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Prediction of the mechanical properties of $MoSi_2$ doped with Cr, Nb and W from first-principles calculations

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ABSTRACT

The influence of Cr-, Nb- and W-doping on the mechanical properties of $C11_b$ $MoSi_2$ has been investigated using first-principles calculations. Firstly, the formation enthalpies of both $C11_b$- and C40-structured $MoSi_2$ with various doping concentrations are calculated and compared, revealing that the $C11_b$ structure can retain good structural stability at low doping concentrations of Cr, Nb or W up to ~9.2 at.%. Based on the calculated elastic constants, the elastic moduli, hardness and several thermodynamic properties of doped $MoSi_2$ have been further predicted. Cr-doping decreases the elastic moduli drastically and W-doping decreases the Debye temperature, while doping with Nb increases the B/G ratio and Poisson ratio significantly, leading to good ductility and strong metallic bonding. As revealed in the three-dimensional contours of the elastic moduli, Cr- and W-doping does not obviously affect the anisotropy of the Young's and shear moduli, but Nb-doping shows a remarkable influence. Finally, in order to clarify the doping effects, the electronic properties of doped $MoSi_2$ are further discussed, based on the analysis of the charge density and density of states.

1. Introduction

$C11_b$ $MoSi_2$ is a promising material for use in heating components and thermal barrier coatings due to its high melting point, pertinent electrical resistance and good high temperature oxidation resistance [1–4]. However, low room temperature toughness and limited elevated temperature strength have hindered its structural applications. Doping with certain alloy elements can be an effective solution to overcome these deficiencies and achieve improved mechanical properties for $MoSi_2$. In past decades, Al-doping has been considered as a method to improve the room temperature fracture toughness and oxidation resistance of $MoSi_2$. As Al is adjacent to Si in the periodic table of elements, the chemical properties of Al are similar to Si to a certain extent, so it is expected that Al will substitute Si in the lattice of $C11_b$ $MoSi_2$ [5]. However, the benefits from Al-doping are still limited to the improvement of mechanical properties, which is not enough to satisfy the complex needs of practical applications.

As an alternative approach, transition elements that would preferentially substitute the Mo sites in $C11_b$ $MoSi_2$ can be considered. Some transition elements that are neighbours to Mo in the periodic table have been focused on extensively, such as Cr, Nb and W. Among them, Cr and W are both in the same group as Mo, and Nb is adjacent to Mo in the periodic table. These elements have very similar chemical and physical properties to Mo, such as an appropriate atomic radius, a high affinity to Si and a wide solubility range in $MoSi_2$ [5]. Another neighbouring element, Tc, however, is ruled out due to its intense radioactivity. Inui [6] suggested that doping with W can improve the yield strength, but decreases the deformability of $MoSi_2$ for temperatures below 1073 K, while doping with Cr or Nb reduces the yield strength, but Nb can effectively enhance the room temperature toughness. It is also suggested that co-doping with Nb and Al can improve the room temperature deformability and oxidation resistance at intermediate temperatures ($T = 750–950$ K) [7]. Xu [8] suggested that Cr can improve the yield strength at elevated temperatures ($T \geq 1573$ K), but seemingly has no influence on the fracture toughness. Zhu [9,10] proposed that Nb-doping or co-doping with Al effectively improves the bending strength and can result in outstanding crack-healing properties under various atmospheres. Recently, it was reported that composing with transition metal disilicides whose

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properties are similar to $MoSi_2$ can also be helpful to enhance the limited mechanical properties of $MoSi_2$ [11]. In particular, Cr can segregate to form a lamellar interface, stabilising the $C11_b$/C40 two-phase microstructure and improving the creep strength and fracture toughness [11,12].

A number of theoretical studies [13–20] have been carried out to understand the influence of substituting elements on the mechanical properties of $MoSi_2$. Liu [21] and Peng [22] employed a phenomenological approach to study the mechanical properties of $MoSi_2$ doped with Nb and W. Hu [23] studied the effects of Al-, Mg- and Ge-doping on the mechanical properties of $MoSi_2$ using first-principles calculations, suggesting that Al or Mg improve the ductility, whereas Ge reduces it. However, knowledge of the doping effects of transition elements on the elastic properties of $C11_b$ $MoSi_2$ is still far from sufficient. In this work, we employ first-principles calculations to investigate the structures and mechanical properties of $C11_b$ $MoSi_2$ doped with various concentrations of Cr, Nb and W. These transition metals always preferentially substitute on the Mo sublattice of $MoSi_2$.

2. Computational methods

All calculations were performed using PAW pseudopotentials with the Perdew-Burke-Ernzerhof (PBE) functionals [24], as implemented in the VASP code [25,26]. The electronic configurations were chosen as Mo $4p^6 4d^5 5s^1$, Si $3s^2 3p^2$, Cr $3d^5 4s^1$, Nb $4s^2 4p^6 5s^1 4d^4$ and W $5p^6 6s^2 5d^4$. The cut-off energy of 400 eV was found to be sufficient in our previous work [27] and thus was employed throughout this work. Intermetallic $C11_b$-type $MoSi_2$ crystallises with a tetragonal structure with the space group *I4/mmm*. The Wyckoff positions of Mo and Si are 2*a* (0, 0, 0) and 4*e* (0, 0, 0.3353), respectively. Supercells of $2 \times 2 \times 2$, $2 \times 2 \times 1$ and $1 \times 1 \times 2$ were constructed for $C11_b$ $MoSi_2$ to analyse the doping effects at different alloying concentrations of 2.08, 4.17 and 8.33 at.%, respectively. A $16 \times 16 \times 6$ k-point mesh was found to be efficient for the conventional cell of $C11_b$ $MoSi_2$, and based on which, appropriate k-point meshes of $8 \times 8 \times 3$, $8 \times 8 \times 6$ and $16 \times 16 \times 3$ were generated for sampling the $2 \times 2 \times 2$, $2 \times 2 \times 1$ and $1 \times 1 \times 2$ supercells, respectively. The C40 phase has a hexagonal structure with the space group $P6_222$. The $2 \times 2 \times 1$, $1 \times 1 \times 2$ and $1 \times 1 \times 1$ supercells of C40 $MoSi_2$ were also constructed for alloying concentrations of 2.78, 5.55 and 11.11 at.%, respectively. Accordingly, appropriate k-point meshes of $8 \times 8 \times 10$, $8 \times 8 \times 5$ and $16 \times 16 \times 10$ were used. During structural relaxation calculations, both the shapes and volumes of the supercells were allowed to fully relax. The Hellman-Feymann force on each atom was converged to within 0.02 eV/Å.

