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# Isothermal section from 50 to 75 at.% Mg of the ternary system Y–La–Mg

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**Abstract**

The ternary system Y–La–Mg has been studied in the 50–75 at.% Mg composition range using microscopic and X-ray diffraction analyses. The sections $(Y_xLa_{1-x})Mg$ (continuous cP2-CsCl-type solid solution), $(Y_xLa_{1-x})Mg_2$ (cF24-$Cu_2Mg$-type solid solution for $0 \leqslant x \leqslant 0.72$ and hP12-$MgZn_2$-type solid solution for $0.82 \leqslant x \leqslant 1$) and $Y_xLa_{1-x}Mg_3$ ($0 \leqslant x \leqslant 0.47$, cF16-$BiF_3$-type solid solution) have been especially studied.

## 1. Introduction

The alloying behaviour of the rare earth (R) metals with magnesium has been described by several authors. Data concerning the binary R–Mg systems (crystal chemistry, phase diagrams), the ternary R–Mg–Me systems (Me ≡ metal) and the properties and applications of these alloys have been summarized by Rokhlin [1]. Assessed versions of several R–Mg binary phase diagrams have been reported by Nayeb-Hashemi and Clark [2]. In our laboratory a systematic investigation and revision of the R–Mg systems has been undertaken. The following systems have been studied and/or assessed: Pr–Mg [3], Nd–Mg [4], Sm–Mg [5], Gd–Mg [6], Tb–Mg [7], Dy–Mg [8], Ho–Mg [9] and Er–Mg [10].

Considering the groups of R–R′–Mg ternary alloys formed by Mg with two different rare earth metals, the following data have been reported in the literature:

(1) phase equilibria in the Mg-rich regions for the systems Y–Sc–Mg [1], Y–La–Mg [11], Y–Ce–Mg [12], Y–Nd–Mg [1], Y–Sm–Mg [13, 14] and Ce–La–Mg [15];

(2) crystal structures and magnetic properties of the continuous solid solutions $Gd_xLa_{1-x}Mg$ [16], $Gd_xLa_{1-x}Mg_2$ [17], $Ce_xR_{1-x}Mg_3$ (R ≡ La,Y) [18] and $Ce_xR_{1-x}Mg$ (R ≡ La,Y) [18, 19], electrical properties of $Ce_xR_{1-x}Mg$ (R ≡ La,Y) [19] and mechanical properties, creep formation [20, 21] and formation and decomposition of supersaturated Y–Nd–Mg alloys [22].

As a contribution to the study of this group of alloys, some data obtained in the investigation of the Y–La–Mg system will be reported.

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## 2. Literature data on the Y–La–Mg system

The binary systems relevant to this investigation are La–Mg and Y–Mg. According to ref. 2, the following phases have been observed.

*La–Mg system.* $LaMg_{12}$, oI338-$CeMg_{12}$(II) type, peritectic formation at about 650 °C; $La_2Mg_{17}$, hP38-$Th_2Ni_{17}$ type, peritectic 672 °C; $LaMg_3$, cF16-$BiF_3$ type, congruent melting at 798 °C; $LaMg_2$, cF24-$Cu_2Mg$ type, peritectic 775 °C; LaMg, cP2-CsCl type, peritectic 745 °C. According to the same assessment, moreover, $LaMg_2$ undergoes a eutectoidal decomposition ($LaMg + LaMg_3$) at 725 °C.

*Y–Mg system.* $Y_5Mg_{24}$, cI58-α-Mn type, peritectic 605 °C; $YMg_2$, hP12-$MgZn_2$ type, peritectic 780 °C; YMg, cP2-CsCl type, peritectic 935 °C.

For the ternary system, Mg-rich alloys have been studied by Padezhnova *et al.* [11] and Dobatkina *et al.* [23]. According to these authors, in the Mg-rich region the $Y_5Mg_{24}$ and $La_2Mg_{17}$ phases are in equilibrium with the magnesium solid solution. The projection of the crystallization surfaces in this composition range and the ternary eutectic ($L \rightarrow (Mg) + Y_5Mg_{24} + La_2Mg_{17}$) have been described. Some discrepancies with the accepted versions of the binary systems can be noticed ($LaMg_{12}$ should be the stable phase in the Mg-rich region). Considering also the complex crystallization processes often reported (metastable phase formation, phase boundary uncertainties), a diagram revision may be useful. As a first contribution, data relevant to the subsolidus equilibria in the 50–75 at.% Mg range will be reported here.


