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THERMODYNAMIC REASSESSMENT OF THE La–Mn SYSTEM

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Abstract

The binary La–Mn system is investigated by CALPHAD approach. The experimental phase diagram and thermodynamic data available in the literature are critically reviewed and assessed using the thermodynamic models for the Gibbs energies of individual phases. A set of consistent thermodynamic data for the La–Mn system is obtained by optimization of the selected experimental data. The miscibility gap is no more existent in the optimized phase diagram. The calculated phase diagram agrees well with the experimental data.

Keywords: La–Mn system; Phase diagram; CALPHAD approach.

1. Introduction

Mg-based alloys are widely used in automotive, railway and aerospace industries due to their low density, excellent specific strength and good recyclability [1]. The addition of a small amount of Mn in Mg-based alloys yields an improvement of corrosion resistance and enhancement of grain refinement [2]. While a small addition of rare earth elements such as lanthanum, cerium or neodymium will lead to attractive properties of Mg-based alloys [3], such as good anti-corrosion [4, 5], high tensile strength [6], and excellent weld ability [7]. To optimize alloy composition and efficiently develop the Mg-based alloys with desirable properties, knowledge of phase equilibria and thermodynamic properties in the La–Mn system is indispensable.

The investigation of the La–Mn system was first carried out by Rolla and Iandelli [8] with the alloys made from 99.5 wt.% La with Fe, Si, Mg, and carbon impurities and 99.8 wt.% Mn with Ni, Zn and sulfur impurities by means of the thermal analysis, micrographic investigation and X-ray diffraction (XRD), and a broader miscibility gap for the liquid phase was found. According to the work of Rolla and Iandelli [8], the monotectic reaction Liquid#2 ↔ Liquid#1 + (βMn) was determined to occur at 1081 °C with the compositions of 38 wt.% Mn and 74 wt.% Mn. The eutectic reaction Liquid#2 ↔ (αLa) + (αMn) was determined to be at 701 °C with the eutectic composition of 7.5 wt.% Mn. But they did not take into account the effects of Mn on the La or of La on the Mn allotropic transformations. And no intermetallic compounds were found in the La–Mn system. Subsequently, based on the data from Rolla and Iandelli [8], Gschneidner [9] published almost the same phase diagram, with slight improvement on the monotectic and eutectic temperatures. Using XRD analysis method, Kripyakevich et al. [10], Wang and Holden [11], and Kirchmayer [12] also approved that no intermediate compounds existed in this system. Gschneidner et al. [13] and Gokcen [14] investigated the melting and transformation temperatures for pure elements. The above experimental data for the La–Mn system was reviewed by Palenzona and Ciraflici [15]. Subsequently, Nikolaenko and Nosova [16] measured the partial enthalpy of mixing for liquid La–Mn alloys at 1600 K using isoperibolic calorimeter, smoothed these data and suggested the integral enthalpy of mixing for liquid. Lately, Kim and Jung [17] evaluated this system by Modified Quasichemical Model with seven parameters for the liquid and the calculated consolute temperature of the miscibility gap which is 1165 °C at 0.28 at.% La.

Since the miscibility gap in the Ce–Mn system proposed by Rolla and Iandelli [8] was not experimentally confirmed by Tang et al. [18, 19] using four key alloys subjected to X-ray analysis and differential thermal analysis (DTA). The present work ignored the report of Rolla and Iandelli [8] on the miscibility gap in the La-Mn liquid phase. In view of the fact that the lanthanide series possess some analogous properties, the La–Mn binary system should be similar to the Ce–Mn, Pr–Mn and Nd–Mn

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Dedicated to the memory of Professor Zbigniew Moser systems. It is reported that no miscibility gap exists in Ce–Mn [18, 19], Pr–Mn [20], and Nd–Mn [21] systems. Consequently, the detected monotectic reaction Liquid#2 ↔ Liquid#1 + (βMn) at 1081 °C [8] and the invariant reaction at 701 °C [8] was regarded as the phase transformation (γMn) ↔ (βMn), Liquid and eutectic reaction Liquid ↔ (βLa) + (αMn), respectively. These data are used in the present modeling.