3. Results and discussion

3.1. Structural stabilities of doped $MoSi_2$

Structural stability is an important quantity for evaluating an alloy system with element substitution or doping [28,29]. For pure $C11_b$ $MoSi_2$, the phase transformation of $C11_b$ to C40 occurs only at high temperatures (above 2173 K). However, when doped with a certain amount of alloying elements, for example, ~10 at.% Al, $C11_b$ $MoSi_2$ may experience a phase transformation into the C40 structure [30]. In this work, the formation enthalpies of both $C11_b$- and C40-structured $MoSi_2$ with various doping concentrations are calculated and compared in order to assess the phase stability of doped $MoSi_2$.

The calculated formation enthalpies of doped C40 $MoSi_2$ are compared with those of doped $C11_b$ $MoSi_2$ in Fig. 1. The formation enthalpy of pure $C11_b$ $MoSi_2$ is −1.47 eV (−141.55 kJ/mol), which is in good agreement with experiment (−135.80 kJ/mol [31] and −131.96 kJ/mol [32]). The formation enthalpy of the pure C40 structure is −1.38 eV (−133.33 kJ/mol), in good agreement with other calculations (−1.32 eV [23]). The $C11_b$ phase has a lower formation enthalpy than C40, suggesting that without any doping, $C11_b$ is the more stable phase of $MoSi_2$.

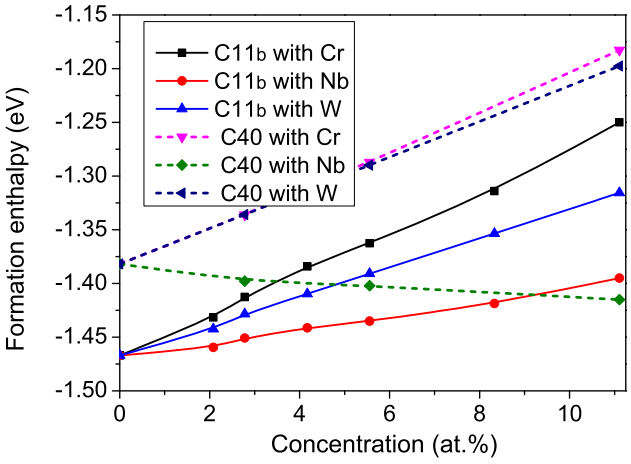

Fig. 1. Calculated formation enthalpies of $C11_b$ and C40 structures for $MoSi_2$ doped with Cr, Nb and W.

From Fig. 1, it can be clearly seen that the formation enthalpy of doped $C11_b$ $MoSi_2$ always increases with increasing doping concentration. The formation enthalpies of doped C40 $MoSi_2$ with Cr or W also increase with increasing doping concentration, and the values are always higher than their $C11_b$ counterparts. However, uniquely, the formation enthalpy of Nb-doped C40 $MoSi_2$ decreases consistently with doping concentration. When the Nb concentration is beyond a critical value of ~9.2 at.%, the C40 phase becomes the more stable phase of $MoSi_2$. In other words, only Nb can stabilise the C40 phase, while all the other dopants decrease the structural stability of $MoSi_2$, no matter which phase it is. A high concentration of Nb may trigger the phase transformation of $MoSi_2$ from $C11_b$ to C40, which has been observed in some previous experiments [7,33]. It can be also concluded that $C11_b$ $MoSi_2$ doped with a low concentration of Cr, Nb or W remains stable. We thus focus on the doping effects of Cr, Nb or W at different concentrations (~2.08, 4.17 and 8.33 at.%) on $C11_b$ $MoSi_2$ in the following calculations.

3.2. Mechanical properties of doped $MoSi_2$

To calculate the elastic constants of undoped and doped $MoSi_2$, both the volumes and shapes of the supercells were allowed to fully relax. The substitution with foreign atoms may also affect the original symmetry of the lattice, which can induce some uncertainty to our calculated results. To assess this uncertainty, one must evaluate the influence of breaking the original lattice symmetry on the total energies of the supercells. For one atom substitution of Cr, Nb or W in the 48-atom $2 \times 2 \times 2$ supercell, the symmetry-unbreaking total energies were calculated as −369.14, −370.32 and −372.77 eV, nearly the same as the symmetry-breaking values of −369.18, −370.33 and −372.78 eV, respectively. All these discrepancies are minimal and are less than 1 meV/atom, within the numerical error range. We further calculated the elastic constants (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}) of the $2 \times 2 \times 1$ supercell with one Cr atom (~4.17 at.%). The symmetry-unbreaking elastic constants were 375.85, 102.91, 81.32, 464.57, 186.47 and 175.10 GPa, respectively, favourably matching the symmetry-breaking values of 375.50,