

Effect of the W addition content on valence electron structure and properties of MoSi₂-based solid solution alloys

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ABSTRACT

Based on the empirical electron theory (EET) of solids and molecules, the valence electron structures (VES) of MoSi₂-based solid solution alloys have been analyzed using the average atom model. The results showed that with the increase of the W addition content, the hybridization steps of Mo and Si atom of the alloys occurred in C3 and 1, respectively. The hybridization step of W was always C5. The bond energy of the main bond branch, the covalence electron number on the strongest bond and the percentage of the total covalent electron numbers accounting for the total valence electron number of (Mo_{1-x}, W_x)Si₂ solid solutions increased with the increase of W addition content. These suggested that the addition of W would increase the melting point, hardness and strength and decrease the fracture toughness of (Mo_{1-x}, W_x)Si₂ solid solutions. Based on those results, MoSi₂-based solid solution alloys were manufactured, and the results of the experiments were in accordance with those of the theory.

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1. Introduction

Transition-metal disilicides have received great attentions as potential high temperature structural materials. In particular, MoSi₂ with the C11_b structure has been considered to be the most promising material because of its high melting temperature, excellent oxidation resistance, relatively low density and high thermal conductivity [1,2]. However, poor fracture toughness at ambient temperature and low strength and creep resistance at elevated temperature (>1200 °C) have seriously limited the development of MoSi₂-matrix structural materials. Thus, many recent studies on the development of MoSi₂-based materials have focused on improving such poor mechanical properties through forming alloys with other elements or composites with a second phase [3,4]. Significant property improvement has been readily gained through alloying MoSi₂ with WSi₂, which also possesses the C11_b structure and forms a complete solid solution with MoSi₂. WSi₂ has been reported to be a suitable addition to MoSi₂ because of the remarkable increase of the elevated temperature strength [5], hardness and fracture toughness of MoSi₂ with the addition of WSi₂ [6]. Bose [7] has demonstrated that high temperature (1200 °C) creep was reduced by a factor of 10 by alloying with WSi₂.

In the theoretical aspects, many researchers have attempted to establish a relationship between the basic crystal structure and macro-properties. For example, Alouani et al. [8] have studied

the elastic constants and structural properties of MoSi₂ by full-potential linear muffin-tin-orbitals (FP-LMTO) method. Friak et al. [9] have simulated the tensile test in ideal crystals of MoSi₂ and WSi₂ loaded along the [001] axis by using first-principles full potential electronic structure calculations. They have found that these compounds have covalent and metallic bonds, and the covalent bond contributes to the macro-properties mostly. However, there is little quantitative analysis on the valence electron structure for these systems that restricts the interpretation of their macro-properties in physical sense. Moreover, for the solid solution, the first principle is not commonly used since the structure type is very limited [10]. On the other hand, the EET of solids and molecules formulated by Yu [11,12] is much simpler and more observable. In this article, the VES of MoSi₂-based solid solution alloys was calculated using the EET of solids and molecules, and the effect of W addition on the VES and the properties of MoSi₂-based alloys have been studied. To simplify the calculation, the average atom model of the EET has been used and assumed that the added content of W increased progressively from 0 to 50 mol% by a step of 10%.

2. Crystalline structure

Both MoSi₂ and WSi₂ have a tetragonal C11_b-type crystal structure with the space group of I4/mmm. Refractory metal atoms occupy the 2a site at the position, (0,0,0), and Si atoms occupy the 4e site at the position, (0,0,u). The cell parameters of MoSi₂ and WSi₂ are as $a=0.32056$ nm, $c=0.78450$ nm, $u=0.3353c$; $a=0.32138$ nm, $c=0.78299$ nm, $u=0.3347c$, respectively [13]. The unit cell of the C11_b structure is shown in Fig. 1.