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TABLE 1. Crystallographic data of Y–La–Mg alloys along the $Y_xLa_{1-x}Mg$, $Y_xLa_{1-x}Mg_2$ and $Y_xLa_{1-x}Mg_3$ sections

| Phase | Pearson symbol and prototype | Lattice parameters (pm) | Reference and comments |
|---|---|---|---|
| $Y_xLa_{1-x}Mg$ | cP2 | | $0 \leqslant x \leqslant 1$ |
| | CsCl | $a = 396.2$ | [28] $x = 0$ |
| | | $a = 396.1$ | [25] $x = 0.11$ |
| | | $a = 391.8$ | [25] $x = 0.333$ |
| | | $a = 385.0$ | [25] $x = 0.667$ |
| | | $a = 381.6$ | [25] $x = 0.889$ |
| | | $a = 379.7$ | [25] $x = 1$ |
| $Y_xLa_{1-x}Mg_2$ | cF24 | | $0 \leqslant x \leqslant 0.72$[a] |
| | $Cu_2Mg$ | $a = 880.1$ | [29] $x = 0$ |
| | | $a = 880.6$ | $x = 0$ |
| | | $a = 879.9$ | $x = 0.11$ |
| | | $a = 877.3$ | $x = 0.22$ |
| | | $a = 865.6$ | $x = 0.55$ |
| | | $a = 866.0$ | $x = 0.556$ |
| | | $a = 862.5$ | $x = 0.64$ |
| | | $a = 862.8$ | $x = 0.667$ |
| | | $a = 861.5$ | $x = 0.72$ |
| $Y_xLa_{1-x}Mg_2$ | hP12 | | $0.82 \leqslant x \leqslant 1$[a] |
| | $MgZn_2$ | $a = 607.7$, $c = 990.3$ | $x = 0.87$ |
| | | $a = 606.5$, $c = 989.0$ | $x = 0.90$ |
| | | $a = 603.8$, $c = 979.0$ | $x = 1$ |
| | | $a = 603.8$, $c = 980.0$ | [29] $x = 1$ |
| $Y_xLa_{1-x}Mg_3$ | cF16 | | $0 \leqslant x \leqslant 0.47$[a] |
| | $BiF_3$ | $a = 749.4$ | [30] $x = 0$ |
| | | $a = 751.0$ | $x = 0$ (La rich) |
| | | $a = 748.8$ | $x = 0$ (Mg rich) |
| | | $a = 747.7$ | $x = 0.20$ |
| | | $a = 745.6$ | $x = 0.30$ |
| | | $a = 743.7$ | $x = 0.40$ |
| | | $a = 741.8$ | $x = 0.47$ |

[a]The reported limiting compositions are those obtained by means of microprobe analysis.

## 3. Experimental details

The metals used were magnesium (99.99 mass% nominal purity), lanthanum and yttrium (99.9 mass% nominal purity), all supplied by Koch Chemicals Ltd. The elements were enclosed in small tantalum crucibles sealed by arc welding under pure argon. The samples were melted in an induction furnace and were then annealed in a resistance furnace at 500 °C for 1 week. Optical and electronic metallographic examinations were carried out on all samples; the samples were prepared by the standard method and etched in alcoholic 2% $HNO_3$ solution. Electronic metallographic examination was carried out using a scanning electron microscope equipped with a microprobe (based on energy-dispersive X-ray spectroscopy). Microprobe examination was carried out to determine phase compositions, using pure elements as standards. For X-ray analysis a vertical diffractometer with Cu K$\alpha$ radiation was used. Annealed ingots were often brittle; therefore powder samples were used for X-ray measurements. The addition of a calibration standard (Si) to the sample was made to achieve higher accuracy in measurements of the $d$ values. The samples were spun during measurements to minimize preferred orientation effects. The observed diffraction intensities were compared with the calculated

