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Thermodynamic optimization of the systems Mn–Gd and Mn–Y using new experimental results

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Abstract

The literature concerning binary systems of manganese and rare earth metals is very scarce. Thermodynamic optimizations using the Calphad method are only available for the Mn–Y system [Flandorfer et al., Z. Metallkd. 88 (1997) 529–538]. In this work, thermodynamic optimizations for the binary systems Gd–Mn and Mn–Y are investigated. New experimental data for the enthalpies of formation of the binary Mn–Y phases were considered. The resulting enthalpies fit in the trend of stabilities within the series of RE–Mn systems described by Saccone et al. [Z. Metallkd. 84 (1993) 563–568].

Keywords: Thermodynamic calculations; Phase diagram; Manganese; Rare earths; Yttrium

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1. Introduction

Manganese and rare earth metals (RE) are important alloying elements for magnesium alloys with high creep resistance and strength. A useful tool to predict new and promising compositions for alloy development is thermodynamic calculation. One premise for these calculations is the thermodynamic description of all the phases in the multicomponent systems formed by Mg, Mn and RE. The binary Mn–RE systems are an essential part of this system because these binary solid phases form important precipitations in the alloys during annealing. These precipitations improve substantially the mechanical properties of the alloys. However, only little is known about the thermodynamics of the Mn–RE systems. Difficulties in alloy preparation and impurity stabilized phases are responsible for various contradicting phase diagrams which can be found in the literature. A conclusive solution of these contradictions is only possible by systematic comparison of the sequence of all RE elements and their binary systems with Mn. Thermodynamic calculations combined with experimental thermodynamic measurements complete the already published systematic review of phase diagram data.

2. Systematics of the binary Mn–RE systems

In the majority of the binary Mn–RE systems three intermetallic phases are stable after the systematic review of the Mn–RE alloys by Saccone et al. [2]. The stoichiometries are Mn_xRE_y with $(x/y)=(12/1)$, $(23/6)$ and $(2/1)$. Exceptions are the divalent RE metals, Eu and Yb. In these systems no compound stable at ambient pressure was found. The binary systems of the two lightest RE metals, La and Ce, show a miscibility gap in the liquid state but no stable compound. The heavier RE form an increasing number of stable intermetallic compounds. The Mn-poorest compound Mn_2RE occurs in two different structure types: Cu_2Mg and $MgZn_2$. In some systems (Sm, Gd, Tb, Dy and Ho) both modifications are stable depending on temperature or pressure. The other compounds $Mn_{23}RE_6$ and $Mn_{12}RE$ crystallize in the $Mn_{23}Th_6$ and $Mn_{12}Th$ structure type, respectively. Only in the Lu–Mn system a Mn_5Lu phase is stable instead of $Mn_{12}RE$.

The thermal stability of the intermediate phases is not settled in the literature. Earlier investigations in the Mn–Nd system by Kirchmayr and Lugscheider [3] measured only the equilibrium with the liquid phase and did not

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consider possible decomposition of the intermetallic phase at lower temperature. This decomposition of all binary phases found by Makhalenko and Kuzma [4] and which was confirmed by Saccone et al. [2]. The non-stability of the $Mn_{12}Nd$ phase was discovered by both works. This phase is possibly stabilized by Al and therefore appeared in the work of Kirchmayr and Lugscheider [3]. The same tendency was found in the Pr–Mn [5] where $Mn_{23}Pr_6$ is stable only in a small temperature range. The other binary phases reported by Chen et al. [6] may be stabilized by Al because Al_2O_3 crucibles were used. In the Sm–Mn system two phases $Mn_{23}Sm_6$ and Mn_2Sm are stable down to room temperature [7].

The stability of the intermetallic phases seems to increase from the light to the heavy RE metals. The number of stable binary phases increase from none (La, Ce) to three (Gd to Tm). The Pr– and Nd–Mn phases decompose at lower temperatures. The compounds of the heavier RE (from Gd to Tm) are stable down to room temperature. The instability at lower temperatures is caused by low enthalpies of formation of all RE–Mn phases. The estimation after de Boer et al. [8] gives enthalpies of formation between -1 and -2 kJ mol^{-1} of atoms for these phases. Experimental data of enthalpies of formation are very scarce in literature. The only value reported is for $Mn_{23}Sm_6$ (-3.17 kJ mol^{-1} of atoms at 1320 K) [9] (see Table 2). Recent measurements of the phases Mn_2Y and $Mn_{23}Y_6$ are obtained by Pisch et al. [10].

