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Influencing factors of atomic order in the binary sigma phase

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ABSTRACT

The sigma phase can serve as a prototype of intermetallic phases when investigating the atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal structure), as the sigma phase bears a broad homogeneity range and there are numerous experimental site occupancy data available for the sigma phase. The present work brings new insights into the influencing factors of atomic order in the binary sigma phase. We calculated the atomic volumes and atomic charges of the constituent elements of 32 stoichiometric end-member compounds (i.e. the complete set of ordered configurations) of the binary sigma phase by using first-principles calculations. The calculation results show that besides the size factor and the number of valence electrons, the total number of electron shells is found as the third factor that affects the atomic order of the sigma phase. Moreover, the calculation results indicate that between the two constituent elements, the one with larger atomic size, smaller number of valence electrons or smaller total number of electron shells prefers occupying large coordination number (CN) sites (i.e. $4f$, $8i_1$ and $8j$) and the other prefers occupying small CN sites (i.e. $2a$ and $8i_2$). Furthermore, we dissociated the effects of individual influencing factors on atomic order of the sigma phase combining with the measured site occupancies from the literature.

1. Introduction

The sigma phase known as topologically close-packed (TCP) phase, is a non-stoichiometric intermetallic compound that crystallizes in a tetragonal structure (space group $P4_2/mnm$) with 30 atoms distributed on five inequivalent sites, namely $2a$, $4f$, $8i_1$, $8i_2$ and $8j$ [1–3]. It is a hard, brittle phase mostly formed between transition elements and deteriorates various properties of many technologically important materials, such as stainless and other high-alloy steels as well as Ni-based superalloys [1,2]. The sigma phase is reported existing in 49 different binary alloy systems, five of which are not confirmed (i.e. Cr-Ni, Ta-V, Ti-Mn, Zr-Ir and Zr-Re). It has attracted great technological and theoretical study interests since the 1950s [4].

The atomic order, i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal structure, is one of the research focuses. There are extensive studies of atomic order in intermetallic and solid state compounds, e.g. mu phase [5], sigma phase [2], chi phase [6], $L1_2$ phase [7] and B2 phase [8]. As an important crystallographic property, the atomic order is closely related to thermodynamic and thermo-physical properties of intermetallic compounds, such as formation enthalpy, volume and elastic modulus [9].

The sigma phase can serve as a prototype of intermetallic phases when investigating the atomic order, as the sigma phase bears a broad homogeneity range and there are abundant experimental site occupancy data available for the sigma phase. Numerous investigations on the atomic order of the sigma phase have been conducted, e.g. Refs. [1,2,10–22], by using XRD (X-ray diffraction), ND (neutron diffraction), mathematical methods or first-principles calculations.

At first, Kasper and Waterstrat [11] indicated that for the sigma phase, $2a$ and $8i_2$ sites should be occupied by elements to the right of Mn in the periodic table; $4f$ site by elements to the left and $8i_1$ and $8j$ sites by a mixture of both. Spooner and Wilson [13] stated that the size of the constituent atoms of the sigma phase was a major factor in governing the filling of $2a$, $4f$, and $8i_2$ sites but in addition some valence electron factor governed the filling of $8i_1$ and $8j$ sites. Afterwards, a systematic review of the sigma phase was conducted by Hall and Algie [1] and then by Joubert [2]. A more thorough argument about the atomic order of the sigma phase was proposed. They indicated that atoms with large size or poor in d-electrons preferentially occupy sites with large coordination number (CN), namely $4f$, $8i_1$ and $8j$; atoms with small size or rich in d-electrons preferentially occupy sites with small CN, namely $2a$ and $8i_2$.