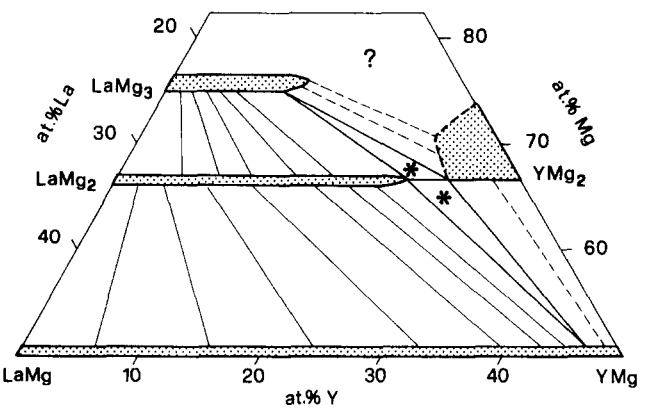


Fig. 1. Y–La–Mg system: isothermal section at 500 °C in the 50–75 at.% Mg range. Asterisks denote three-phase regions. Dotted areas are one-phase regions. In the two-phase regions a few tie-lines are indicated.

TABLE 2. Crystallographic data of the binary Y–Mg system (50–75 at.% Mg)

| Phase | Pearson symbol and prototype | Lattice parameters (pm) | Reference and comments |
|---|---|---|---|
| $YMg_{1+x}$ | cP2 | $a=380.9(1)$ | [31] (Y-rich) |
| | CsCl | $a=378.1(1)$ | [31] (Mg-rich) |
| $YMg_{2+x}$ | hP12 | $a=603.8$, $c=980.0$ | [29] $x=0$ |
| | $MgZn_2$ | $a=603.8$, $c=979.0$ | $x=0$ |
| | | $a=603.4$, $c=978.6$ | $x=0.12$ |
| | | $a=603.0$, $c=977.2$ | $x=0.57$ |
| | | $a=602.7$, $c=976.3$ | $x=0.70$ |
| | | $a=602.3$, $c=974.7$ | $x=0.82$ |

The reported compositions are those obtained by means of microprobe analysis.

values obtained using the program PULVERIX [24]. The values of the lattice parameters, reported in Table 1, were refined using a least-squares routine.

## 4. Results and general remarks

Figure 1 summarizes the results obtained after annealing the alloys at 500 °C for 1 week (metastable equilibria, however, have possibly been included).

A few comments may be especially noteworthy for the following sections.

*$Y_xLa_{1-x}Mg$ section.* The CsCl-type solid solution, continuous over the complete composition range ($0 \leqslant x \leqslant 1$), already described by Zanicchi *et al.* [25], has been confirmed.

*$Y_xLa_{1-x}Mg_2$ section.* Two phases have been observed in this section: the $LaMg_2$-based, cF24-$Cu_2Mg$-type solid solution (extending up to $x \approx 0.72$) and the $YMg_2$-based, hP12-$MgZn_2$-type solid solution (extending from $x \approx 0.82$ to $x = 1.0$). Notice, however, that the homogeneity field of the $YMg_2$-based solid solutions extends also towards Mg-richer compositions (up to about 73 at.% Mg). This may be compared with the lattice parameter data of the binary Y–Mg phases reported in Table 2 (notice the lattice constant decreasing with increasing Mg content). This trend is different from that reported in the literature ($YMg_2$ was reported as a point compound). In order to obtain further confirmation of this behaviour, a revision of the binary Y–Mg diagram has been started. The preliminary data obtained so far (by differential thermal analysis, micrography, etc.) are in agreement with the existence of a homogeneity field for $YMg_2$. Also for the $LaMg_2$-based solid solutions we have to mention disagreement between the data reported in Fig. 1 and the literature description of the binary La–Mg system. For $LaMg_2$, in fact, a eutectoidal decomposition occurring either at 626 °C [26] or at 725 °C [27] has been described in the literature. In this investigation, however, even after very lengthy annealing treatments

