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Thermodynamic assessments of the Mn–Sm and Mn–Ho systems

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ABSTRACT

By using the calculation of phase diagrams (CALPHAD) method, the thermodynamic assessments of the Mn–Sm and Mn–Ho systems were carried out based on the experimental data including thermodynamic properties and phase equilibria. Gibbs free energy of the solution phase (liquid, fcc, bcc, hcp, cbcc, rhombohedral and cub) were modeled by the subregular or regular solution model with the Redlich–Kister formula, and those of the intermetallic compounds ($Mn_{23}Sm_6$, Mn_2Sm, $HoMn_2$, Ho_6Mn_{23}, $HoMn_{12}$) were described by the sublattice model. An agreement between the present calculated results and experimental data is obtained.

1. Introduction

The intermetallic compounds formed by rare earth elements (RE) and transition metals are of particular interest regarding their outstanding magnetic properties [1]. Moreover, Manganese and RE are important alloying elements for magnesium alloys with high creep resistance and strength. 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 [2]. Therefore, it is important to understand the phase equilibria in the Mn–RE alloy system.

The CALPHAD method, which is a powerful tool to cut down on cost and time during development of materials [3], effectively provides a clear guideline for materials design. In order to develop the thermodynamic database of phase equilibria in the multicomponent alloys containing Mn and rare earth elements, the thermodynamic description of each lower-order system which forms a part of this thermodynamic database is necessary. However, only little is known about the thermodynamics of Mn–RE systems. The purpose of the present work is to present the thermodynamic descriptions of the Mn–Sm and Mn–Ho binary systems by the CALPHAD method. The thermodynamic parameters of each phase in the Mn–Sm and Mn–Ho systems are optimized by fitting the experimental data on the thermodynamic properties and phase equillibria.

2. Thermodynamic models

The information of the stable solid phases and the used models in the Mn–Sm and Mn–Ho systems is listed in Table 1.

2.1. Solution phases

In the Mn–Sm and Ho–Mn systems (A–B system), the Gibbs free energies of the solution phases (liquid, fcc, bcc, hcp, cbcc, rhombohedral and cub) were described by the subregular or regular solution model with the Redlich–Kister formula [4], The molar Gibbs free energy of each solution phase in A–B system is given as follows:

$$G_m^{\phi} = \sum\nolimits_{i=\mathrm{A,B}} {}^{0}G_i^{\phi} x_i + RT \sum_{i=\mathrm{A,B}} x_i \ln x_i + x_\mathrm{A} x_\mathrm{B} \sum_{m=0}^{n} {}^{m}L_{\mathrm{A,B}}^{\phi} (x_\mathrm{A} - x_\mathrm{B})^m + \Delta^{mag} G_m^{\phi}, \quad (1)$$

where ${}^{0}G_i^{\phi}$ is the molar Gibbs free energy of pure component i in the respective reference state with the structure ϕ in a nonmagnetic state, which is taken from the compilation by Dinsdale [5]. x_i denotes the mole fraction of the component i; R is the gas constant; T is the absolute temperature; and ${}^{m}L_{A,B}^{\phi}$ is the interaction energy between A and B atoms, and is expressed as:

$${}^{m}L_{\mathrm{A,B}}^{\phi} = a + bT, \quad (2)$$

the parameters of a and b are evaluated based on the experimental data in the present work.

In the Mn–Sm and Ho–Mn systems, the magnetic contributions to the Gibbs free energies are considered in the bcc, cbcc, fcc and

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Table 1
Information on the stable solid phases and the used models in the Mn–Sm [10] and Mn–Ho [13] systems.

System	Phase	Prototype	Strukturbericht designation	Modeling phase
Mn–Sm	δMn	W	A2	(Mn,Sm)
	γMn	Cu	A1	(Mn,Sm)
	βMn	βMn	A13	(Mn,Sm)
	αMn	αMn	A12	(Mn,Sm)
	$Mn_{23}Sm_6$	$Mn_{23}Th_6$	$D8_a$	$(Mn)_{23}(Sm)_6$
	Mn_2Sm	$MgZn_2$	C14	$(Mn)_2(Sm)$
		Cu_2Mg	C15	
	γSm	W	A2	(Mn,Sm)
	βSm	Mg	A3	(Mn,Sm)
	αSm	αSm	C19	(Mn,Sm)
Mn–Ho	(Ho)	Mg	A3	(Ho,Mn)
	$HoMn_2$	Cu_2Mg	C15	$(Ho)(Mn)_2$
	Ho_6Mn_{23}	$Mn_{23}Th_6$	$D8_a$	$(Ho)_6(Mn)_{23}$
	$HoMn_{12}$	$Mn_{12}Th$	$D2_b$	$(Ho)(Mn)_{12}$
	δMn	W	A2	(Ho,Mn)
	γMn	Cu	A1	(Ho,Mn)
	βMn	βMn	A13	(Ho,Mn)
	αMn	αMn	A1	(Ho,Mn)

hcp phases. $\Delta^{mag}G_m^{\phi}$ is the magnetic contribution to the Gibbs free energy, which is described by the following equation [6]:

$$\Delta^{mag}G_m^{\phi} = RT\ln(\beta+1)f(\tau), \tag{3}$$

where $\tau = T/T_C^{\phi}$, T_C^{ϕ} is the Curie temperature of solution for ferromagnetic ordering and β is the Bohr magneton number per mole. The function $f(\tau)$ is formulated by the polynomial of the normalized temperature, as follows:

$$f(\tau) = 1 - \frac{1}{D}\left[\frac{79\tau^{-1}}{140p} + \frac{474}{497}\left(\frac{1}{p}-1\right)\left(\frac{\tau^3}{6}+\frac{\tau^9}{135}+\frac{\tau^{15}}{600}\right)\right], \quad \text{for } \tau < 1 \tag{4}$$

$$f(\tau) = -\frac{1}{D}\left(\frac{\tau^{-5}}{10}+\frac{\tau^{-15}}{315}+\frac{\tau^{-25}}{1500}\right), \quad \text{for } \tau \geq 1 \tag{5}$$

where $D = \frac{518}{1125} + \frac{11692}{15975}((1/p)-1)$, p depends on the structure, 0.40 for bcc structure and 0.28 for others.