However, all the conclusions above, focusing on the size factor and the number of valence electrons, cannot explain the measured site occupancies or atomic order satisfactorily. Taking Re-Mn system as an example, the numbers of valence electrons of Re ($5d^5 6s^2$) and Mn ($3d^5 4s^2$) are the same so the size factor should be the primary influencing factor on the atomic order based on the argument from Hall and Algie [1] and Joubert [2]. However, large differences can be observed in the site occupancies measured for sites with the same CN ($8i_1$ vs $8j$, CN = 14) and thus with similar size, as discussed in the following Section 4.2. In fact, the experimental site occupancies show that the atomic order among the large CN sites (i.e. $4f$, $8i_1$ and $8j$) or between the small CN sites (i.e. $2a$ and $8i_2$) can be very large, more examples being Nb-Re ($4f$ vs $8i_1/8j$) [2], Re-Fe ($8i_1$ vs $8j$) [2]. The early conclusions [1,2] about the atomic order cannot explain the occupancy preference among the large CN sites or the small CN sites.

Later on, Sluiter et al. calculated the site occupancies of the sigma compounds in Cr-Fe [19], Os-Cr [22], Re-Ta [20], Re-W [20,21] and Ru-Cr [22] systems by using a first-principle statistical thermodynamic approach. Their calculation results do not fit the experimental data very well, especially for Cr-Fe [19] and Os-Cr [22] systems because of their simplified assumptions. They confirmed the influencing factors on atomic order of Ru-Cr and Os-Cr systems from the perspective of the crystal structure [22]. They considered 1) the size factor (the size difference among the five inequivalent sites), 2) electronic degeneracy arguments and 3) the pairwise interaction (*A-A*, *A-B* or *B-B*) within the sigma unit cell. It was indicated that their conclusion has no predictive value [22]. Actually, their argument about the pairwise interaction was based on the deduction that all five crystal sites were equivalent as Cr and Ru/Os do not have an overwhelming preference for any of the sites. However, this deduction is not totally correct, which will be discussed in Section 4.2.3.

Recently, Crivello et al. [10] systematically discussed the site occupancy behavior of the sigma phase in binary Re-*X* (*X* = Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Os, Ru, Ta, Tc, Ti, V, W and Zr) systems by using the compound energy formalism (CEF) combined with first-principles calculations. These studied systems include stable sigma compounds (Re-V, Re-Cr, Re-Mn, Re-Fe, Nb-Re, Mo-Re, Ta-Re and W-Re) as well as some hypothetically unstable ones (Ti-Re, Zr-Re, Hf-Re, Re-Co, Re-Ni, Re-Tc, Re-Ru and Re-Os). The site occupancies of the above binary sigma compounds were calculated at 2000 K (see Fig. 9 in Ref. [10]) and Crivello et al. [10] proposed that the site occupancy behavior of the binary sigma phase is related to whether Re bears a larger size than the other constituent element or not. If Re bears a larger size (e.g. for Re-V, Re-Cr, Re-Mn, Re-Fe, Re-Co, Re-Ni, Re-Tc, Re-Ru and Re-Os systems), the site occupancy preference for Re atom follows $4f > 8i_1 > 8j > 8i_2 > 2a$ and if Re bears a smaller size (e.g. for Nb-Re, Mo-Re, Ta-Re, W-Re, Ti-Re, Zr-Re and Hf-Re systems), the site occupancy preference for Re atom follows $8i_2/2a > 8i_1/8j > 4f$. However, for Re-Os, Re-Ru and Re-V systems where Re bears a larger size, the calculation results show that the site occupancy preference for Re atom follows $8j > 8i_1$ (for Re-Os and Re-Ru systems) and $8i_2 > 8j$ (for Re-V system) which is inconsistent with their above conclusion. On the other hand, from the experimental perspective, for Re-V system the site occupancy sequence for Re atom follows $8i_2 > 2a > 8i_1 > 4f > 8j$ (see Section 4.2) which is almost the opposite sequence as the one proposed by Crivello et al. [10]. Moreover, the site occupancy behavior between the same CN (i.e. CN12: $2a$ vs $8i_2$; CN14: $8i_1$ vs $8j$) sites was not clearly clarified in that work.