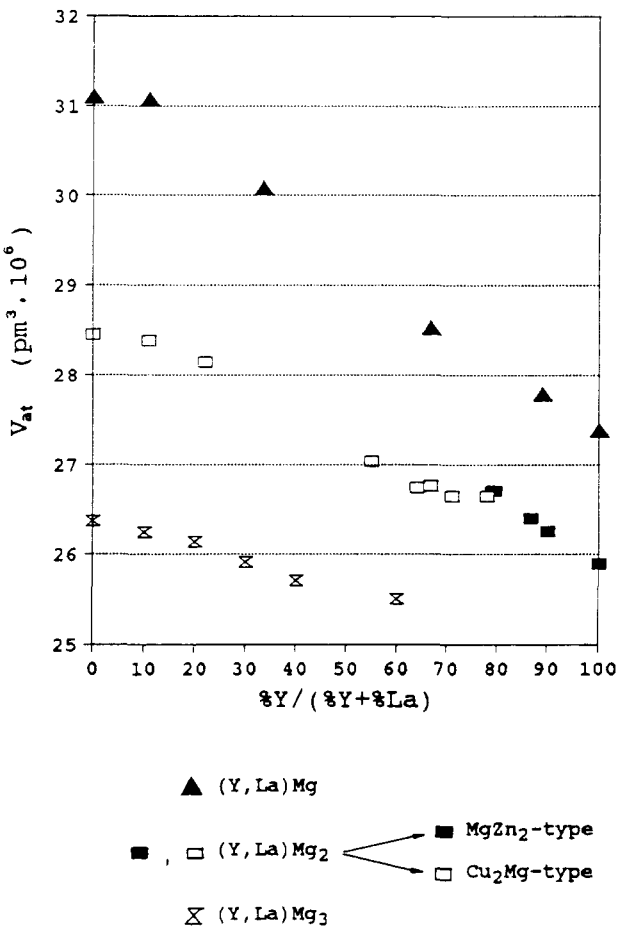


Fig. 2. Average atomic volumes of Y–La–Mg alloys along the continuous $Y_xLa_{1-x}Mg$ solid solution region and along the $Y_xLa_{1-x}Mg_2$ and $Y_xLa_{1-x}Mg_3$ sections.

(*e.g.* 720 h at 500 °C, 480 h at 650 °C) no significant decomposition was observed in either the binary $LaMg_2$ or the ternary $Y_xLa_{1-x}Mg_2$ phases (only for an alloy with a composition corresponding to $x=0.49$ was a partial decomposition observed after 192 h at 500 °C). We may therefore not exclude a metastable character

of a certain portion (near $LaMg_2$) of the isothermal section presented in Fig. 1.

*$Y_xLa_{1-x}Mg_3$ section.* Along this section an $LaMg_3$-based phase of the cF16-$BiF_3$ type is formed from $x=0$ up to $x\approx 0.47$.

*Two- and three-phase regions.* On the basis of the microprobe analysis carried out on the different phases observed in two- and three-phase alloys, possible trends of the tie-lines (and triangles) have been obtained. These are sketched in Fig. 1 even though within the limits of the uncertainties relative to the metastability of the phases.

In conclusion, we may mention the data obtained from the lattice parameter measurements (see Table 1). A summary of these data is given in Fig. 2, where the average atomic volumes of the various alloys are reported as function of the Y/(La+Y) relative content. We may notice in the single-phase fields the smooth trends of the curves and in the (Y, La)$Mg_2$ section the miscibility gap between the $MgZn_2$-type and $Cu_2Mg$-type fields.