3. Assessment of the experimental data

The only available literature concerning the binary Gd–Mn phase diagram is due to Kirchmayr and Lugscheider [11]. They prepared several alloys using a special method called 'amalgamization'. An amalgam with RE–Mn was prepared, free Hg was distilled and the obtained products were heat treated at temperatures between 900 and 1100°C. Thermoanalysis was performed in Ta crucibles with heating rates smaller than 6°C min^{-1}. Three intermetallic phases were observed: Mn_2Gd, $Mn_{23}Gd_6$ and $Mn_{12}Gd$. No solubilities were observed and a possible thermal decomposition at lower temperatures was not investigated. Table 1a shows the reported invariant temperatures and compositions. Nikolaenko and Nosova [12–14] measured partial enthalpies of mixing in the liquid phase at 1600 K by heat flux high temperature isoperibolic calorimetry. They reported widely scattering data points especially for the Mn–Gd system [12]. The partial enthalpy of Mn is measured from 0 to 60 at% Mn. The values scatter between $+5$ and -12 kJ mol^{-1} and are mostly negative. The partial enthalpy of Gd is measured from 70 to 100 at% Mn. The date points scatter between $+25$ and -18 kJ mol^{-1} and are mostly positive. A clear compositional trend cannot be detected in the original data [12].

The assessment of the binary Mn–Y system by Palenzona and Cirafici [15] is based on the work of Myklebust and Daane [16]. Similar to the Gd–Mn system, three intermetallic phases were observed: Mn_2Y, $Mn_{23}Y_6$ and $Mn_{12}Y$. Thermal decomposition at lower temperatures was not found. For the phase $Mn_{23}Y_6$ a synthectic formation is assumed. Table 1b shows the invariant reactions for this binary system. Valishev et al. [17] measured the partial and integral enthalpy of mixing of liquid binary Mn–Y at 1600°C using high-temperature isoperibolic calorimetry. Samples were prepared in corundum crucibles in pure He atmosphere. The measured enthalpies are about twice lower compared to the calculated ones by deBoer et al. [8].

Previous optimization of the binary system including literature assessment was published by Flandorfer et al. [1]. Recently new calorimetric measurements of the enthalpy of formation of the binary phases Mn_2Y and $Mn_{23}Y_6$ were investigated by Pisch [10]. Their samples have been prepared by levitation melting starting from the pure elements under controlled atmosphere. The enthalpy of formation has been determined by aluminium solution calorimetry at 850°C in a Calvet-type calorimeter under

Table 1
Invariant reactions: experimental and calculated

Reaction	Experimental: Gd–Mn [11], Mn–Y [13]		Calculated: this work	
	T (°C)	Composition of liquid (at% Mn)	*T* (°C)	Composition of liquid (at% Mn)
Gd–Mn				
$L=\alpha\text{-}Gd+Mn_2Gd$	830	35.3	828	33.8
$L+Mn_{23}Gd_6=Mn_2Gd$	950	52	941	52.7
$L+Mn_{12}Gd=Mn_{23}Gd_6$	1050	79		
$L=Mn_{12}Gd+Mn_{23}Gd_6$			1052	79.5
$L+\beta\text{-}Mn=Mn_{12}Gd$	1085	89	1085	88.7
Mn–Y				
$L=\alpha\text{-}Y+Mn_2Y$	878	35.3	897	35.9
$L=Mn_{23}Y_6+Mn_2Y$	1100	71.6	1103	70.2
$L=Mn_{12}Y+Mn_{23}Y_6$	1075	88.1	1093	88.3
$L+\gamma\text{-}Mn=Mn_{12}Y$	1100	89	1099	90.1

Table 2
Enthalpy of formation of binary compounds Mn–RE in kJ mol^{-1} of atoms at 298 K

RE	$Mn_{12}RE$	$Mn_{23}RE_6$	Mn_2RE	Type and reference
Sm	Not stable	−3.17	No data	Experimental (1320 K) [9]
Gd	−4.0	−6.4	−6.4	Calculation [this work]
Y	−1	−2	−2	Miedema estimation [8]
		−5.1±1.7	−0.9±2.5	Calorimetry [10]
	−2.1	−5.0	−2.8	Calculation [this work]

flowing argon gas to prevent oxidation. The values are given together with the estimation after de Boer et al. [8] and all available enthalpy data of Mn–RE (including Sc and Y) systems in Table 2.