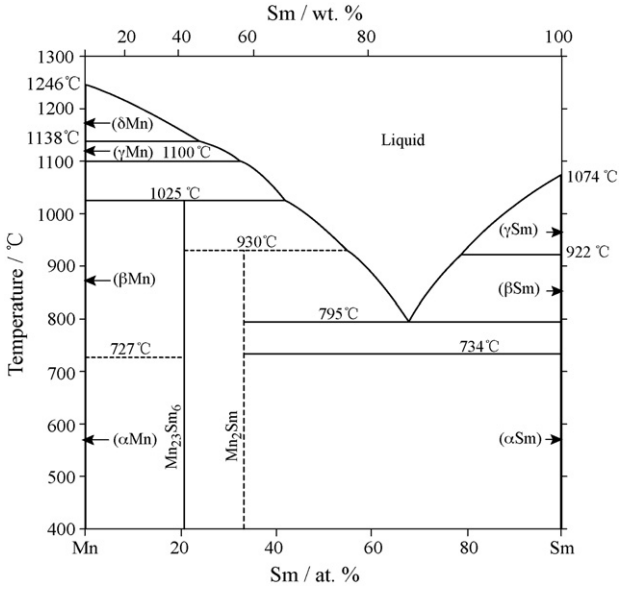

Fig. 1. The phase diagram of the Mn–Sm system reviewed by Massalaski et al. [10].

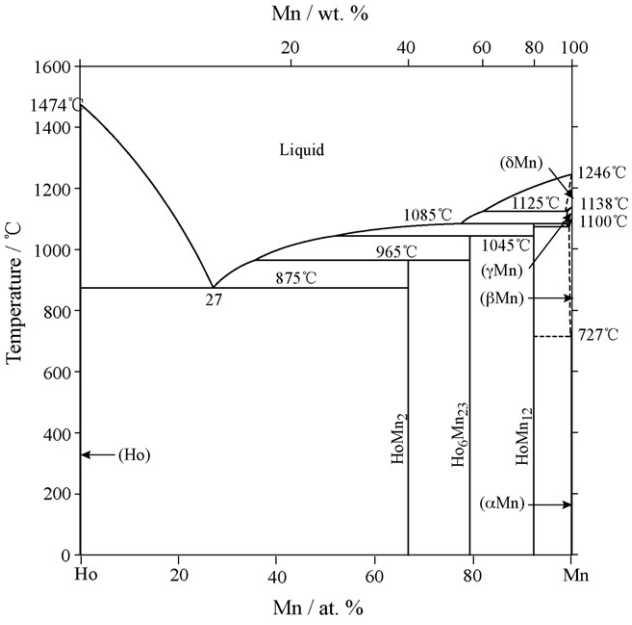

Fig. 2. The phase diagram of the Mn–Ho system reviewed by Massalaski et al. [13].

2.2. Stoichiometric intermetallic compounds

The intermetallic compounds of the $Mn_{23}Sm_6$, Mn_2Sm, $HoMn_2$, Ho_6Mn_{23} and $HoMn_{12}$ in the Mn–Sm and Mn–Ho binary system are treated as stoichiometric compounds. The Gibbs free energy per mole of formula unit $(Mn)_m(RE)_n$ can be expressed by the two-sublattice model [7], as the following equation referring to the pure element in their nonmagnetic state:

$$G^{Mn_mRE_n}_{Mn:RE} = \Delta^0 G^{Mn_mRE_n}_{Mn:RE} + m^0G^{ref}_{Mn} + n^0G^{ref}_{RE} + \Delta^{mag}G_m^{Mn_mRE_n}, \tag{6}$$

where the $\Delta^0 G^{Mn_mRE_n}_{Mn:RE}$ denotes the standard Gibbs free energy of formation of the stoichiometric compound form the pure elements at temperature T, which is described as:

$$\Delta^0 G^{Mn_mRE_n}_{Mn:RE} = a' + b'T, \tag{7}$$

where the parameters of a' and b' are evaluated in the present optimization.

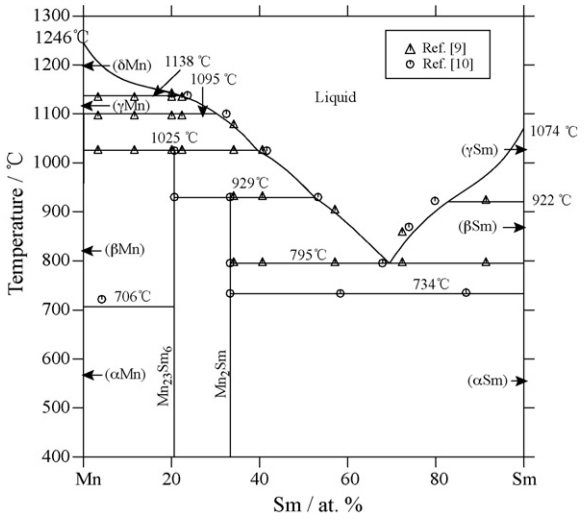

Fig. 3. Calculated phase diagram of the Mn–Sm system compared with the experimental data [9,10].