Influence of atomic mixing and atomic order on molar volume of the binary sigma phase

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ABSTRACT

The present work systematically clarifies the influence of the atomic mixing and the atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal) on the molar volume of the binary sigma phase. We calculated the molar volumes of 21 binary sigma compounds with different atomic order by using EMTO-CPA (Exact Muffin-Tin Orbitals - Coherent Potential Approximation) method. The calculation results follow a similar trend as the experimental data. Moreover, the calculated molar volumes with respect to the composition of the sigma phase in disordered states show that the sigma compounds do not comply with the linear volume-composition relationship. This is due to the influence of the atomic mixing and the deviation can be either negative or positive depending on the tendency of electron loss or gain of the two constituent elements. Additionally, we compared the molar volume difference ($\Delta Vm = V_{disorder} - V_{order}$) between the hypothetically disordered and ordered states of the binary sigma compounds. The results indicate that the effect of the atomic order on the molar volume of the sigma phase depends on the size difference and the electron configurations of the two constituent elements.

1. Introduction

The sigma phase is a nonstoichiometric intermetallic compound with tetragonal structure (space group P4$_2$/mnm) containing 30 atoms distributed on five inequivalent sites [1–3] as shown in Table 1. This phase exists in 49 different binary systems, among which Cr-Ni, Ta-V, Ti-Mn, Zr-Ir and Zr-Re are not confirmed. It is a hard brittle phase mostly formed between transition elements and when presenting in stainless and other high-alloy steels as well as Ni-based superalloys, it deteriorates the properties of products [1,2].

As an important physical property, the molar volume (or lattice parameters) of the sigma phase has attracted great interests of investigations [1–5], by using XRD (X-ray diffraction), ND (neutron diffraction), CALPHAD [6–8] or first-principles calculation methods.

From the 1950s–2010s, there are numerous measurements (see e.g. Ref. [5] and references therein) on the lattice parameters of the sigma compounds by using XRD or ND methods. The measured data from the 2000s–2010s are more accurate. Most measured volumes with respect to composition present linear relationship within the homogeneity range [5].

Besides, Crivello et al. [4] calculated the cell volumes of the stoichiometric end-member compounds (i.e. the complete set of ordered configurations) of Re-X (X = Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Os, Ru, Ta, Tc, Ti, V, W and Zr) by using first-principles calculations. They indicated that for most systems, the cell volume with respect to composition present an approximately linear relationship, while for Hf-Re, Nb-Re, Ta-Re, Ti-Re and Zr-Re, a negative deviation from linearity was observed (see Fig.5 in Ref. [4]), which indicates a denser packing with atomic mixing [4]. However, Crivello et al. [4] did not further discuss the origin of the deviation.

In a recent work, Liu et al. [5] modeled and evaluated the molar volume of the binary sigma phase at room temperature and atmospheric pressure by using the CALPHAD method and establishing a CALPHAD-like database. The adopted model expresses the molar volume of a nonstoichiometric sigma phase as a linear average of volumes of the constituent elements in their hypothetic sigma structure [5]. The proposed linear model can well reproduce most experimental data. It has interesting features in developing databases, such as reducing the

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Table 1
Crystal structure of the sigma phase with assignment of the site occupancy of atom A corresponding to the ordered and disordered compounds A_2B and $A_xB_{(1-x)}$ (V(A) > V(B)), where V(A) and V(B) are the molar volumes of A and B, respectively, in their hypothetic sigma phase structure from the CALPHAD assessments [5,9]).

Space group	P4₂/mnm (no. 136)				
Wyckoff position	2a	4f	8i₁	8i₂	8j
Coordination number (CN)	12	15	14	12	14
Completely ordered compound (A_2B) [2]	0	1	1	0	1
Disordered compound ($A_xB_{(1-x)}$)	x	x	x	x	x

number of assessed parameters and separating the volume data from the corresponding thermodynamic databases. The proposed linear model works well as a phenomenological method, which however does not present any physical and chemical insights.

In fact, two influencing factors were neglected in the above linear model, namely atomic mixing and atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal). Both the atomic mixing and atomic order may lead to a deviation from the linearity mentioned above. Unlike solution phases, the molar volume of the sigma phase can vary with the atomic order even at a fixed composition. The purpose of the present work is to study how the atomic mixing and atomic order affect the molar volume of the sigma phase.

Hall and Algie [1], Joubert [2] and then Liu et al. [9] systematically investigated the atomic order of the binary sigma phase. Liu et al. [9] indicates that between the two constituent elements, the one with larger size, smaller number of valence electrons or smaller total number of electron shells prefers occupying large coordination number (CN) sites and the other one prefers occupying small CN sites.

In the present work, we calculated the molar volume of the A-B binary sigma phase with different atomic order by using EMTO-CPA approach. The atomic order involves the completely ordered and disordered states as defined in Table 1, as well as the experimental site occupancies. We used the molar volume difference between the A_2B sigma compounds in the ordered and disordered states to describe the influence of atomic order on molar volume. On the other hand, we describe the influence of atomic mixing on molar volume by studying deviation of the volume of the hypothetically disordered sigma phase from linear volume-composition relationship, which describes volume variations of the hypothetically disordered sigma phase spanning from pure sigma A to pure sigma B. Notably, the disordered state is the closest state to solid solution. Thus it excludes the influence of atomic order on molar volume.

