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Thermodynamic assessment of Mg/Zr unary systems

Yongxin Ruan, Changrong Li*, Chengliang Xu, Cuiping Guo, Zhenmin Du

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

With consideration of the phase equilibrium dependency upon temperature (T) and pressure (P), the P-T type phase diagrams of Mg and Zr unary systems are constructed. The gaseous phase of the Mg system consists of the species Mg (g) and Mg_2 (g), and the condensed phases are liquid, hexagonal close-packed (HCP_A3) and body centered cubic (BCC_A2). Similarly, the gaseous phase of the Zr system consists of the species Zr (g) and Zr_2 (g), and the condensed phases are liquid, HCP_A3 (α), BCC_A2 (β) and a more open hexagonal structure (ω). The ω phase has a hexagonal lattice with three atoms per unit cell at (0, 0, 0), (1/3, 2/3, c/2a) and (2/3, 1/3, c/2a), where the c/a ratio is ~0.62. The real solution model is applied to describe the molar Gibbs free energy of gaseous species by taking the fugacity coefficient into account to ensure the validity of the calculated phase diagrams under high temperature and high pressure. As for the description of the molar Gibbs free energy for condensed phases, the temperature and pressure dependent Murnaghan equation is employed, which is represented by G_{press} and is correlated with the molar volume, the variations of voluminal thermal expansivity and compressibility with temperature, and the variation of bulk modulus with pressure. Based on the literature data available, the parameters of the pressure contribution part G_{press} for the condensed phases are optimized by use of Pandat Software package. The calculated phase diagrams are well comparable with the experimental and theoretical reports. The favorable consistency between the calculated results for the optimized mechanical and thermophysical properties, such as the variations of the molar volume and the volume ratio with pressure and the molar heat capacity with temperature, and the experimental measurements from literatures further proves the reliability of the present thermodynamic assessment. According to the calculated results, it is indispensable for the contribution of G_{press} to the global molar Gibbs free energy to be taken into consideration as the magnitude of pressure exceeds the order of 10^9 Pa. This CALPHAD method for developing the phase diagrams of Mg/Zr unary systems at high temperature and high pressure can be extended to study other unary systems.

1. Introduction

Magnesium alloys with various aspects of remarkable properties, such as excellent specific strength, low density and high modulus of elasticity, have been paid close attention over the past decade in the fields of hydrogen storage apparatuses [1], light weight and high strength structural materials [2], degradable biomedical materials [3], and so on. With Zr addition, Mg-based multicomponent alloys dramatically achieve better mechanical properties as well as satisfactory heat resistance on account of the refinement of crystalline grains [4]. However, the high melting point of Zr results in a serious burning loss of Mg matrix and other alloying elements with low melting points during the process of metallurgy. Therefore, it is helpful to have a good knowledge of the thermodynamic properties and phase diagrams at high temperature and high pressure for both of the Mg and Zr unary systems.

During the practical sintering process, the phase equilibrium in the prepared alloy is often critically controlled by the relationship between temperature and pressure, especially for the alloys consisting of the components with a large discrepancy between melting points. As it is mentioned in Ref. [5], the thermodynamic parameters related to the gaseous species and the condensed phases can be obtained from SSUB database, SGTE (Scientific Group Thermodata Europe) substance database, of Thermo-Calc Software package [6] and PURE database taken from SGTE compilation by Dinsdale [7], respectively. Unfortunately, high pressure databases are sorely lacking and cannot be retrieved from available thermodynamic software packages and literature reports.

The main objective of the present work is to obtain a set of reasonable thermodynamic descriptions of all the phases for each of the Mg and Zr unary systems and to develop the corresponding thermodynamic database for both of them, by taking account of the effect of high temperature and high pessure on the globle molar Gibbs free

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* Corresponding author.
E-mail address: crli@mater.ustb.edu.cn (C. Li).

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energy and using PanPhasediagram module [8] and PanOptimizer module [9] of Pandat Software package.