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## References

1 L.L. Rokhlin, *Magnesium Alloys with Rare Earth Metals,* Nauka, Moscow, 1980.
2 A.A. Nayeb-Hashemi and J.B. Clark (eds.), *Phase Diagrams of Binary Magnesium Alloys,* ASM International, Metals Park, OH, 1988.
3 A. Saccone, A.M. Cardinale, S. Delfino and R. Ferro, *Intermetallics, 1* (1993) 151–158.
4 S. Delfino, A. Saccone and R. Ferro, *Metall. Trans. A, 21* (1990) 2109–2114.
5 A. Saccone, S. Delfino, G. Borzone and R. Ferro, *J. Less-Common Met., 154* (1989) 47–60.
6 G. Cacciamani, A. Saccone, G. Borzone, S. Delfino and R. Ferro, *Thermochim. Acta, 199* (1992) 17–24.
7 A. Saccone, S. Delfino, D. Macciò and R. Ferro, *J. Phase Equilib., 14* (1993) 479–484.
8 A. Saccone, S. Delfino, D. Macciò and R. Ferro, *Z. Metallkd., 82* (1991) 568–573.
9 A. Saccone, S. Delfino, D. Macciò and R. Ferro, *J. Phase Equilib., 14* (1993) 280–287.
10 A. Saccone, S. Delfino, D. Macciò and R. Ferro, *Metall. Trans. A, 23* (1992) 1005–1012.
11 E.M. Padezhnova, T.V. Dobatkina and E.V. Muratova, *Izv. Akad. Nauk SSSR, Met.,* (4) (1983) 194–197.
12 E.M. Padezhnova, E.V. Mel'nik, V.V. Kinzhibalo and T.V. Dobatkina, *Izv. Akad. Nauk SSSR, Met.,* (4) (1981) 220–223.
13 M.E. Drits, L.L. Rokhlin and N.P. Sirchenko, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.,* (6) (1983) 78–82.
14 M.E. Drits, L.L. Rokhlin and N.P. Abrukina, *Izv. Akad. Nauk SSSR, Met.,* (5) (1984) 199–204.
15 L.L. Rokhlin and N.R. Bochvar, *Izv. Akad. Nauk SSSR, Met.,* (2) (1972) 193–197.
16 K.H.J. Buschow and C.J. Schinkel, *Solid State Commun., 18* (1976) 609–612.
17 E. Dormann, H. de Graaf, R.C. Thiel and K.H.J. Buschow, *J. Magn. Magn. Mater., 30* (1982) 231–237.
18 R.M. Galera, J. Pierre and A.P. Murani, *J. Magn. Magn. Mater., 47–48* (1985) 155–158.
19 J. Pierre, R.M. Galera and E. Siaud, *J. Phys. (Les Ulis, Fr.), 46* (1985) 621–626.
20 I. Stulikova, P. Vostry, B.L. Mordike and B. Smola, *Proc. 5th Int. Conf. on Progress on Heat Treatment of Materials, 1986,* IFHT, Budapest, Vol. 3, pp. 1993–2000.
21 W. Henning and B.L. Mordike, *Strength of Metallic Alloys, Proc. 7th Int. Conf., 1985,* Pergamon, Oxford, 1986, Vol. 1, pp. 803–808.
22 P. Vostry, I. Stulikova, B. Smola, M. Cieslar and B.L. Mordike, *Z. Metallkd., 79* (1988) 340–344.
23 T.V. Dobatkina, E.V. Muratova, V.V. Kinzhibalo and A.T. Tyvanchuk, *Izv. Akad. Nauk SSSR, Met.,* (1) (1984) 211–214.
24 K. Yvon, W. Jeitschko and E.J. Parthé, *J. Appl. Crystallogr., 10* (1977) 73–74.
25 G. Zanicchi, V. Contardi, R. Marazza, D. Mazzone and R. Ferro, *J. Less-Common Met., 142* (1988) L31–L36.
26 R. Vogel and T. Heumann, *Z. Metallkd., 38* (1947) 1–8.
27 P. Manfrinetti and K.A. Gschneidner Jr., *J. Less-Common Met., 123* (1986) 267–275.
28 K.H.J. Buschow, *J. Less-Common Met., 33* (1973) 239–244.
29 K.H.J. Buschow, R.C Sherwood and F.S.L. Hsu, *J. Appl. Phys., 49* (1978) 1510–1512.
30 G. Berger and A. Weiss, *J. Less-Common Met., 142* (1988) 109–121.
31 J.F. Smith, D.M. Bailey, D.B. Novotny and J.E. Davison, *Acta Metall., 13* (1965) 889–895.