On the basis of the above analytic results, the evaluation of Kim and Jung [17], who took the miscibility gap into consideration, is not reasonable. Moreover, the description of the liquid phase in our multicomponent Mg alloys database [22-23] is based on the regular solution model [24]. So the present work will provide a self-consistent set of thermodynamic parameters for this binary system using regular solution model for the liquid phase by means of CALPHAD approach.

2. Thermodynamic model

2.1 Unary phases

The Gibbs energy functions ${}^{o}G_i^{\Phi}(T) = G_i^{\Phi}(T) - H_i^{SER}$ for the pure elements La and Mn are taken from the SGTE (Scientific Group Thermodata Europe) unary database [25] and expressed by an equation of the form:

$$ {}^{o}G_i^{\Phi}(T) = a + b\cdot T + c\cdot T\cdot ln\,(T) + d\cdot T^2 + e\cdot T^3 + f\cdot T^{-1} + g\cdot T^7 + h\cdot T^{-9} \qquad (1)$$

in which H_i^{SER} is the molar enthalpy of element i (i = La, Mn) at 298.15 K and 1 bar in its standard element reference (SER) state, and T is the absolute temperature. The last two terms in Eq. (1) are used only outside the ranges of stability [26], the term $g\cdot T^7$ is for a liquid below the melting point and $h\cdot T^{-9}$ is for solid phase above the melting point.

2.2. Solution phases

In the La–Mn system, there are five solution phases, viz. liquid, (δMn), (γMn), (βMn) and (αMn). The liquid phase is modeled as completely disordered solution phase, and its Gibbs energy is expressed as follows:

$$G^L - H^{SER} = x_{La}\cdot {}^0G^L_{La} + x_{Mn}\cdot {}^0G^L_{Mn} + R\cdot T\cdot[x_{La}\cdot \ln(x_{La}) + x_{Mn}\cdot \ln(x_{Mn})] + {}^E\mathrm{G}^L_M \qquad (2)$$

where H^{SER} is the abbreviation of $x_{La}\cdot {}^0\mathrm{H}^{\mathrm{SER}}_{La} + x_{Mn}\cdot {}^0\mathrm{H}^{\mathrm{SER}}_{Mn}$, R is the gas constant, and the x_{La} and x_{Mn} are the mole fractions of La and Mn, respectively ${}^E\mathrm{G}^L_M$. is the excess Gibbs energy which is described by the Redlich-Kister (R-K) polynomial [27]:

$${}^E\mathrm{G}^L_M = x_{La}\cdot x_{Mn}\cdot \sum_{j=0}^{n} {}^jL^{\varphi}_{La,Mn}(x_{La} - x_{Mn})^j \qquad (3)$$

in which ${}^jL^{\varphi}_{La,Mn}$ is the j_{th} R-K parameter of liquid phase and can be expressed as ${}^jL^{\varphi}_{\mathrm{La,Mn}} = a_j + b_j\cdot T$. The coefficients a_j and b_j (j=0, 1, 2) are the parameters to be optimized.

3. Results and discussion

The thermodynamic parameters were optimized by using the PARROT module of the Thermo-Calc software package [28], which was based on a least square method. The step-by-step optimization procedure carefully described by Du et al. [29] was utilized in the present assessment. In the optimization procedure, each piece of experimental information was given a certain weight.

The optimization begins with the liquid phase. The parameters for liquid, a_0 and a_1 in Eq. (3), are adjusted to reproduce the experimental data of partial enthalpy of mixing for liquid at 1600 K. In order to fit the partial and integral enthalpy of mixing for liquid phase better, the parameters b_0 and a_2 needed to be optimized. Afterwards, the obtained parameters were used as starting values for subsequent optimization of the liquid and related degradation equilibria reactions at 861 or 1138 °C. Considering the reaction (δMn) ↔ (γMn), Liquid, one parameter, $a_0^{\mathrm{Bcc\_A2}}$, was introduced to describe the Bcc_A2 (δMn) phase. Similarly, one parameter, $a_0^{\mathrm{Fcc\_A1}}$, was used to adjust the description of Fcc_A1 (γMn) phase. In the present work, it was found that the introduction of further parameters (b_1 and b_2) for liquid can improve the description for the phase diagram. Finally, the thermodynamic parameters for all the phases were adjusted simultaneously by taking into account all of the selected phase diagram and thermodynamic data.