2. Thermodynamic models

2.1. Gaseous phase

The gaseous phase of the Mg unary system consists of the species Mg (g) and Mg_2 (g), while that of the Zr unary system consists of Zr (g) and Zr_2 (g). The real solution model is used to describe the molar Gibbs free energies of the gaseous species for both of the unary systems to ensure the rationality of the *P-T* phase diagrams and the thermodynamic properties under high pressure. The integrated expression of the pressure contribution to the molar Gibbs free energy can be described as the following [5,10–12]:

$$G_m^{\mathrm{gas}}(T) = \sum y_i\,[{}^0G_i^{\mathrm{gas}} + \mathrm{RTln}(y_i) + \mathrm{RTln}(f_i/P_0)] \tag{1}$$

where y_i and ${}^0G_i^{gas}$ refer to the molar fraction and the molar Gibbs free energy of the gaseous species *i* (*i* = Mg (g) and Mg_2 (g) for the Mg unary system, and Zr (g) and Zr_2 (g) for the Zr unary system). *T* and *R* are the absolute temperature and the gas constant, respectively. $f_i = f(T, P)$ is the fugacity of the gaseous species *i*, which must be taken into consideration when the pressure exceeds the standard pressure. *P* and P_0 are the real pressure and the standard pressure (101.325 kPa) of the gaseous phase, respectively.

The degree of the deviation from the standard pressure to the real pressure is always evaluated by the fugacity coefficient $\gamma = f/P_0$ in thermodynamics. The expression of the fugacity coefficient in logarithmic form is shown as the following [5,10–12]:

$$\ln(\gamma) = \ln\left(\frac{f}{P_0}\right) = A \times \frac{P}{1 \times 10^5\ \mathrm{Pa}} + B \times \frac{P^2}{(1 \times 10^5\ \mathrm{Pa})^2} \tag{2}$$

where *A* and *B* are the parameters related to temperature, both of which are endowed with relatively small values on account of the reason that *f* should infinitely approach to the real pressure *P* when *P* is not higher than the standard pressure of 101.325 kPa.

It is a priority to reasonably estimate the values of the parameters *A* and *B* before optimization. In the present optimization, since there is no fugacity expression available for either of the Mg and Zr unary systems, that of nitrogen is adopted as the substitution for all the gaseous species in both of the Mg and Zr unary systems. The expressions of the parameters *A* and *B* are given in the following form [10,12,13], which are completely temperature dependent:

$$A = \frac{0.3926\mathrm{K}}{T} - \frac{39.23\mathrm{K}^2}{T^2} + \frac{2800\mathrm{K}^3}{T^3},\ B = \frac{3.805 \times 10^{-6}\ \mathrm{K}}{T} + \frac{0.00113\mathrm{K}^2}{T^2} - \frac{0.07\mathrm{K}^3}{T^3} (T \geqslant 300\ \mathrm{K}) \tag{3}$$

2.2. Condensed phases

The pressure contribution G_{press} to the molar Gibbs free energy of pure element can be expressed as the function of temperature and pressure by Murnaghan equation [7]:

$$G_{\mathrm{press}} = \frac{A\exp(A_0T + A_1T^2/2 + A_2T^3/3)}{(K_0 + K_1T)(n-1)}\{[1 + \mathrm{nP}(K_0 + K_1T)]^{(1-1/n)} - 1\} \tag{4}$$

where, the parameter *A* is equivalent to the molar volume of the specified phase at a temperature of 0 K and a pressure of 0 Pa. The parameters A_0, A_1, A_2 and K_0, K_1, K_2 are the coefficients of the temperature polynomials, $\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = A_0 + A_1T + A_2T^2$ and $\kappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T = K_0 + K_1T + K_2T^2$, for the thermal expansivity and the compressibility of the phase at a pressure of 0 Pa. The parameter *n* is pressure-independent but temperature-dependent, and is used to describe the linear function of *P* for the bulk modulus of a condensed phase, *B* = *B*(*T*,*P*), which was suggested by Guillermet [14]:

$$B(T, P) = B(T, 0) + \mathrm{nP} \tag{5}$$

where *B*(*T*,0) is the bulk modulus at a pressure of 0 Pa.

