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First-principles investigation of new structure, mechanical and electronic properties of Mo-based silicides

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ABSTRACT

The adjustment of strength and ductility of high-temperature ceramics is still a big challenge. Although Mo-based silicides are promising high-temperature materials, the influence of Mo concentration on the mechanical and electronic properties of Mo-based silicides is unclear. In addition, it is necessary to explore the novel Mo-based silicides. In this paper, we present results of novel phases, mechanical and electronic properties of the stable Mo-based silicides within various stoichiometries. Two new Mo-based silicides: MoSi (*Cmcm* and *Pnma*) and Mo_2Si (*I4/mcm*) are predicted. The calculated results show that the volume deformation resistance of Mo-based silicides increases with increasing Mo concentration. $MoSi_2$ shows the strongest elastic stiffness and shear deformation resistance due to the strong Mo-Si bonds. The calculated intrinsic hardness of $MoSi_2$ (37.7 GPa) is much larger than that of other Mo-based silicides. In particular, $MoSi_2$ and MoSi show brittle behavior. However, other silicides exhibit ductility. We further find that high concentration of Mo can improve the electronic properties of Mo-based silicides because of the formation of Mo-Mo metallic bond. Finally, our works indicate that the adjustment of the Mo stoichiometric ratio to improve the mechanical and electronic properties of Mo-based silicides.

1. Introduction

With the development of the advanced automobile, aerospace and gas-turbine industries, transition metal silicides are increasingly important high-temperature materials because of the excellent mechanical properties, low cost, better thermodynamically stable and high melting-point etc [1–6]. However, the improvement of mechanical properties is still a great challenge for the applications. Although transition metal silicides have been widely investigated over the last years, the adjustment of strength and ductility is difficult to meet the requirement of the industrial applications [7–10]. To solve the key problem, it is necessary to reveal the nature of mechanical properties of transition metal silicides and explore the novel transition metal silicides.

Among those silicides, molybdenum silicides (Mo-Si) have attracted considerable attention in recent years [11–14]. According to the Mo-Si binary phase diagram, there are three different phases: $MoSi_2$ with tetragonal structure [15], Mo_5Si_3 with tetragonal structure [16] and Mo_3Si with cubic structure [17], respectively. The operated temperature of hexagonal $MoSi_2$ is up to 2173 K [18]. In addition, $MoSi_2$ shows better oxidation resistance in the temperature range of 873–1473 K [19]. However, the application of hexagonal $MoSi_2$ is hindered by the worse ductility. Although the ductility of cubic Mo_3Si is better than that of $MoSi_2$, the mechanical properties of Mo_3Si are lower than that of $MoSi_2$. The structural configuration of tetragonal Mo_5Si_3 (I4/mcm) is similar to Nb_5Si_3 [20]. Unfortunately, the mechanical properties of Mo_5Si_3 are unclear. Naturally, the mechanical and physical properties of transition metal silicides sensitively depend on the structure and composition. Therefore, structural configuration plays an important role in mechanical properties. Although the microstructure of Mo_5Si_3 and $MoSi_2$ has been studied over the last years [21–23], the correlation between structure and mechanical properties of Mo-based silicides is unclear.

In the present paper, we use the first-principles method to investigate the effect of Mo concentration on the structure, mechanical and electronic properties of Mo-based silicides. Based on the stoichiometric ratio and structural characteristics, we predict two novel Mo-based silicides: Mo_2Si with Ta_2Si-type structure and MoSi with orthorhombic structure. We find that the structural stability and elastic modulus of Mo-based silicides strongly rely on the Mo concentration. Mo-based silicides not only show high strength but also exhibit better ductility (except for $MoSi_2$). Therefore, we can adjust the stoichiometric ratio of Mo-based silicides to design suitable Mo-based high-temperature materials.

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2. Model and methods

As we know, the structural stability of crystal structure depends not only on the stoichiometric ratio and interaction between atoms, but also on the elemental feature of the main group or neighbor elements. To search for the novel Mo-based silicides, we examine the known phases and design possible unknown phases. According to the Mo-Si binary phase diagram, there are three different Mo-Si silicides: $MoSi_2$ with WSi_2-type structure (space group: *I4/mmm*, No. 139) [15], Mo_5Si_3 with Nb_5Si_3-type structure (space group: *I4/mcm*, No. 140) [16] and Mo_3Si with Nb_3Si-type structure (space group: *Pm-3n*, No. 223) [17], respectively. To explore the possible novel structure, we design many similar structures: $MoSi_2$ with $NbSi_2$-type structure (space group: *P6222*, No. 180), MoSi with YSi-type structure (space group: *Cmcm*, No. 63), MoSi with HfSi-type structure (space group: *Pnma*, No. 62), MoSi with RuSi-type structure (space group: *Pm-3 m*, No. 221), MoSi with NaCl-type structure (space group: *Fm-3m*, No. 225), Mo_3Si with Fe_3Al-type structure (space group: *Fm-3m*, No. 225) and Mo_3Si with Au_3Cu-type structure (space group: *Pm-3m*, No. 221), respectively. We examine the structural stability of these structures based on the thermodynamic model and phonon dispersion, respectively. The stable Mo-based silicides with various stoichiometric ratios are shown in Fig. 1.