Table 1 lists the thermodynamic parameters finally obtained in the present work. The calculated La–Mn phase diagram according to the present thermodynamic parameters is shown in Fig.1. It can be seen that less thermodynamic parameters were used in the present assessment compared with the

Table 1. *Summary of the optimized thermodynamic parameters of the La–Mn system*

Liquid: Model $(\mathrm{La,Mn})_1$

${}^0L^{\mathrm{Liquid}}_{\mathrm{La,Mn}} = 30665 - 14.903{*}T$

${}^1L^{\mathrm{Liquid}}_{\mathrm{La.Mn}} = -11157 + 2.764{*}T$

${}^2L^{\mathrm{Liquid}}_{\mathrm{La.Mn}} = -17502 + 15.983{*}T$

Bcc_A2: Model $(\mathrm{La,Mn})_1(\mathrm{Va})_3$

${}^0L^{\mathrm{Bcc\_A2}}_{\mathrm{La,Mn:Va}} = 100000$

Fcc_A1: Model $(\mathrm{La,Mn})_1(\mathrm{Va})_1$

${}^0L^{\mathrm{Fcc\_A1}}_{\mathrm{La,Mn:Va}} = 100000$

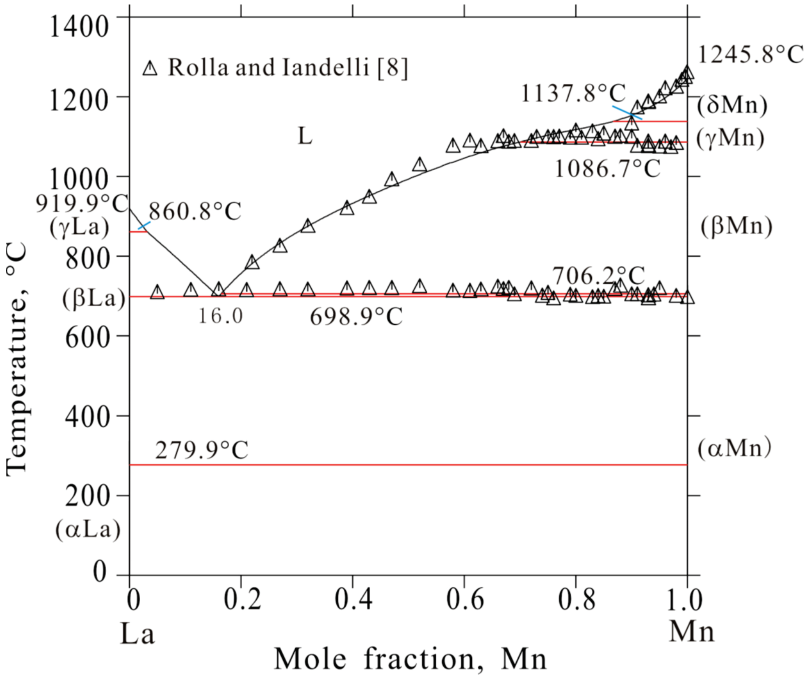

Figure 1. *Calculated phase diagram of La–Mn system compared with the experimental data from the literature [8]*

work of Kim and Jung [17]. Since the melting temperature of La reported by Rolla and Iandelli [8] is lower than the accepted melting temperature by about 100 °C, their liquid data in the La-rich region was not included in the present work. Calculated temperatures and compositions for invariant equilibria in the La–Mn system are listed in Table 2 along with the experimental data [8, 30, 31].

Fig. 2 shows the calculated partial enthalpies of mixing for the liquid at 1600 K compared with the experimental data from Nikolaenko and Nosova [16], which fits the experimental data reasonably within the estimated experimental errors. Fig. 3 presents the calculated enthalpies of mixing for the liquid at 1600 K along with the experimental data from Nikolaenko and Nosova [16], showing a good agreement.

