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Ab-initio calculations of mechanical and thermodynamic properties of TM (transition metal: 3d and 4d)-doped Pt_3Al

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ABSTRACT

The cubic Pt_3Al has received considerable attention for high temperature applications. However, it is a great challenge to improve the balance between the mechanical properties and thermal stability. By means of *ab-initio* calculations, here, we systematically investigate the influence of transition metals on the mechanical and thermodynamic properties of Pt_3Al. Owing to the *d*- orbit effect, we select 18 transition metals: nine 3 d-transition metals and nine 4 d-trantion metals, respectively. The results show that those dopant elements prefer to occupy the Al site in comparison to the Pt site because of the valence electronic density. We further find that Nb-doping is more thermodynamically stable than that of other transition metals. Importantly, those transition metals can effectively enhance the bulk modulus of Pt_3Al. In particular, Nb-doping shows high bulk modulus in comparison to other transition metals. In addition, we find that the calculated Debye temperature of the Co-doping, Fe-doping, Ni-doping, Rh-doping and Ru-doping is larger than that of the parent Pt_3Al. Therefore, we predict that Nb is an effective element to improve the balance between the mechanical and thermodynamic properties of the parent Pt_3Al.

1. Introduction

The development of advanced high temperature material has received growing interest due to the increasing demands for the next generation aerospace gas turbine, rocket engines and blades etc [1–10]. In addition to the high strength, for high temperature materials, the thermal stability plays an important role in high temperature environment. Therefore, it is a big challenge to adjust the balance between the thermal stability and high temperature strength [11,12].

Platinum group metals (PGMs) are attractive candidates among those high temperature structural materials because of their excellent thermal stability, high strength, high melting point, good corrosion and oxidation resistances etc [13–20]. Pt-Al compounds have been widely investigated over the last years [21–25]. For example, Alam et al. have been studied the tensile behavior of Pt-Al bond coat [26]. They have found that the brittle to ductile transition temperature (BDTT) of this coating increases with increasing strain rate. Stahl et al. have investigated the oxidation behavior of Pt-Al coating based on the magnetron sputtering [27]. They have found that the oxidation resistance of Pt-Al coating strongly depends on the formation of Al_2O_3 particle. The microstructure, high temperature strength and oxidation resistance of Pt-based alloys have been studied by Wenderoth et al. [28]. They have found that those dopant elements (Mo, Re and W) improve the high temperature strength of Pt-Al compounds when the temperature is up to 1273 K. It is obvious that Pt-Al compounds can be regarded as the promising candidates for high temperature applications.

Among Pt-Al compounds, Pt_3Al has received great attention because of its cubic structure (*Pm*-3m) [29–32]. The thermodynamic properties of Pt-Al binary compounds have been studied by the CALPHAD model and first-principles approach [33]. The calculated formation enthalpy of Pt_3Al with cubic structure is −6.1451 eV/atom, which is smaller than that of other Pt-Al compounds. Recent work has showed that γ-Pt_3Al phase in Pt-based superalloy exhibits the configuration of super-dislocations [34]. The experimental antiphase boundary energy of Pt_3Al is about 344–456 mJ/m^2. The first-principles calculations have showed that the calculated antiphase boundary energy of Pt_3Al is 205 mJ/m^2 for [111] boundary and 414 mJ/m^2 for [010] boundary, respectively. In particular, this single crystal Pt_3Al exhibits better plastic deformation [35]. Feng et al. have investigated the structural, mechanical and thermodynamic properties of Pt-Al compounds [36]. The calculated bulk modulus, shear modulus and Young's modulus of Pt_3Al is 262.5 GPa, 94.3 GPa and 273.2 GPa, respectively. Unfortunately, the

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industrial applications of Pt_3Al are limited by the low strength and high cost. In addition, the thermal stability also plays a crucial role in high temperature environment. Therefore, it is significant to improve the thermodynamic properties of Pt_3Al. To solve those key problems, it is obvious that doping is an effective method to improve the strength and reduce the cost of Pt-Al compounds. However, the influence of dopant elements on the mechanical and thermodynamic properties of Pt_3Al is unknown.

In the present work, we apply *ab-initio* calculations to study the mechanical and thermodynamic properties of Pt_3Al with doping of transition metals. Owing to the *d*- orbit effect, we select 18 transition metals (TM): nine 3 d-TMs and nine 4 d-TMs, respectively. To estimate the dopant effect, we design two possible dopant models: Pt site and Al site, respectively. The stability of dopant elements is measured by the impurity formation energy. We find that those dopant elements prefer to occupy the Al site in comparison to the Pt site. Importantly, Nb-doping not only improves the bulk modulus but also enhances the Debye temperature of the parent Pt_3Al. As mentioned above, the main purpose of this work will help to guide and improve the correlation between mechanical and the thermodynamic properties of Pt-Al based high temperature materials.

2. Model and method

2.1. Model

Pt_3Al belongs to a cubic structure with the space group of *Pm*-3m (No. 221). The experimental lattice parameter is $a = 3.876$ Å [37]. In this structure, Al and Pt occupy the Wyckoff 1*a* (0, 0, 0) and 3*c* (0, 0.50, 0.50) sites, respectively. To investigate the dopant effect, we first consider the unit cell and then design $1 \times 2 \times 1$ supercell model with dopant elements of transition metals. As a result, we find that there is a structural transition from the cubic structure to a tetragonal structure both unit-cell and supercell model. Therefore, we build the $1 \times 2 \times 1$ supercell model in this paper. The dopant concentration of transition metals in Pt_3Al is 12.5 at%. Therefore, the structural model of TM-doped Pt_3Al is showed in Fig. 1. Here, we consider two possible dopant models: TM doped Pt site ($TM_{\text{-Pt site}}$) and TM doped Al site ($TM_{\text{-Al site}}$), respectively.

