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Modeling of molar volume of the sigma phase involving transition elements

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A R T I C L E I N F O

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The molar volume of the sigma phase has been modeled and evaluated at room temperature and atmospheric pressure for binary systems concerning 19 transition elements Au, Co, Cr, Fe, Ir, Mo, Nb, Ni, Os, Pd, Pt, Re, Rh, Ru, Ta, Tc, V, W and Zr by using the CALPHAD approach. The volume model proposed in this work expresses the molar volume of a non-stoichiometric sigma phase as a linear average of volumes of the constituting elements in their hypothetic sigma structure, which can be assessed as model parameters based on experimental data from the literature. Reasonable model parameters have been obtained giving a best description of most experimental data. For comparison, volumes of the 19 transition elements in the sigma structure have been calculated by first-principles calculations. The results are compatible with the assessed values.

1. Introduction

The sigma phase is an intermetallic compound with tetragonal structure. The space group of the sigma phase is generally designated as $P4_2/mnm$ [1,2], except for β-Ta and β-U (see e.g. [2] and references therein). It is a hard, brittle phase mostly precipitated in transition alloy systems and deteriorates various properties of stainless and other high-alloy steels [1,2]. In this connection there are numerous researches on how to avoid or control the amount of the sigma phase, as well as its crystal structure, physical properties, ordering and phase stability (see e.g. [2] and references therein). In addition, thermodynamic properties of the sigma phase have been intensively studied by the CALPHAD approach [3–5]. Multi-component phase diagrams involving the sigma phase have been measured experimentally and critically assessed to establish comprehensive thermodynamic databases. As an important physical property, molar volume has also been modeled and evaluated by the CALPHAD approach mostly for solution phases [6–10]. The resulting volume databases act as an indispensable complement to the growing CALPHAD databases. Various CALPHAD models of molar volume have been reviewed by He et al. [11] recently. However, for the sigma phase, modeling of molar volume is still a vacancy.

At certain temperature and pressure, the molar volume of a disordered solution phase is dependent on the composition of this phase. For an intermetallic compound which is ordered or partially ordered, the volume is dependent on the site fractions of its sublattices, i.e. detailed site occupancies of constituents on all inequivalent sites. In order to obtain molar volumes of involving phases in a multi-component and multi-phase material system, phase equilibrium calculations based on thermodynamic databases should be performed firstly to determine the amounts and compositions or site fractions of all constituting phases of the system. One can then calculate the molar volumes of individual phases as well as the overall volume of the system by taking a linear average of volumes of all phases with the phase amounts as the linear coefficients.

Databases for thermodynamics, diffusional mobility and molar volume are developed and integrated within the framework of the CALPHAD approach. This integration greatly facilitates the practice of materials design. However, a problem may arise that any updates of thermodynamic databases may predict different site occupancies for ordered or partially ordered compounds and thus it necessitates modifications of model parameters for volume data.

In the present work, a method to conveniently model molar volume of the sigma phase is proposed. With this method, the molar volumes of sigma phases at room temperature and atmospheric pressure involving 19 transition elements were systematically assessed by using the CALPHAD approach based on experimental data from the literature. The volumes of sigma phases in real alloy systems can be calculated conveniently by using the established volume database, which is independent of the thermodynamic data for the sigma phases studied in the present work.

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2. Methodology

2.1. CALPHAD modeling

On the basis of the compound energy formalism (CEF) [12,13] in the CALPHAD approach, the sigma phase is preferably modeled using three sublattices with a stoichiometric ratio of 10:4:16, although the atoms in the unit cell occupy 5 inequivalent sites and other sublattice models are proposed [2,13–17].

For a binary non-stoichiometric sigma phase concerning elements A and B, the sublattice model adopted in the present work is $(A, B)_x(A, B)_y(A, B)_z$, with x, y and z equaling 10, 4 and 16, respectively. In CEF, the Gibbs free energies for totally eight ($2^3 = 8$) stoichiometric end-member compounds (e.g. $A_xA_yA_z$, $A_xB_yA_z$) and the possible interaction energy have to be assessed to represent the total Gibbs energy of the sigma phase. Similar to CEF, molar volumes of the stoichiometric end-member compounds, denoting V_{ijk}, are assessed to model the molar volume of the non-stoichiometric sigma phase as follows:

$$V_m = \sum y'_i y''_j y'''_k V_{ijk} + V_m^E, \tag{1}$$

where y', y'' and y''' are the site fractions in the first, second and third sublattice, respectively. The subscripts i, j and k represent the constituent elements A or B. V_m^E is the excess molar volume. In the present work, molar volume means volume per mole of atoms instead of per mole of formula units containing 30 atoms in the unit cell.

