Theoretical study of the Mo–Ru sigma phase

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Abstract

The thermodynamic properties of the Mo–Ru binary σ-phase are investigated using a combination of *ab initio* calculations and CALPHAD modeling. Total energy calculations have been performed for the complete set of 32 end-member compounds of a 5-sublattice compound energy model. The internal crystallographic parameters for each end-member compound have been determined by minimising the total energy. A simpler, 3-sublattice model of the Mo–Ru σ-phase is formulated on the basis of calculated total energies. The site occupancy is acquired by minimising the free energy given by the compound energy model. A strong preference of Mo and Ru towards high-coordination sites and icosahedral sites in the Mo–Ru σ-phase is found and analysed in terms of the electronic structure.
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1. Introduction

The σ-phase occurs in transition metal alloys with a total number of valence electrons between 6.2 and 7.4 per atom. The structure type is complex tetragonal, with space group $P4_2/mnm$ [1]. The effects of this very hard and brittle phase on the mechanical properties are mainly deleterious, therefore the mechanisms that govern the σ-phase formation are important for the metallurgy of steels and superalloys. Usually, the stability of the σ-phase is discussed in terms of electronic structure and atomic size factors. Recently it was shown that the thermodynamic functions of σ-CrFe, as well as those of other σ-phases containing 3d transition elements, contain sizeable magnetic contributions [2,3].

The case of the Mo–Ru σ-phase is of particular interest in connection with the development of next generation superalloys (containing platinum group metals such as Ru, Rh, Pd, Pt and Ir) [4], but also because its constituents are non-magnetic and isoelectronic with those of the magnetic σ-CrFe. Also, the atomic radii of the components are more similar in Mo–Ru than in the other non-magnetic isoelectronic σ-phases such as

Cr–Ru or Cr–Os. Therefore, the stability of the Mo–Ru σ-phase appears to be governed mainly by the electronic structure factor.

Experimental studies of the Mo–Ru σ-phase are complicated because of the refractory nature of this material. *Ab initio* calculations may be used as a complementary source of data for thermodynamic modeling [5,6]. They also allow one to investigate the relationship between the electronic and atomic structure of the σ-phase. Several successful studies have been conducted in which *ab initio* calculations are combined with the CALPHAD modeling [3,7] or the Connolly–Williams cluster expansion approach [8–10], aiming to analyse the site occupancy in the σ-phase as a function of composition and temperature. The purpose of the present study is to calculate the electronic structure and ground-state properties of the Mo–Ru σ-phase, as well as to develop a model for the thermodynamic description for this phase using first-principles calculations as the only input. It is worth noting that *ab initio* and CALPHAD methods have also been used to improve the description of the σ-phase in the phase diagram of Re–W [7], Co–Mo and Fe–Mo [11].

There are five crystallographically inequivalent sites in the crystal structure of the σ-phase; see Table 1. These sites can be grouped into two larger categories according to the coordination number Z, icosahedrally coordinated (IC) sites 1 and 4 (for

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Table 1
Inequivalent sites in the unit cell of the σ-phase

Site	1	2	3	4	5
Multiplicity (Wyckoff index)	2(a)	4(f)	8(i)	8(i)	8(j)
Coordination number	12	15	14	12	14

which $Z = 12$) and high-coordination number (high-CN) sites 2, 3 and 5 (for which $Z = 15$, 14 and 14, respectively). If all five sites are treated as independent sublattices; the site occupancy in the Mo–Ru case may be expressed by a general formula $(Mo, Ru)_2(Mo, Ru)_4(Mo, Ru)_8(Mo, Ru)_8(Mo, Ru)_8$. Here (Mo, Ru) denotes a mixture of Mo and Ru on a certain sublattice, and the subscript gives the number of atoms belonging to that sublattice in the unit cell of the σ-phase (the unit cell contains 30 atoms in total). The $2^5 = 32$ cases of integral site occupancy (where each site is completely occupied by either Mo or Ru) have special meaning within the compound energy formalism (CEF) [12] as so-called end-member compounds, the parameters of a five-sublattice model. Hereafter we use a short notation for the end-member compounds, e.g. we write RuMoMoRuMo instead of writing the full formula $Ru_2Mo_4Mo_8Ru_8Mo_8$. In this study we calculate the complete set of 32 total energies for the end-member compounds, whose energies are then used in order to model atomic ordering in the Mo–Ru σ-phase as well as to estimate its thermodynamic properties.