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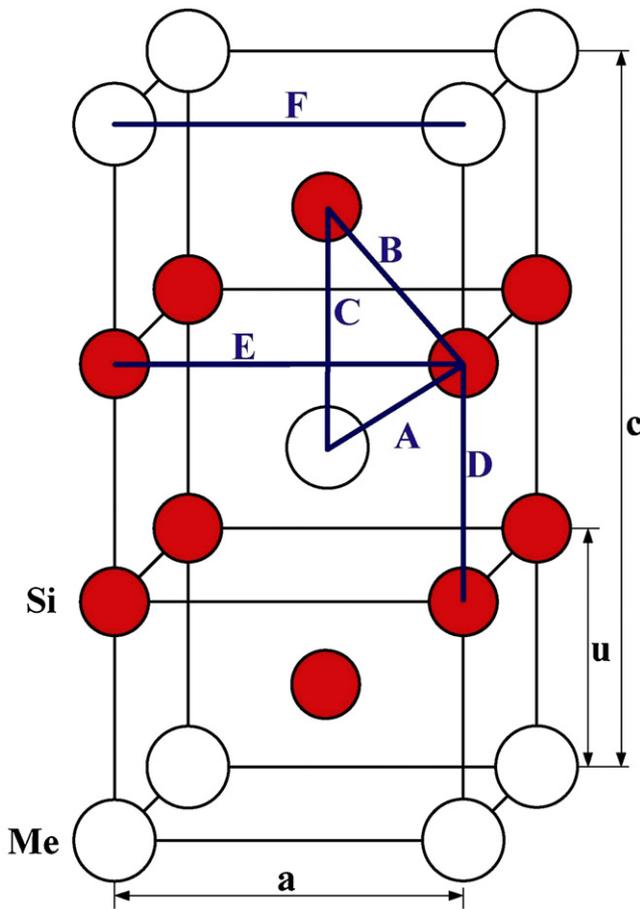


Fig. 1. Crystal structure of MeSi_2 with the C11_b structure.

A previous investigation has showed that the crystal structure of $(\text{Mo}, \text{W})\text{Si}_2$ is the same as that of MoSi_2 . The lattice parameters of $(\text{Mo}_{1-x}, \text{W}_x)\text{Si}_2$ solid solution can be calculated by Vegard's law [14]. The equations for calculating lattice parameters a_x and c_x are as follows:

$$a_x = (1-x)3.2056 + x3.2138 \quad (1)$$

$$c_x = (1-x)7.8450 + x7.8299 \quad (2)$$

where x is the mole fraction of W atoms.

3. VES of MoSi_2 -based solid solution alloys

3.1. VES results of MoSi_2

The VES of MoSi_2 has been analyzed in detail based on the bond length difference (BLD) method of EET. The calculated results are listed in Table 1 [15].

3.2. Meaning of average atom model

For the binary alloy or solid solution, because of its disordered atomic arrangement, we assume in the first order approximation that all positions in the solid solution were the same atoms, and the atoms were neither the matrix atom nor the solute atom, but a 'virtual' atom. The characteristic parameter of this atom was the weighted average of the characteristic parameter of the matrix atom and that of the solute atom. This kind of atom with the characteristic parameter of weighted average was called 'average atom'.

The $(\text{Mo}, \text{W})\text{Si}_2$ solid solution is formed by substituting Mo by element W. Thus, it is reasonable to consider that Mo and W atoms

have randomly occupied the stations of the Mo atoms. The distribution should be statistical. The single-bond semilengths, $R^{\text{Me}}(l)$, and the total covalence-electron pairs, $n_c^{\text{Me}}(l)$, of the solid solutions can be calculated according to the average atom theory [12]. The equations for calculating $R^{\text{Me}}(l)$, $n_c^{\text{Me}}(l)$ and $n_l^{\text{Me}}(l)$ are as follows:

$$R^{\text{Me}}(l) = (1-x)R^{\text{Mo}}(l) + xR^{\text{W}}(l) \quad (3)$$

$$n_c^{\text{Me}} = (1-x)n_c^{\text{Mo}} + xn_c^{\text{W}} \quad (4)$$

$$n_l^{\text{Me}} = (1-x)n_l^{\text{Mo}} + xn_l^{\text{W}} \quad (5)$$

Here, $R^{\text{Me}}(l)$, $R^{\text{Mo}}(l)$, and $R^{\text{W}}(l)$ represent the single-bond semilengths of metallic atoms (or average atoms composed $(1-x)\text{Mo}$ and $x\text{W}$), Mo atom, and W atom, respectively; and n_c^{Me} , n_c^{Mo} , and n_c^{W} denote the total number of covalent electron pairs of metallic atoms, Mo atom, and W atom, respectively; and n_l^{Me} , n_l^{Mo} , and n_l^{W} denote the lattice electron number of metallic atoms, Mo atom, and W atom, respectively.