It is difficult to evaluate all eight values for V_{ijk} as some of the compounds are metastable or non-stable. The number of the end-member compounds increases sharply to n^3 when describe a n-component sigma phase. In the following we propose a convenient way to avoid the difficulty:

$$V_{ijk} = \frac{x}{x+y+z}V_i + \frac{y}{x+y+z}V_j + \frac{z}{x+y+z}V_k + V_{ijk}^E, \tag{2}$$

where V_i, V_j and V_k represent molar volumes of pure elements in the hypothetic sigma structure, either V_A or V_B. V_{ijk}^E is the deviation from the linear combination for pure elements. When there is no experimental evidence, V_{ijk}^E is set to zero. It is then possible to calculate all values for V_{ijk} by using only V_A and V_B.

As shown in Appendix A, when both V_m^E and V_{ijk}^E equal zero, meaning a linear relation exists between the molar volume and the composition of the constituting elements, the molar volume of the non-stoichiometric sigma phase is:

$$V_m = x_A V_A + x_B V_B, \tag{3}$$

which means V_m is a function of mole fraction (x_A and x_B) of the constituting elements (A or B) and independent of site fractions in each sublattice. This method can be extended beyond binary systems and reduces the n^3 unknowns for end-member compounds to n values for n elements for a n-component sigma phase. Another practical significance is that the development of volume database can be separated from thermodynamic databases since the volume is dependent only on mole fraction instead of site occupancy.

For the binary sigma phases concerning transition elements Au, Co, Cr, Fe, Ir, Mo, Nb, Ni, Os, Pd, Pt, Re, Rh, Ru, Ta, Tc, V, W and Zr, we performed a systematic evaluation of the volume data and found that V_m^E and V_{ijk}^E are indeed negligible showing the linearity. Actually, this linearity has been noticed by Joubert [2] based on the experimental information and by Crivello et al. [18] based on the first-principles calculations of the stoichiometric end-member compounds of the Re-related sigma phases. However, the preliminary study of the Mn–X systems (X = Cr, Mo, Re, Tc, Ti and V) shows that the linear relation does not hold for the Mn–X sigma phases. In addition, experimental data for ternary and high-order sigma phases should be examined to verify the linearity. A separate work is conducted on these systems.

2.2. First-principles calculations

In Eqs. (2) and (3), molar volumes of pure elements in the hypothetic sigma structure are used. These data can be evaluated from the experimental data as fitting model parameters. On the other hand, it is not difficult to obtain these values from first-principles calculations. In the present work, we compare data from both methods and try to reveal the physical significance of the evaluated parameters in order to make reliable predictions for multi-component systems.

The first-principles calculations were performed using the plane wave method with projector augmented wave (PAW) pseudopotentials [19], as implemented in the Vienna ab initio simulation package (VASP) [20]. We used the exchange–correlation functional within the generalized gradient approximation (GGA) as parameterized by Perdew and Wang [21]. The k-point meshes (8 * 8 * 15) for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme [22]. A large plane-wave cutoff energy of 400 eV was used. Spin-polarized calculations were conducted. To facilitate the calculations, ZenGen script-tool was used to automatically generate input files for VASP calculations [18].

3. Results and discussion

Each end-member compound was assigned a volume following Eq. (2), i.e. the composition average of the volumes of the relevant elements in the sigma phase structure. These elemental volumes were served as the model parameters and assessed simultaneously by using the PARROT module [23] in the Thermo-Calc software package [24,25] and considering all experimental data for all binary systems. By reviewing experimental conditions and sample quality, different weights were assigned to the experimental data from the literature during the assessment. Experimental data were mostly lattice parameters measured by X-ray or neutron diffraction and were converted to molar volumes in the present work. Some experimental data measured by X-ray diffraction in the 1950–1960s with unit of kX were converted to absolute length [8,26–27]. Parameters that can best represent the experimental data were obtained and listed in Table 1.

Assessed molar volumes of the 19 transition elements in the sigma phase structure compared with the first-principles calculations are shown in Fig. 1. It is obvious that the molar volumes of 4d and 5d transition elements decrease and then increase with increasing atomic number. It should be mentioned that Cu-, Hf- and Ti- related systems are not evaluated in the present work since the experimental data are scarce and mostly for ternaries (e.g. Al–Cu–Nb, Al–Mo–Ti, Cu–Ga–Nb and Hf–Mo–Ru). For Mn- related systems, as mentioned in Section 2.1, a separate work is conducted. The assessment results are discussed below. For the convenience of comparison and discussion, all assessed binary systems are grouped in the following 10 categories.

3.1. General discussion

Greenfield and Beck [28] measured the lattice parameters of sigma phases in many binary systems, i.e. Cr–Re, Cr–Ru, Mo–Re, Mo–Ru, Nb–Pd, Nb–Pt, Nb–Re, Nb–Rh, Pt–Ta, Re–Ta, Re–W and Rh–Ta. They mentioned that the analyzed compositions were not accurate. Moreover, alloys with different compositions were prepared for each binary system but it is not clear which alloys were used for X-ray diffraction detection. For systems (i.e. Mo–Ru, Nb–Pd, Nb–Pt, Nb–Re, Re–Ta and Rh–Ta) that sigma phases