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An updated thermodynamic modeling of the Ga–Ti system

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ABSTRACT

The thermodynamic description for the Ga–Ti system has been updated using the CALPHAD approach. By combining the existing experimental data and newly obtained results from *ab initio* calculations and cluster variation method (CVM), the Gibbs energy functions of the individual phases of the Ga–Ti system have been evaluated. Compared with the previous thermodynamic modeling, the present assessment shows a better agreement with the experiments and the calculated enthalpies of formation of the intermetallic compounds obtained from *ab initio* calculations.

1. Introduction

The latest published phase diagram of the Ga–Ti system as shown in Fig. 1 was given by Okamoto [1] based on the work from Li et al. [2] and Antonova and Tretyachenko [3]. Li et al. [2] redetermined the Ga-rich corner of this system and assessed the phase diagram by the CALPHAD method, which convinced well with most of the experiments at that time. However, this modeling has the shortcomings discussed below:

(i) A congruent melting region of β-Ti(A2) was presented in the former evaluated phase diagram [2].
(ii) The homogeneity composition range of Ga_4Ti_5 was underestimated by Li et al.[2].
(iii) The predicted enthalpies of formation of compounds showed large difference with the results from *ab initio* calculations [4] (see Fig. 2).

In the present work, the thermodynamic models of the compounds proposed by Li et al. [2] were adopted but the model parameters were refined to overcome the above shortcomings with the aid of enthalpies of formation obtained recently by *ab initio* calculations [4]. Additionally a combination of *ab initio* and the cluster variation method (CVM) [5] calculations have allowed an estimation of the Gibbs energies of mixing of the hcp and bcc solid solutions based on titanium.

2. Literature

Since the literature data on the Ga–Ti system has been reviewed by Li et al. [2] up to 2001, this part is brief in the present paper, and a summary of the literature and the new obtained theoretical data is given in Table 1 to facilitate reading.

2.1. Phase diagram data

There are twelve phases in the Ga–Ti system: the liquid phase (L), three terminal solid solutions (β-Ti(A2), α-Ti(A3) and Ga(A11)) and eight binary compounds: $GaTi_3(D0_{19})$, $GaTi_2(B8_2)$, $Ga_3Ti_5(D8_m)$, Ga_4Ti_5, $GaTi(L1_0)$, Ga_3Ti_2, Ga_2Ti and $Ga_3Ti(D0_{22})$.

Liquidus and solidus boundaries have been determined by several authors [2,3,6 and 7]. Each of them determined different parts of the boundaries and no obvious conflicts were observed, so these data were used in the optimization.

The phase boundaries for the solid phases have also been exhaustively studied. The composition ranges for intermetallics were determined with diffusion couples [2] and annealing alloys [3], and several other values were reported by [2,8,9]. Data for the A2/$GaTi_2$ phase boundary was given by [3,6]. The A2/$GaTi_3$ phase boundaries were measured by [2,3,8,9]. The A2/A3 phase boundaries were studied by [3,6,8,9]. The A3/$GaTi_3$ phase boundaries were examined by [3,8–10]. However, the determined boundaries by [8–10] were located on the Ti-rich side of [3] and [11,12]'s results, and the calculation by Kaufman and Nesor [13] and Li et al. [2] fitted somewhat better with Antonova [3] and Anderko's

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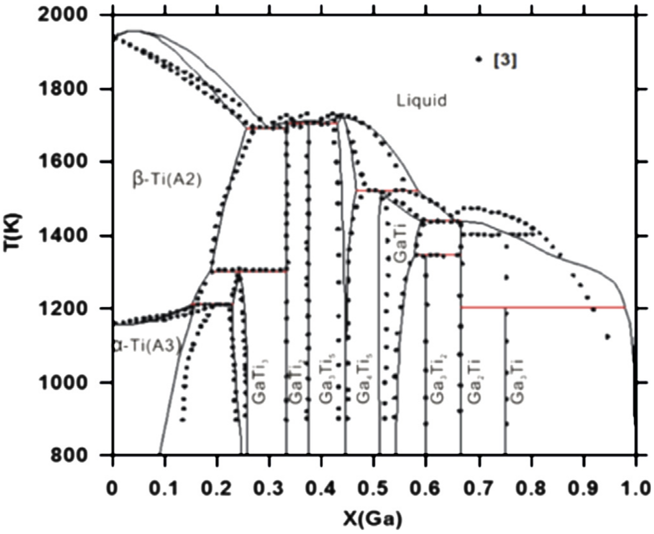

Fig. 1. Ga–Ti phase diagram from Li et al. [2] and Antonova [3]. The solid line stands for the calculated phase diagram form Li et al. [2].