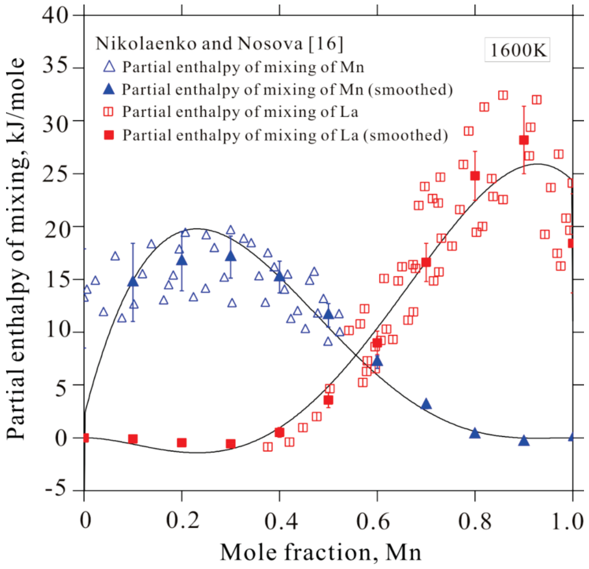

Figure 2. *Calculated partial enthalpies of mixing for the liquid at 1600 K with the experimental data from Nikolaenko and Nosova [16]. The reference states are liquid La and liquid Mn.*

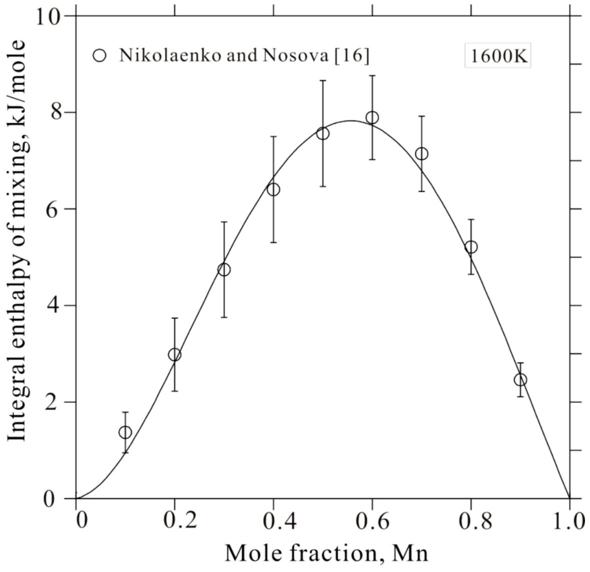

Figure 3.*Calculated integral enthalpies of mixing for the liquid at 1600 K with the experimental data from Nikolaenko and Nosova [16]. The reference states are liquid La and liquid Mn.*

Table 2. *Calculated invariant reactions compared with the literature data in the La–Mn systems*

Invariant reactions	T, °C	Composition (at.% Mn)			Reference
(δMn) ↔ (γMn), Liquid	1137.9	100	---	100	[30]
	1137.8	99.9	86.7	99.9	This work
(γMn) ↔ (βMn), Liquid	1086.8	---	100	100	[30]
	1086.7	70.1	99.9	99.9	This work
(γLa) ↔ (βLa), Liquid	860.9	0	---	0	[30]
	860.8	0	3.2	0	This work
(βMn) ↔ (αMn), Liquid	706.9	---	100	100	[31]
	706.2	16.5	100	99.9	This work
Liquid ↔ (βLa) + (αMn)	701	16	0	100	[8]
	698.9	17	0	100	This work
(βLa) ↔ (αLa)	276.9	0	0		[31]
	276.9	0	0		This work

4. Conclusion

In summary, the thermodynamic description of the La–Mn system has been performed by the CALPHAD method. A self-consistent set of thermodynamic parameters has been obtained by critically evaluated literature data. The calculated phase diagram and thermodynamic properties agree well with the experimental data. Compared to the previous published work, less number of parameters are used for the description of the liquid phase in the present work.

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References

[1] B.L. Mordike, T. Ebert, Mater. Sci. Eng. A, 302 (2001) 37.

[2] H.E. Friedrich, B.L. Mordike: Magnesium Technology, Springer-Verlag, Berlin Heidelberg (2006) 63.