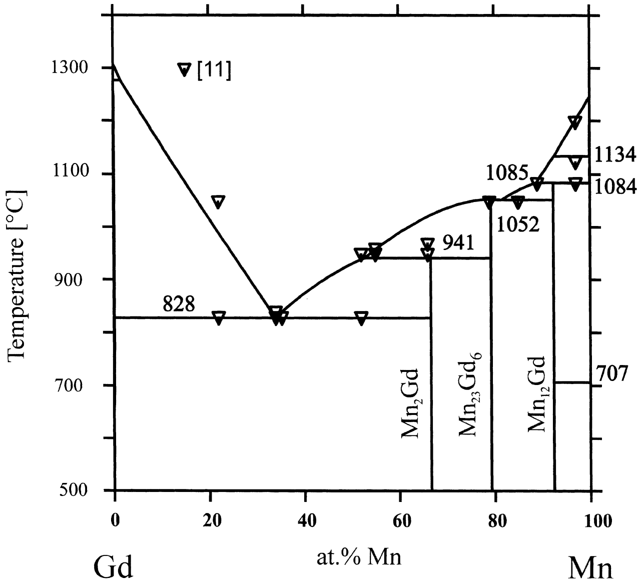

Fig. 1. The binary system Gd–Mn including experimental data of Kirchmayr and Lugscheider [11].

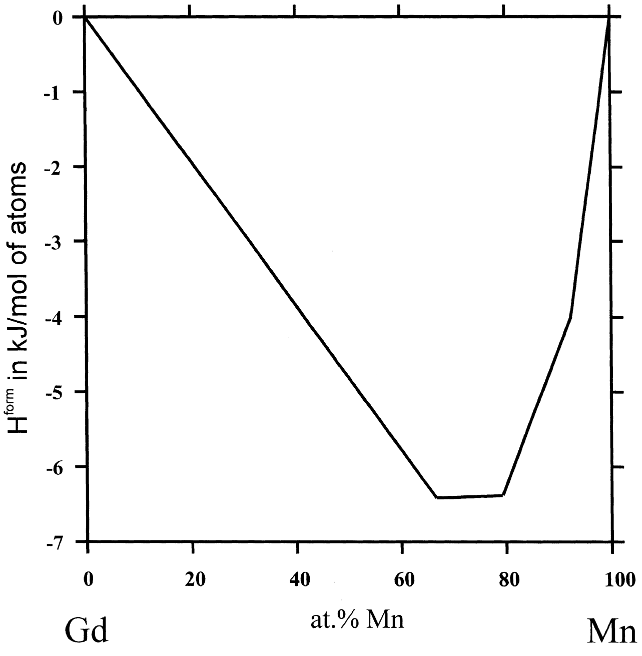

Fig. 2. Calculated room-temperature enthalpy of formation of the intermetallic phases in the binary system Gd–Mn.

4. Thermodynamic optimization

The Calphad method was applied for the thermodynamic modeling of the two binary systems. Doing so, the Gibbs energy for every phase in the system is described by a function with adjustable parameters. These parameters were fitted by a least squares method to all the available experimental values related to the Gibbs energies. Suitable data are all phase diagram information (temperatures of liquidus and solidus, invariant temperatures, solubilities) and thermodynamic functions (enthalpy of formation, partial enthalpies, etc.).

Gibbs energy functions for the elements in their different modifications have been taken from the compilation of Dinsdale [18]. The binary systems Gd–Mn and Mn–Y were optimized using the Program BINGSS [19,20]. The terminal solid solutions and the liquid were modeled as solution phases using the Redlich–Kister formalism [21]. All binary solid compounds were treated as stoichiometric since no solubilities were reported.

The experimental values of Kirchmayr and Lugscheider [11] were the only data available for optimization in the Gd–Mn system. Enthalpies of formation of the binary solid phases were estimated regarding the known values of Mn–Y. The partial enthalpies of liquid of Nikolaenko and Nosova [12] were not used for the optimization because of their wide scattering. For the parameter $^{\circ}L = A + B \cdot T$ of the liquid regular solution the relation for enthalpy/entropy after Tanaka et al. [22,23] for $A/B = H/S = -12\,000$ K was used during optimization. The immiscibility in the HCP (α-Gd), bcc (β-Gd, δ-Mn) and fcc (γMn) was estimated with a large value $L_{Gd,Mn} = 50\,000$ J mol^{-1} to fit the very small solubilities of the elements. The calculated binary system Gd–Mn including experimental data of Kirchmayr and Lugscheider [11] is shown in Fig. 1. The calculated trend of the enthalpy of formation at room temperature of the intermetallic phases is presented in Fig. 2.