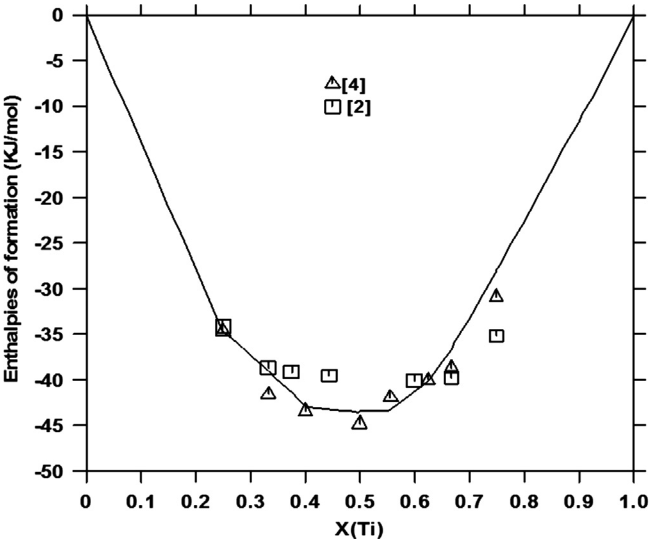

Fig. 2. Enthalpy of formation of the phases in the Ga–Ti system. Reference states are A3-Ti and A11-Ga.

[11,12] results, respectively. So the results from Ref. 8 and Ref. 10,11 were not included in the present optimization.

Invariant reactions from the literature are listed in Table 2. The values of temperature and composition for these equilibria were used for the assessment.

2.2. Thermodynamic data

The enthalpies of mixing as a function of composition for the A2 and A3 phases were calculated by combining *ab initio* calculations and the CVM [5]. They will be given in detail in the next section. Thermodynamic activities in the A2 were determined at 1623–1773 K by Gegel and Hoch [14] using the method of the Knudsen effusion technique with coupled a time-of-flight mass spectrometer. The partial enthalpies of Ti(A2) with 0–13 at% Ti in Ga melts were examined by Niklolaenklo et al. [15]. All the data were accepted in the assessment.

The enthalpies of formation of the stoichiometric ordered compounds were calculated by *ab initio* approach [4] using the Vienna *Ab initio* Simulation Package (VASP) [22], Fig. 2. The calculated enthalpy of formation of $GaTi_2$ is consistent with the value obtained by direct calorimetry [17,18] and adopted in the optimization. According to the measured solubility of Ti in molten Ga, Natanzon et al. [16] estimated the formation enthalpy of Ga_3Ti to be -40.2 kJ/mol. Based on the area of the differential peak in the DTA curve, Lobova and Syrvacheva [19] calculated the thermal effect of the $GaTi_3$ formation as -43.9 ± 2.1 kJ/mol. These results which considerably differ from the *ab initio* results were not adopted in the optimization. Finally low-temperature phase of the $GaTi_3$ compound was discovered by Simic and Marinkovic [21]; Rokuro et al. [20] reported a phase of Ga_5Ti_3 which was believed to be an ordered phase based on $L1_0$ according to their results of electron diffraction and XRD.

3. *Ab-initio* data and modeling of the Ti based solid solutions

The three most widely employed approaches for calculating the properties of disordered alloy solid solutions are: (i) the cluster expansion [23–28], (ii) the supercell method using either conventional supercells or special quasi-random structures (SQS) [27–29], or (iii) direct methods based on the coherent potential approximation [28,30,31]. In the present work we have combined the two first methods.

3.1. Strategy

In each lattice, the total energies of selected ordered structures have been calculated from *ab-initio*. Tables 3 and 4 present the characteristics of the hcp and bcc structures which have been considered. As we want to obtain the thermodynamic data of hcp and bcc solid solutions, we have not allowed shape relaxations of the structures because these relaxations can lead to structures which have lost the symmetry of the underlying lattice. Therefore volume and atomic positions relaxations have been allowed. However, the values reported in Table 3 for the hcp phases correspond to equal first nearest neighbor distances of the atoms in the hexagonal plans and between the hexagonal planes. As in the hcp solid solution these distances are more often different, we have optimized the hexagonal c/a parameter for each hexagonal structure.

For each structure-type, a cluster expansion was fit to formation energies [24,25] via the Connoly Williams method [32]. This method also allows to obtain the value of the enthalpy of formation of the disordered solid solution by considering a random distribution of the atoms.

Ab-initio calculations have also been performed for 16 atoms-SQS structures [33,34]. A volume relaxation followed by a relaxation of the positions of the atoms has been performed in order to keep the symmetry of the underlying lattice. The difference between the two energy values allows an estimation of the lattice relaxation energy.

Finally, *ab-initio* calculations have been performed in supercells for dilute solutions. In the hcp lattice, we have considered a 64 atom supercell, in the bcc lattice the supercell contains 54 atoms.

In each lattice, the values of the enthalpy of formation of the disordered solid solution, of the cluster interactions, and of the relaxation energy are the input of a CVM [5,35,36] calculation of the thermodynamic data.

3.2. Computational details

The density functional (DFT) calculations have been carried out using the Vienna *ab initio* simulation package (VASP) [22]. The