Based on the above description of G_{press}, the integrated molar Gibbs free energy of the pure element *i* (*i* = Mg and Zr) in the condensed phase ϕ, ${}^0G_i^{\phi} = G_i^{\phi} - H_i^{SER}$, takes the following form:

$$\begin{aligned} {}^0G_i^{\varphi}(P, T) &= G_i^{\varphi}(P, T) - H_i^{\mathrm{SER}}(101.325\ \mathrm{kPa}, 298.15\ \mathrm{K}) \\ &= a + \mathrm{b}T + \mathrm{c}T\ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \\ &\quad + G_{\mathrm{press}} \end{aligned} \tag{6}$$

where H_i^{SER} is the molar enthalpy of the element *i* at 298.15 K and 101.325 kPa in its standard element reference state which is HCP_A3 for both Mg and Zr. The coefficients from *a* to *h* in order are the parameters of the temperature polynomial for the molar Gibbs free energy when the pressure approaches to or falls below 101.325 kPa (1 atm).

3. Literature data on both unary systems

3.1. Magnesium system

Under the condition of $P \leq 101.325$ kPa, it is widely acknowledged that the gaseous phase of Mg consists of the species of Mg (g) and Mg_2 (g), and the condensed phases are hexagonal close-packed (HCP_A3) and liquid. Kennedy and Newton [15] determined the melting curve of Mg (HCP_A3) by resistivity measurement up to 12 GPa, which was further confirmed by Errandonea [16] and has reached a widespread consensus [15–18].

By contrast, the phase transitions of Mg at higher temperature and pressure have attracted intensive investigations not only on the methods of experiments (such as synchrotron X-ray diffraction [19] and high shock loading [20]) but also on the approaches of calculations (such as first principle calculation [18,21], *ab initio* calculation [22,23] and generalized pseudopotential theory [24]). The particular interest in the studies on Mg is mainly due to the great controversy about whether the phase transitions of Mg at high pressure follow the transition sequence of HCP_A3 → BCC_A2 (body centered cubic) or HCP_A3 → DHCP (double hexagonal close-packed) →BCC_A2, which is also the issue of the present focuses. In the research on the phase behavior and the *P–V–T* equation of state for Mg up to 18.6 GPa and 1527 K with in-situ energy-dispersive X-ray diffraction, Errandonea et al. [19] observed the phenomenon of the peak splittings and attributed it to the existence of DHCP phase. However, a subsequent experimental study up to 25 GPa and 1900 K, performed by Cynn et al. [25] using the similar method as that by Errandonea et al., specifically indicated no proof for the appearance of this DHCP phase. The relative stability study on HCP_A3, BCC_A2 and DHCP structures with metadynamics method revealed no stability range for DHCP in ambient temperature, but the structural fluctuations for Mg were found only at 15 GPa and 500 K [26]. The authors suggested that the alternate appearances of HCP_A3, BCC_A2 and DHCP structures were driven by kinetics. According to the enthalpy calculations, it was much more energetically favorable for DHCP than BCC_A2, leading to the experimental observation of DHCP at the above mentioned pressure and temperature [26]. However, Liu et al. [21] pointed out that the BCC_A2 phase may be the most stable structure for Mg under higher pressure than 65 GPa and at 0 K, with no interim structure transition of HCP_A3-DHCP. In view of the above analysis, the present work tends to accept the exclusion of the DHCP phase from the condensed phases at high pressure and high temperature when the *P-T* phase diagram of the Mg unary system is constructed.

In addition, the triple point of three-phase equilibrium and the onset pressure of HCP_A3-BCC_A2 transition at ambient temperature have not reached an unanimous conclusion yet. *Ab initio* calculations predicted