)$_{17}$ solid solutions. The solubility of zinc in La(Mg,Zn)$_3$ is limited to 42 at.%.

In light of Dobatkina's results, the cubic $La_2Mg_3Zn_3$ phase observed by Melnik et al. [13] belongs to the $La(Mg,Zn)_3$ solid solution.

As shown by De Negri et al. [12], La_2Mg_{17} is more accurately described as a $LaMg_{10.3}$ ($CeMg_{10.3}$-type, space group $P6_3/mmc$) disordered structure. It differs from the structure of La_2Zn_{17} (Th_2Zn_{17}-type, space group $R\bar{3}m$ [17]). Consequently, the existence of a continuous solid solution between these structures put forward by Dobatkina et al., is not possible.

The existence of a ternary compound is also mentioned by Tsai et al. [18] with a composition slightly different from the one of the V phase mentioned by Dobatkina et al. ($La_8Mg_{42}Zn_{50}$).

Li and Huang and co-workers investigated the Mg-rich corner of the La–Mg–Zn system at 573 K [19], 623 K [20] and 673 K [21]. According to these authors, the V-phase is in fact a linear solid solution $La_8(Mg,Zn)_{92}$ labelled T-phase, stable in a domain extending from at least 16 at.% to 43 at.% Zn at 673 K, with a C-centred orthorhombic structure which is consistent with the determination by electron diffraction of Wei et al. [22] on the pseudo ternary T-phases in Mg–Zn–RE alloys.

Recent results of Pavlyuk et al. [23,14] evidenced the existence of two new ternary phases:

- the orthorhombic (Immm) $La_3(Zn_{0.874}Mg_{0.126})_{11}$ [23];
- the hexagonal ($P6_3/mmc$) $La_{4.27}Mg_{2.89}Zn_{30}$ with strong positional disorder [14].

To our knowledge, no thermodynamic functions of the phases in the La–Mg–Zn ternary system have been reported so far in the literature.

2.2. Assessment

A Calphad assessment of the La–Mg–Zn system was performed by Qi et al. [24] on the basis of Dobatkina et al. data [15,16].

The ternary phase named T_1 is modelled with the $La_5Mg_{42}Zn_{53}$ stoichiometry. The isothermal sections of the system calculated at 298 K and 500 K are drawn in Fig. 1. The calculated results reproduce the experimental information of Dobatkina et al.
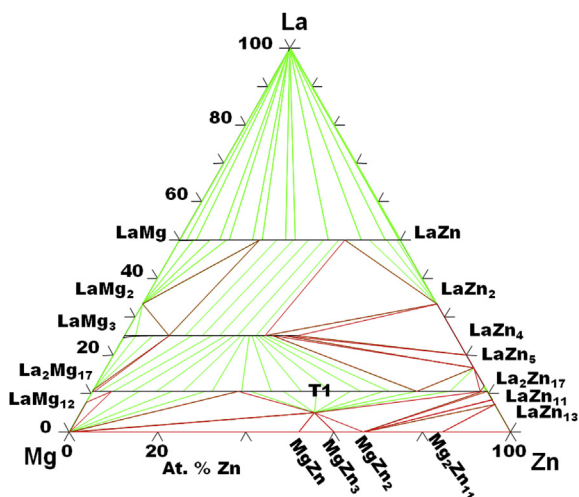
However, the extended stability range of the T-phase by Mg/Zn substitution as evidenced by Li and Huang [20,21] is not taken into account in the Qi's work. As pointed out in paragraph 2.1, the continuous solid solution between La_2Mg_{17} and La_2Zn_{17} contradicts available crystallographic data. Moreover, two new ternary phases ($La_3(Mg,Zn)_{11}$ and $La_{4.27}Mg_{2.89}Zn_{30}$) were discovered after the publication of Qi's assessment.

The La–Mg and La–Zn binary systems have been recently reassessed by the present authors [9–11] on the basis of their new experimental data [5,6,8,10].

Before performing a new ternary assessment based on the new binary assessments, further ternary experimental investigations are necessary. Especially, the isothermal section at low temperature must be made clearer and the mixing enthalpy of the ternary solid solutions must be measured.

3. Experimental

3.1. Elaboration of the samples

The alloys are prepared from the pure constitutive elements: La (99.9%+, Huhhot Jinrui Rare Earth Co. Ltd), Mg (99.98%, Aldrich) and Zn (99.999%, Alfa Aesar).

In the following, the samples are denominated as x/y/z where x, y, z are respectively the La, Mg and Zn atomic fractions in percent.

Since both La and Mg have a strong affinity with oxygen and the vapour pressures of Mg and Zn are high, the samples are prepared in sealed crucibles.

These crucibles (18 mm in diameter and 11 mm in height) are cold-stamped from a pure tantalum sheet of 0.25 mm thickness, supplied by Technicome. They are filled in and sealed by Tungsten Inert Gas welding, under argon atmosphere (<1 ppm O_2 and <20 ppm H_2O) in a glove box.

The mixtures are heated up to 1220 K for about 30 min. This temperature chosen as higher than the highest melting temperature of the constitutive elements (1193 K for La) allows for complete mixing of the elements in the liquid state.

After the melting stage, three samples are air quenched down to 298 K. These alloys are labelled HT.

The other samples are slowly cooled down to 595 K and hold at this temperature for 40 days. This temperature is lower than the lowest invariant temperature reported in any of the 3 constitutive binaries (598.2 K in Mg–Zn).

3.2. Characterization of the samples

The samples are characterized by X-Ray powder Diffraction (XRD) and Electron Probe Micro-Analysis (EPMA).

Powder diffraction patterns are recorded in the [10°–100°] 2θ range, with a step size of 0.01671° and a step time of 130 ms on a Philips Expert diffractometer equipped with a copper $K_{\alpha 1}$ anticathode.

The phases are indexed from the experimental X-Ray diffraction patterns using the PowderCell software [25]. The lattice parameters are calculated using the UnitCell software [26].

Electron Probe Micro-Analyses are performed with a CAMECA SX100 Analyser equipped with five Wave Dispersion Spectrometers (WDS).

3.3. Calorimetric measurements

The dissolution calorimetric measurements are carried out in a home-made Tian–Calvet high temperature differential microcalorimeter extensively described in the literature [27,28].

Fig. 1. Isothermal section of the La–Mg–Zn calculated at 500 K from the assessed parameters of Qi [24].