2.2. Method

In this paper, the total energy, elastic properties and electronic structure of TM-doped Pt_3Al were calculated by using the *ab-initio* calculations with density function theory (DFT), as implemented in the CASTEP code [38,39]. The interactions between electrons and the ions were described by the ultrasoft pseudopotentials [40]. The exchange correlation functional of TM-doped Pt_3Al was adopted by the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof functional (PBE) [41]. After convergence test, the cut off energy of all systems was 350 eV. The Brillouin zone of TM-doped Pt_3Al and the parent Pt_3Al was sampled with $12 \times 12 \times 6$ mesh grids. The Broyden-Fletcher-Golddarb-Shanno (BFGS) scheme was introduced. The electronic energy tolerance of the SCF was treated by the 1×10^{-6} eV/atom. In particular, all atoms, lattice parameters and atomic coordinates of all systems were fully relaxed during the process of structural optimization [42].

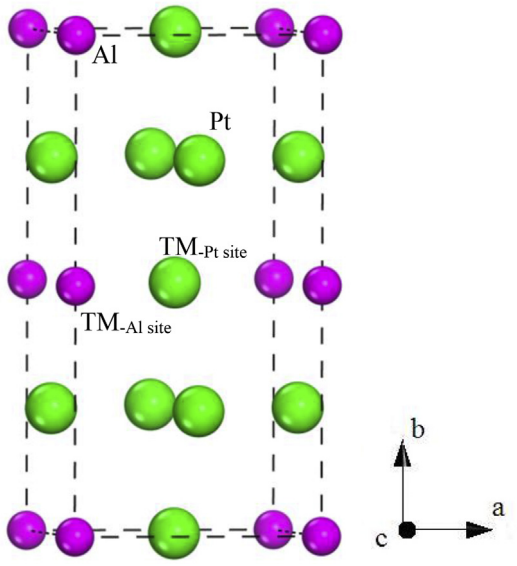

Fig. 1. Structural model of TM-doped Pt_3Al with $1 \times 2 \times 1$ supercell.

2.3. Theory

Naturally, the stability of TM-doped Pt_3Al is related to the chemical potential between TM atom and the Pt_3Al compound, which is defined as the impurity formation energy (E_f). To explore the influence of transition metals on the mechanical and thermodynamic properties of Pt_3Al, we firstly examine the stability of those transition metals in Pt_3Al. Here, the equation of impurity formation energy is given by:

$$E_f = E_{\mathrm{PtAl3}}^{M \to TM} - E_{PtAl3} + \mu_M - \mu_{TM} \quad (1)$$

where $E_{\mathrm{PtAl3}}^{M \to TM}$ and E_{PtAl3} are the calculated total energy of TM-doped $PtAl_3$ and the parent $PtAl_3$. μ_M (M = Pt and Al) and μ_{TM} are the total energy of the isolated Pt atom, the isolated Al atom and the isolated TM atom, respectively.

To the best of our knowledge, the mechanical properties of high temperature materials are well measured by the elastic modulus and shear strength, respectively. Generally speaking, the elastic modulus of high temperature material is estimated by the bulk modulus (*B*), shear modulus (*G*) and Young's modulus (*E*), respectively [43,44]. In fact, the elastic modulus of TM-doped Pt_3Al is further calculated by the elastic constants (C_{ij}). In this paper, the elastic constants of TM-doped Pt_3Al are calculated by the stress *vs* strain method [45,46]. To study the influence of transition metals on the mechanical properties of Pt_3Al, we should be examined the mechanically stable of TM-doped Pt_3Al firstly. For cubic structure, it has three elastic constants: C_{11}, C_{12} and C_{44}. Therefore, the mechanically stable of a cubic structure satisfies the following equations [47]:

$$C_{11} > 0,\ C_{44} > 0,\ C_{11}\text{-}C_{12} > 0,\ C_{11} + 2C_{12} > 0 \quad (2)$$

It is worth noticing that the transition metal-doping results in structural transition from the cubic structure to a tetragonal structure. Therefore, we must estimate the mechanically stable of the tetragonal structure. For tetragonal structure, it has six important elastic constants: C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}. The mechanically stable of a tetragonal structure is given by:

$$C_{11} > 0,\ C_{33} > 0,\ C_{44} > 0,\ C_{66} > 0$$

$$C_{11} - C_{12} > 0,\ C_{11} + C_{33} - 2C_{13} > 0, 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0 \quad (3)$$

In this paper, the bulk modulus and shear modulus of TM-doped Pt_3Al are calculated by the Voigt-Reuss-Hill (VRH) approximation method [48,49]. Therefore, the Young's modulus of TM-doped Pt_3Al is given by:

$$E = \frac{9BG}{3B + G} \quad (4)$$

On the other hand, the shear strength plays an important role in high temperature material. Therefore, the shear strength of TM-doped Pt_3Al is given by Ref. [50]:

$$T \approx G/2\pi \quad (5)$$