In the Mn–Y system the experimental values of Myklebust and Daane [16] and the enthalpies of mixing of

Valishev et al. [17] were used for the thermodynamic optimization. The synthectic formation of $Mn_{23}Y_6$ reported by Palenzona and Cirafici [15] seems to be very unlikely since it requires a very narrow liquid miscibility gap. This reaction type was therefore not modeled. The parameters from the previous optimization [1] were used as starting values for the least-square optimization. The calorimetric measurements of the enthalpy of formation by Pisch et al. [10] were treated with 10 times higher weight. Fig. 3 gives the calculated binary phase diagram Mn–Y compared with the experimental data of Myklebust and Daane [16]. The partial enthalpies of Valishev et al. [17] is slightly in contradiction with the other experimental data and were therefore not fitted exactly. The comparison of the calculated partial enthalpy of mixing of the liquid Mn–Y at 1600°C with the experimental points of Valishev et al. [17] is shown in Fig. 4. Considering the measured enthalpy of formation of the Mn_2Y phase [10], this phase should decompose at lower temperatures. In this calculation Mn_2Y is stable down to 257°C. Fig. 5 gives the trend of the room-temperature enthalpy of formation of the intermetallic phases. Experimental data [10] and estimations after de Boer et al. [8] are included for comparison. It can be seen that the calculated values are within the uncertainties of the experimental data. The estimations derived from Miedema's model [8] are too positive for all binary phases. Mn_2Y shows an enthalpy of formation within the uncertainty of the measurement, however, it will not be stable at room temperature.

All calculated and experimental temperatures and compositions of the invariant reactions are summarized in Table 1.

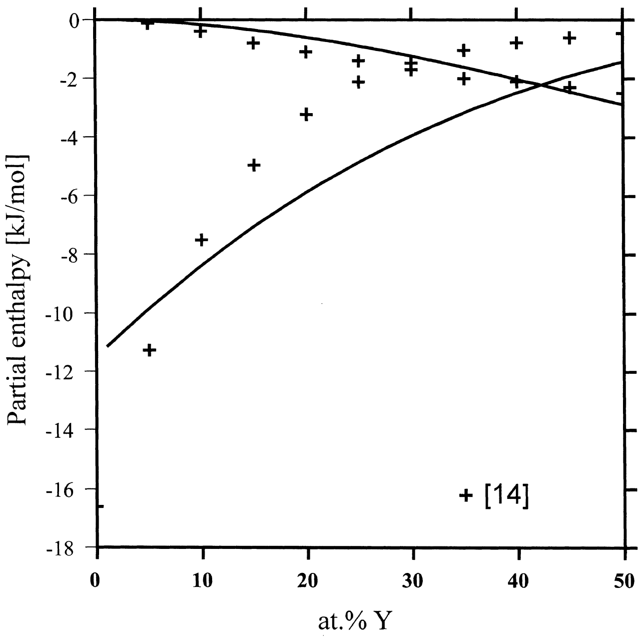

Fig. 4. Calculated partial enthalpy of mixing of the liquid Mn–Y at 1600°C with the experimental points after Valishev et al. [17].

5. Conclusion

Thermodynamic optimizations for the two binary systems Gd–Mn and Mn–Y are given. New experimental data for the enthalpies of formation of the binary Mn–Y phases considered for the reoptimization indicate lower enthalpy values than for the previous calculation of this system [1]. The resulting enthalpies fit in the trend of stabilities within

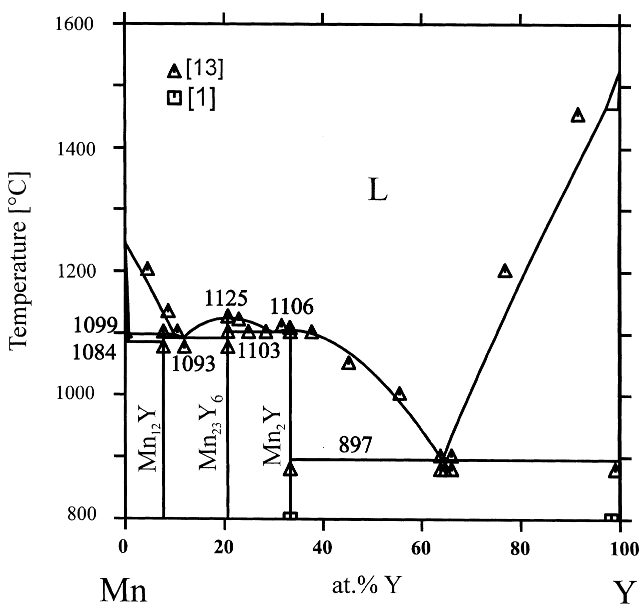

Fig. 3. The binary system Mn–Y including experimental data of Flandorfer et al. [1] and Mylkebust and Daane [16]. Mn_2Y decomposes at 257°C into $Mn_{23}Y_6$ and Y.