To facilitate explanation, all the binary sigma compounds investigated are designated as A-B where atom A always has a larger size than atom B (i.e. V(A) > V(B)). The size of atom A or B is determined by the molar volume of pure A or B in their hypothetic sigma phase structure from the CALPHAD assessments [5,9]. Besides, we introduced

different categories of the sigma phase divided by Liu et al. [9] as shown in Table 2. It is classified according to the electron configurations of the two constituent elements. There exist six different categories, i.e. SMe, SMs-SMe, LAs, LAs-SMe, LAs-LAe, A-Al (A = Nb, Ta), where SMe or LAe indicates that atom A has smaller or larger number of valence electrons than atom B, respectively; SMs or LAs indicates that atom A has smaller or larger total number of electron shells than atom B, respectively.

2. Methodology and calculation details

First-principles calculations were performed using the exact muffin-tin orbitals (EMTO) method [10,11] based on the density-functional theory (DFT) [12]. With this method, Green's function technique is used to solve the one electron Kohn-Sham equation. The effective potential in the one-electron equation is treated with the optimized overlapping muffin-tin approximation. Besides, the total energy is corrected with the full charge density (FCD) method [10]. The basis sets of the exact muffin-tin orbitals [10,11] are used to expand the wave function. The coherent potential approximation (CPA) [13–15] is incorporated within the EMTO code, which facilitates the calculations dealing with chemical disordered alloys. With these techniques, the EMTO-CPA method holds a great higher accuracy than the linear muffin-tin orbital (LMTO) method [16] and ensures the reliability of calculations dealing with atomic and magnetic disordered systems [17].

In the present work, Green's function was calculated for 16 complex energy points distributed exponentially on a semicircular contour. The scalar-relativistic and soft-core approximations were employed. We used the electronic exchange-correlation functional within the generalized-gradient approximation (GGA) parameterized by Perdew et al. [18]. The Brillouin zone was sampled by a uniform k-point mesh without any smearing technique. The k-point mesh was set to $3 \times 3 \times 6$. For Cr-Fe and V-Fe, the magnetic parameters for ferromagnetism were set.

3. Results and discussion

The binary sigma compounds chosen to perform EMTO-CPA calculations are Cr-Co, Cr-Fe, Cr-Mn, Mo-Co, Mo-Mn, Mo-Os, Mo-Re, Nb-Al, Nb-Ir, Os-Cr, Re-Cr, Re-Mn, Re-V, Ru-Cr, Ta-Al, Ta-Pd, Ta-Rh, V-Co, V-Fe, V-Mn and V-Ni. The molar volumes of the pure elements in a hypothetic sigma phase structure obtained from first-principle calculations are compared in Fig. 1 with those obtained from the CALPHAD assessments. This figure shows that the volumes calculated by EMTO-CPA and VASP methods follow a similar trend. Besides, it indicates that for most elements, the differences between the first-principles calculations and the CALPHAD assessed ones are within 10%. The small deviations validate our calculations.

Fig. 2 shows the calculated molar volumes of the A-B (V(A) > V(B)) binary sigma compounds compared with the experimental data. The

Table 2
A-B (V(A) > V(B)) binary sigma systems in different categories divided by Liu e al [9] according to electron configurations of the two constituent elements. An instance of the electron configurations for each category is given at the bottom. The systems labelled with italic are not confirmed to form the sigma phase.

SMe			SMs-SMe		LAs	LAs-SMe		LAs-LAe	A-Al (A=Nb, Ta)
Cr-Co	Nb-Rh	V-Co	Mo-Ir	*Zr-Ir*	Re-Mn	Mo-Co	Tc-Fe	Os-Cr	Nb-Al
Cr-Fe	Ta-Au	V-Fe	Mo-Os	*Zr-Re*	*Ta-V*	Mo-Fe	W-Ru	Re-Cr	Ta-Al
Cr-Mn	Ta-Ir	V-Mn	Mo-Re		Tc-Mn	Mo-Mn	W-Tc	Re-V	
Cr-Ni	Ta-Os	V-Ni	Nb-Ir			Re-Fe		Ru-Cr	
Mo-Ru	Ta-Pt	W-Ir	Nb-Os			Ta-Pd		Tc-Cr	
Mo-Tc	Ta-Re	W-Os	Nb-Pt			Ta-Rh			
Nb-Pd	*Ti-Mn*	W-Re	Nb-Re						
			e.g. Mo-Ir: $4d^55s^1$ -		e.g. Re-Mn:	e.g. Mo-Co:		e.g. Os-Cr:	e.g. Nb-Al
e.g. Cr-Co: $3d^54s^1$ - $3d^74s^2$			$5d^76s^2$		$5d^56s^2$ - $3d^54s^2$	$4d^55s^1$ - $3d^74s^2$		$5d^66s^2$ - $3d^54s^1$	$4d^45s^1$ - $3s^23p^1$