First-principle approach is a strong tool to predict the crystal structure, mechanical, physical and chemical properties of a solid at atomic or electronic level. In this paper, we applied the first-principles method within CASTEP code [24] to calculate the total energy, elastic modulus, intrinsic hardness, band structure and electronic structure of Mo-based silicides with various concentrations. We used the LDA within CA-PZ functional [25] to treat the electronic interaction between Mo atom and the Si atom. The charge interaction between electron and ion was treated by the Ultrasoft pseudopotentials. The cut off energy of all systems was 350 eV. The *k*-points of $16\times16\times20$, $12\times12\times7$, $12\times12\times12$, $7\times13\times9$, $16\times16\times16$, $14\times14\times14$, $12\times12\times7$, $12\times12\times11$, $10\times10\times10$, $14\times14\times14$ and $12\times12\times12$ were selected for $MoSi_2$ with WSi_2-type structure, $MoSi_2$ with $NbSi_2$-type structure, MoSi with YSi-type structure, MoSi with HfSi-type structure, MoSi with RuSi-type structure, MoSi with NaCl-type structure, Mo_5Si_3 with Nb_5Si_3-type structure, Mo_2Si with Ta_2Si-type structure, Mo_3Si with Nb_3Si-type structure, Mo_3Si with Fe_3Al-type structure and Mo_3Si with Au_3Cu-type structure, respectively. The elastic strain and elastic modulus of a solid are related to the stress *vs* strain [26]. Therefore, the elastic modulus of Mo-based silicides was calculated by the stress *vs* strain method. The phonon dispersion of Mo-based silicides was calculated by the PHONON code [27].

3. Results and discussions

It is obvious that the structural stability of a material is estimated by the thermodynamically and dynamically, respectively. The thermodynamically stable of a material is calculated by the formation enthalpy (ΔH). Therefore, the equation of formation enthalpy of Mo-based silicides is given by:

$$\Delta H = \frac{E(\mathrm{Mo}_x Si_y) - xE(Mo) + yE(Si)}{x+y} \quad (1)$$

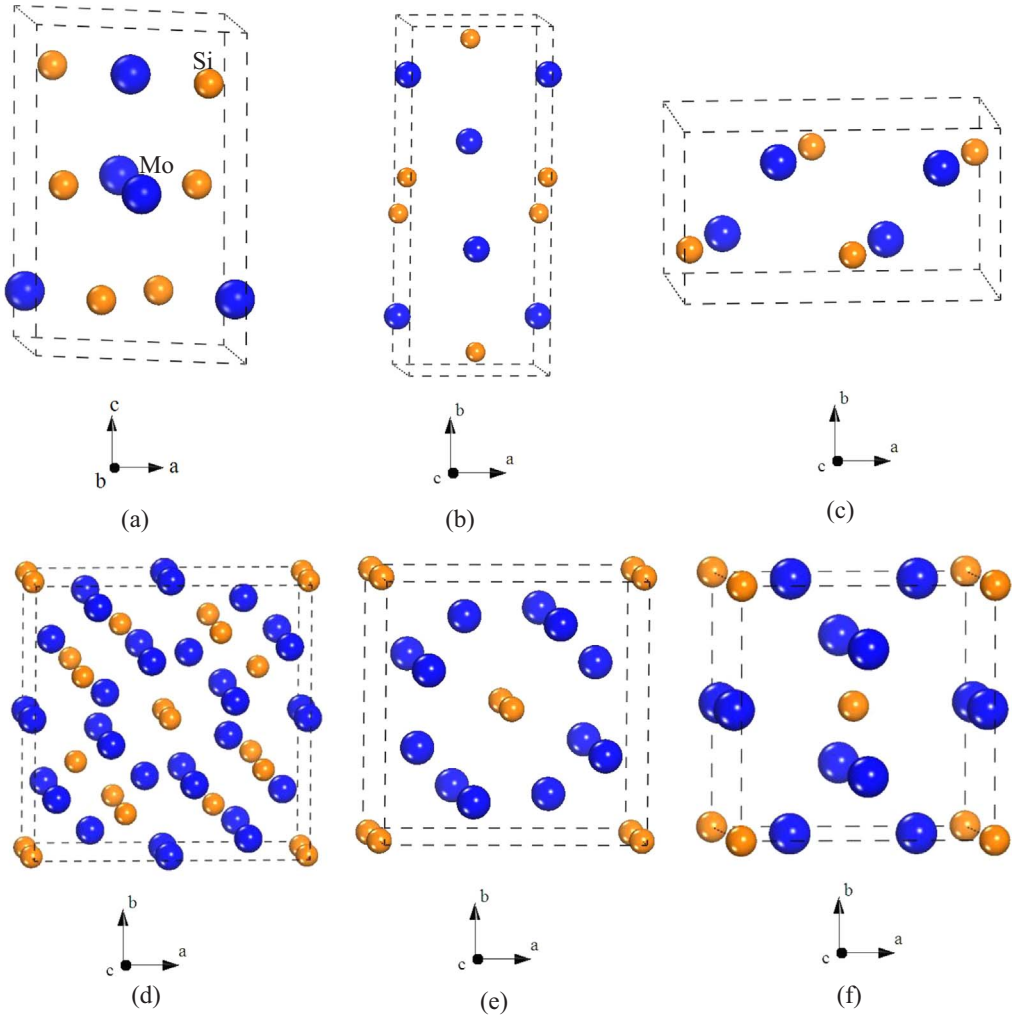

Fig. 1. Structural model of Mo-based silicides. (a) $MoSi_2$ with WSi_2-type structure, (b) MoSi with YSi-type structure, (c) MoSi with HfSi-type structure, (d) Mo_5Si_3 with Nb_5Si_3-type structure, (e) Mo_2Si with Ta_2Si-type structure and (f) Mo_3Si with Nb_3Si-type structure, respectively.

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