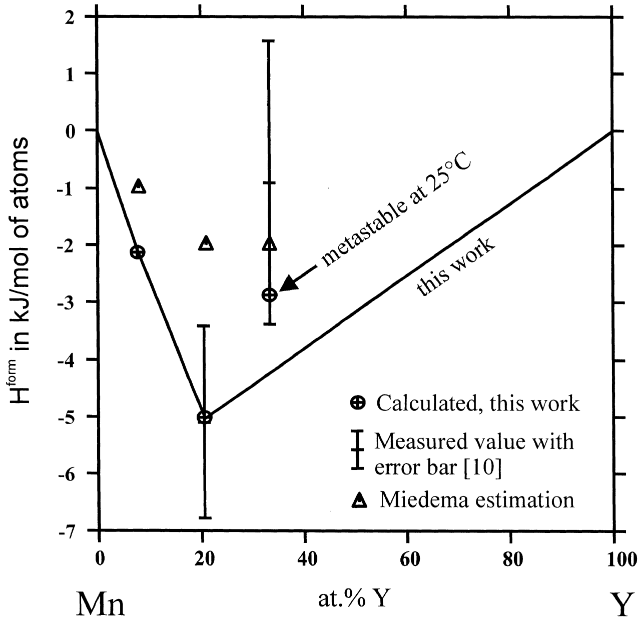

Fig. 5. Room-temperature enthalpy of formation of the intermetallic phases in the binary system Mn–Y with the experimental data of Pisch et al. [10] and estimations after Miedema [8].

Table 3
Assessed binary parameters (J mol^{-1})

Mn–Gd

L(LIQUID,GD,MN;0) = −5020.87 + 0.56166*T
L(LIQUID,GD,MN;1) = 1041.42

G(MN12GD,MN:GD;0) = −52 000 + 12.1*T + 12*GHSERMN + GHSERGD

G(MN23GD6,MN:GD;0) = −185 000 + 27.6*T + 23*GHSERMN + 6*GHSERGD

G(MN2GD,MN:GD;0) = −19 242 + 2.87*T + 2*GHSERMN + GHSERGD

G(FCC_A1,GD;0) = 10 000 + GHSERGD

L(BCC_A2,GD,MN;0) = 50 000
L(HCP_A3,GD,MN;0) = 50 000
L(FCC_A1,GD,MN;0) = 50 000

Mn–Y

L(LIQUID,MN,Y;0) = −8613.87 + 0.71782*T
L(LIQUID,MN,Y;1) = −2877.73 + 0.23981*T

L(HCP_A3,MN,Y;0) = 50 000

G(Mn12Y,MN:Y;0) = −27 200.00 − 9.500*T + 12*GHSERMN + GHSERYY

G(Mn23Y6,MN:Y;0) = −145 792.86 − 33.1200*T + 23*GHSERMN + 6*GHSERYY

G(Mn2Y,MN:Y;0) = −8485.94 − 10.7900*T + 2*GHSERMN + GHSERYY

the series of RE–Mn systems described by Saccone et al. [2]. The small values for the enthalpies of formation of the solid phases measured by Pisch et al. [10] require decomposition of the Mn_2Y phase at low temperatures. The small enthalpies of formation of the Mn–Y binary solid phases suggest that these phases have to be entropy stabilised. And indeed, the positive entropies of formation (negative B values) for the Mn–Y binary solid phases (Table 3) are caused by the fact that these high melting phases show a small enthalpy of formation. This tendency increases with decreasing atomic weight of the RE elements. In the Nd–Mn and Pr–Mn systems no binary solid phase was found to be stable down to room temperature [2,5]. And for the lightest RE–Mn systems (La and Ce) no binary solid phase is stable at all. The heavier RE seem to form binary phases with Mn with more negative enthalpies of formation. Therefore the intermetallic Mn-phases of the RE elements Gd to Er are supposed to be stable at room temperature. Further investigations are necessary to verify this statement.

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