3.3. Calculation of the VES

With the known crystal structure, experimental covalent bond length, i.e., the distance between any two atoms in the unit cell, can be calculated by knowledge of solid geometry. Each kind of covalent bond has its own number of equivalent bond, l_α , which is very important for the rest calculation. l_α was calculated using the formula in Ref. [11]. The equivalent bond numbers of $(\text{Mo}, \text{W})\text{Si}_2$ solid solution are the same to those of MoSi_2 as shown in Table 1.

Based on the EET of solids and molecules, the theoretical covalent bond length $D_{uv}(n_\alpha)$ between atom u and atom v is as follows [11]:

$$D_{uv}(n_\alpha) = R_u(l) + R_v(l) - \beta \lg n_\alpha \quad (6)$$

where $R_u(l)$ and $R_v(l)$ are the single bond radii of the atom u and v , respectively; n_α is pair number of bond covalent electrons, $\alpha = \text{A}, \text{B}, \text{C}, \dots, \text{F}$, and $\beta = 0.060 \text{ nm}$ is the empirical constant. The theoretical bond lengths in C11_b crystal are represented as:

$$D_{\text{Me-Si}}(n_A) = R_{\text{Me}}(l) + R_{\text{Si}}(l) - \beta \lg n_A \quad (7a)$$

$$D_{\text{Si-Si}}(n_B) = 2R_{\text{Si}}(l) - \beta \lg n_B \quad (7b)$$

$$D_{\text{Me-Si}}(n_C) = R_{\text{Me}}(l) + R_{\text{Si}}(l) - \beta \lg n_C \quad (7c)$$

$$D_{\text{Si-Si}}(n_D) = 2R_{\text{Si}}(l) - \beta \lg n_D \quad (7d)$$

$$D_{\text{Si-Si}}(n_E) = 2R_{\text{Si}}(l) - \beta \lg n_E \quad (7e)$$

$$D_{\text{Me-Me}}(n_F) = 2R_{\text{Me}}(l) - \beta \lg n_F \quad (7f)$$

Eq. (7a) subtracts Eqs. (7b)–(7f), respectively, and we can get:

$$\lg r_B = \lg \frac{n_B}{n_A} = \frac{D_{\text{Me-Si}}(n_A) - D_{\text{Si-Si}}(n_B) + R_{\text{Si}}(l) - R_{\text{Mo}}(l)}{\beta} \quad (8a)$$

$$\lg r_C = \lg \frac{n_C}{n_A} = \frac{D_{\text{Me-Si}}(n_A) - D_{\text{Me-Si}}(n_C)}{\beta} \quad (8b)$$

$$\lg r_D = \lg \frac{n_D}{n_A} = \frac{D_{\text{Me-Si}}(n_A) - D_{\text{Si-Si}}(n_D) + R_{\text{Si}}(l) - R_{\text{Mo}}(l)}{\beta} \quad (8c)$$

$$\lg r_E = \lg \frac{n_E}{n_A} = \frac{D_{\text{Me-Si}}(n_A) - D_{\text{Si-Si}}(n_E) + R_{\text{Si}}(l) - R_{\text{Mo}}(l)}{\beta} \quad (8d)$$

$$\lg r_F = \lg \frac{n_F}{n_A} = \frac{D_{\text{Me-Si}}(n_A) - D_{\text{Me-Me}}(n_F) - R_{\text{Si}}(l) + R_{\text{Mo}}(l)}{\beta} \quad (8e)$$

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