At present, plentiful site occupancy measurements have been conducted on the binary sigma compounds with high accuracy, but the influencing factors on the atomic order of the sigma compounds are still not clear. Apparently, the size factor and the number of valence electrons are not enough for the explanation of the atomic order. Another obstacle to sort out the connections is that the experimental site occupancies are results of competition and cooperation of the influencing factors on atomic order, and it is difficult to dissociate the effects of individual influencing factors, as sometimes, for a specific system

different factors have similar effects [19] (e.g. for Cr-Fe system, larger size and also poorer in *d*-electrons of Cr comparing to Fe both cause Cr to preferentially occupy sites with large CN, namely $4f$, $8i_1$ and $8j$).

In the present work, besides the size factor and the number of valence electrons, we also considered the total number of electron shells as an influencing factor affecting the atomic order of the sigma compounds. Finally, we dissociated the effects of individual influencing factors on atomic order. To facilitate explanation, all the binary sigma compounds investigated are designated as *A-B* where the size of atom *A* is always larger than that of atom *B*. The sizes of the constituent elements (*A* and *B*) are determined by the cell volumes of their pure elements in the sigma phase structure from the first-principles calculations [10,23]. Besides, the site occupancy of atom *A* is given in the present work. Atom *B* complements atom *A* on different sites. We use $Y_S(A)$ to denote the site occupancy of atom *A* on site *S*. The site occupancy of atom *B* on site *S*, $Y_S(B)$, is equal to 1- $Y_S(A)$. The sequence of atomic order of atom *A* was given in the present work. For example, the sequence of atomic order, $4f_{(A)} > 8i_{1(A)} > 8j_{(A)} > 8i_{2(A)} > 2a_{(A)}$, denotes a descending site occupancy preference of atom *A* from the site $4f$ to $2a$. The sequence of atomic order of atom *B* is opposite. Moreover, five different colours are assigned to the five different crystal sites, namely $2a$ (red), $4f$ (blue), $8i_1$ (orange or magenta), $8i_2$ (black) and $8j$ (green), and they are used consistently throughout the present work.

2. Crystal structure of sigma phase

The sigma phase crystallizes in a tetragonal structure (space group $P4_2/mnm$) with 30 atoms distributed on five inequivalent sites, namely $2a$, $4f$, $8i_1$, $8i_2$ and $8j$. Fig. 1 presents the crystal structure of the sigma phase, which is stacked by coordination polyhedrons of CN 12, 14 and 15. Coordination polyhedrons around five inequivalent sites of the crystal structure are clearly clarified in Fig. 2 and Table 1 lists the nearest neighbor (NN) sites for the five inequivalent sites. More details about the crystal chemistry of the sigma phase can be found in Ref. [2].

3. Methodology and calculation details

3.1. First-principles calculations

First-principles calculations were performed using the plane wave method with projector augmented wave (PAW) pseudo-potentials [24], as implemented in the Vienna ab initio simulation package (VASP) [25]. We used the exchange-correlation functional within the
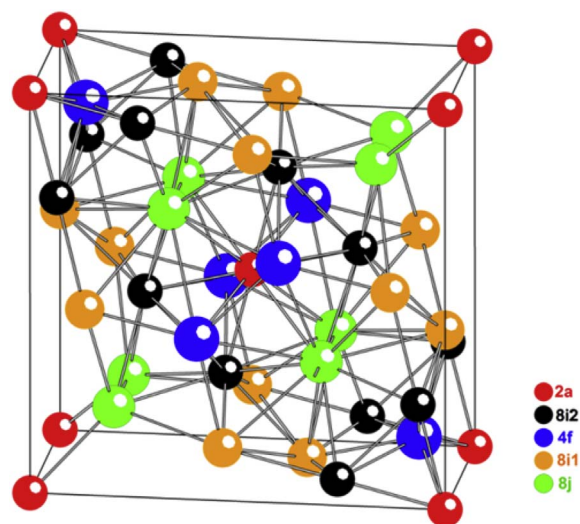

Fig. 1. Crystal structure of the sigma phase. Atoms occupying on different Wyckoff positions, namely $2a$, $4f$, $8i_1$, $8i_2$ and $8j$, are indicated by different fillings.