[3] V. Goryany, P.J. Mauk, J. Min. Metall. B, 43 (2007) 85-97.

[4] W.J. Liu, F.H. Cao, Z. Zhang, J.Q. Zhang, Fushi Kexue Yu Fanghu Jishu, 21 (2009) 82-84.

[5] D.Q. Wan, J.C. Wang, G.F. Wang, X.Y. Chen, L. Lin, Z.G. Feng, G.C. Yang, Mater. Sci. Eng. A, 494 (2008) 139-142.

[6] Y. Fan, G.H. Wu, H.T. Gao, G.Q. Li, C.Q. Zhai, J. Mater. Sci., 41 (2006) 5409-5416.

[7] K.I. Portnoi, A.A. Lebedev, Metallurgizdat, Moscow (1952).

[8] L. Rolla and A. Iandelli, Ber. Deut. Chem. Ges., 75 (1942) 2091-2095.

[9] K.A. Gschneidner, Jr., Rare Earth Alloys, Van Nostrand, New York, 1961, 215-217.

[10] P.I. Kripyakevich, D.P. Frankevich, Y.V. Voroshilov, Poroshk. Metall., 11 (1965) 55-61.

[11] F.E. Wang, J.R. Holden, Trans. Metall. Soc. AIME, 233 (1965) 731-736.

[12] H.R. Kirchmayer, Z. Kirstallogr., 124 (1967) 152-160.

[13] K.A. Gschneidner, Jr., and F.W. Calderwood., Handbook on the Physics and Chemistry of Rare Earths, 8 (1986) 1-161.

[14] N.A. Gokcen, Bull. Alloy Phase Diagrams, 10 (1989) 313.

[15] A. Palenzona and S. Ciraflici, Bull. Alloy Phase Diagrams, 11 (1990) 491-492.

[16] I.V. Nikolaenko, V.V. Nosova, Rasplavy, 1 (1993) 76-79.

[17] J. Kim, I.H. Jung, J. Alloys Compd., 525 (2012) 191-201.

[18] C.Y. Tang, Y. Du, H.H. Xu, S.M. Hao, L.J. Zhag, J. Min. Metall. B, 43 (2007) 21-28.

[19] C.Y. Tang, Y. Du, L.J. Zhang, H.H. Xu, Z. Zhu, J. Alloy Compd., 437 (2007) 102-106.

[20] C.P. Wang, Z. Lin, X.J. Liu, J. Alloys Compd., 469 (2009) 123-128.

[21] H. Okamoto, J. Phase Equilib., 12 (1991) 148-168.

[22] P.S. Wang, J.R. Zhao, Y. Du, H.H. Xu, T. Gang, J.C. Fen, L.J. Zhang, C.Y. He, S.H. Liu, H.W. Ouyang, Int. J. Mater. Res., 102 (2011) 6-16.

[23] M.J. Bu, P.S. Wang, H.H. Xu, S.H. Liu, C.S. Sha, Y. Du, F.S. Pan, A.T. Tang, J. Min. Metall. B, 46 (2010) 181-192.

[24] J.H. Hildebrand, J. Am. Chem. Soc., 51 (1929) 66-80.

[25] A.T. Dinsdale, Calphad, 15 (1991) 317-425.

[26] J.O. Andersson, A.F. Guillermet, P. Gustafson, M. Hillert, B. Jansson, B. Sunderman, J. Ågren, Calphad, 11 (1987) 93-98.

[27] O. Redlich, A.T. Kister, J. Ind. Eng. Chem., 40 (1948) 84-88.

[28] B. Sundman, B. Jansson, J.O. Andersson, Calphad, 9 (1985) 153–190.

[29] Y. Du, R. Schmid-Fetzer, H. Ohtani, Z. Metallkd., 88 (1997) 545–556.

[30] T.B. Massalski, J.L. Murray, L.H. Bennett, H. Baker, Binary Alloy Phase Diagrams, ASM International, 1986.

[31] H.W. King, Crystal Structures of the Elements at 25 °C, Bull. Alloy Phase Diagrams, 2 (1981) 401-4044