2. Methodology

2.1. Ab initio calculations

The *ab initio* calculations were performed using Density Functional Theory (DFT) [13,14] as implemented in the Projector Augmented Wave (PAW) code Vienna Ab initio Simulation Package (VASP) [15–17]. The energy cut-off for the PAWs was set to 300 eV, the exchange correlation was treated within the generalised gradient approximation (GGA) as parametrised by Perdew, Burke and Ernzerhof [18]. A Monkhorst-Pack mesh with 112 k-points in the irreducible wedge of the Brillouin zone was used [19]. The c/a ratio was optimised for the RuMoMoRuMo (most stable) configuration; the optimum value was found to be $c/a = 0.514$. The increase in energy for a deviation of 1% in the c/a ratio (shifted to 0.509 instead of 0.514) was about 0.2 kJ/mole; this dependence was regarded as weak. Therefore, the calculated optimum value $c/a = 0.514$ was used for all the other compounds. To confirm the validity of this assumption for other compounds, we carried out several additional tests. For instance, for the configuration RuRuRuRuMo, which was representative of Ru-rich phases, the energy was lowered by 0.1 kJ/mole as a result of the relaxation of the c/a ratio. The change is small enough, and does not have any impact on subsequent analysis. The equilibrium volume for each compound was calculated, followed by full relaxation of the internal atomic positions. Relaxation energies were found to be as high as a few kJ/mole for some compounds.

The reference states of Mo and Ru were chosen to be their respective ground states. The structural parameters were first optimised, followed by an accurate calculation of the total energy. The k-points were distributed according to a Monkhorst-Pack mesh consisting of 744 and 432 and k-points in the irreducible wedge of the Brillouin zone for bcc Mo and hcp Ru respectively.

The volume was equilibrated for every end-member compound, assuming a zero-pressure environment. The enthalpy of formation for each end-member compound $ijlkm$, where $(i, \ldots, m) = \{Mo, Ru\}$, was then calculated from the total energies, E, as:

$$H_{ijklm} = E_{ijklm} - c_{Ru}E_{Ru} - (1 - c_{Ru})E_{Mo}. \tag{1}$$

Here c_{Ru} is the overall concentration (mole fraction) of Ru in the end-member compound. The procedure of finding the equilibrium volume also gave us access to the energy versus volume relation, hence, the ground-state properties such as the lattice parameters and the bulk modulus were directly available.

2.2. Free energy estimation

In the compound energy formalism, which is a generalised Bragg–Williams approximation, the components are assumed to be randomly distributed within each crystallographic site [7, 12]. The Gibbs free energy may be written as

$$G = H^{srf} - TS^{conf}, \tag{2}$$

where the enthalpy of the σ-phase is represented in configurational space by H^{srf}, the so-called *surface of reference* [5]. Within the 5-sublattice model, where the five crystallographically inequivalent sites of the σ-phase are treated as independent sublattices, the H^{srf} reads as:

$$H^{srf} = \sum_{ijklm} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} y_m^{(5)} H_{ijklm}. \tag{3}$$

Here the H_{ijklm} is the *ab initio* enthalpy of formation for every end-member compound calculated at zero temperature (vibrational contribution is neglected here and thereafter) and $y_i^{(s)}$ is the mole fraction of component i on the sublattice s.

It is worth noting that in principle the mixing enthalpies of compounds with partial disorder at sublattices can be calculated directly from first principles using the so-called coherent potential approximation (CPA) [20] or using the effective cluster interactions determined from the CPA calculations, as was recently demonstrated for the hcp Ru-rich MoRu alloys [21]. However, for the Mo–Ru σ-phase the optimisation of the internal positions within the unit cell turns out to be important. For example, the energy gain due to such an optimisation for the most stable compound RuMoMoRuMo is of the order of 0.8 kJ/mole, to be compared with the enthalpy for this compound of 1.8052 kJ/mole. Unfortunately, the CPA does not allow one to perform the above-mentioned optimisation within the present-day implementations.