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The effect of metal transition dopant on electronic and mechanical properties of titanium nitride: First principle method

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ABSTRACT

This paper theoretically describes the structural, mechanical and electronic properties and the phase stability of titanium nitride doped with metal transition elements denoted as Ti_7TMN_8 (TM = V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re and Os). The hardness and erosion resistance (based on H^3/E^2 ratio) of TiN and Ti_7TMN_8 were investigated. Among doped compounds, Ti_7VN_8 and Ti_7MnN_8 possessed the highest hardness (H = 30.7 GPa) which is still 2.1 GPa lower than pure TiN (H = 32.8 GPa) whereas Ti_7OsN_8 owned the lowest hardness equal to 20.2 GPa. In order to further understand the mechanical properties of Ti_7TMN_8, the electronic properties, which are widely used for describing the mechanical properties, were thoroughly investigated. Although the bond population plays an essential role in hardness, it is seen that the value of the population is not the only factor to estimate or compare the hardness. Finally, it was shown that the doped atom has no substantial effect on nitrogen charge whereas titanium charge is quite dependent on the doped atom.

1. Introduction

Fabrication of materials with superior mechanical properties is continuously of much interest for many researchers. It originally stems from both the potential industrial and technological application of such material and the human being's thirst for developing the harder and harder material. A typical application of hard compounds is applying them as a wear-resistance coating for cutting tools and compressor vanes and blades [1–12]. TiN-based coatings have already been approved to have proper erosion and wear resistance. Many experimental studies have been so far carried out to enhance the mechanical properties of TiN-based coatings by optimization of the deposition parameters [13–15]. Alloying the compounds with other elements is another way to further enhancement of properties [16–19].

On the other hand, Ab initio calculations are such fascinating tool employed to design new materials with better properties [20,21]. Along with theoretical approach, physical vapor deposition (PVD) and chemical vapor deposition (CVD) are two powerful methods to deposit many stoichiometric, non-stoichiometric, equilibrium and non-equilibrium compounds designed by first principle method. Many first principle studies of metal transition nitrides in the literature are approved by experimental results. Ou et al. [22] investigated the elastic and structural properties of $Ti_{1-x}TM_xN$ (TM = Y, Zr, Nb, Hf, and Ta) and showed that calculated results are in good agreement with available experimental data. Besides, by employing Pugh's index of ductility, they concluded that adding Ta and Nb (unlike Y) into TiN increases the ductility. Brik et al. [23] studied the electronic and elastic properties of XN (X = Sc, Ti, V, Cr, Zr, Nb), demonstrating that there is a great anisotropy of Young modulus (especially for CrN) despite the fact that their structure is cubic.

However, the literature lacks the systematic study of structural, mechanical and electronic properties of metal transition-doped TiN, which it motivates us to model the doped TiN. In order to judge the erosion and wear resistance of doped TiN, it is essential to possess $\frac{H^3}{E^2}$ ratio, which the higher the $\frac{H^3}{E^2}$ ratio, the more durable and resistant the coatings [16,17,24]. Although, the elastic constants can be easily calculated via first principle method [22,25–28], the hardness, with intrinsic and extrinsic nature, is more difficult to obtain. However, the hardness is usually estimated by some semi-empirical equations that is reported to have good accordance with experimental measurements [29].

The aim of this paper is to investigate the electronic and mechanical properties of metal transition-doped TiN to introduce such new materials with the potential industrial application. Because this research is more concerned about mechanical properties, the hardness and $\frac{H^3}{E^2}$ ratio were computed based on semi-empirical equations and elastic constants. Moreover, the electronic

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properties were employed to determine the nature character of bonding so as to explain the variation of mechanical properties.

2. Computational method

First principle calculations were carried out based on the pseudo-potential plane-wave within the density functional theory (DFT), as implemented in the Cambridge Serial Total Energy Package (CASTEP) [30]. The exchange-correlation energy was evaluated by generalized gradient approximation of Perdew Wang (GGA-PW91) [31]. The energy calculations in the first Brillouin zone were performed using a $6 \times 6 \times 3$ k-point grid of the Monkhorst-Pack scheme and the cut-off energy set to 350 eV where the calculation has appropriately converged. The geometry of unit cell was optimized while the convergence thresholds for energy change, maximum force, maximum displacement and maximum stress were 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å and 0.02 GPa, respectively. In addition, the minimization process was performed within Brodyden-Fletcher-Doldfarb-Shanno (BFGS) algorithm [32].

The 16-atom supercell (Fig. 1) with tetragonal structure was built to study the mechanical and electronic properties of doped TiN (Ti_7TMN_8) where TM = V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re, and Os). Since chromium and manganese have magnetic behavior, the calculation for Ti_7CrN_8 and Ti_7MnN_8 were carried out with polarized spin. The dopants in this research were selected from 3 different rows (rows 4–6) of the periodic table to examine the influence of valence electron configuration, atomic radius, and electronegativity on the structure. The elastic constants were calculated by Hook's law and then based on Voigt-Reuss-Hill (VRH) approximation [28,33]; bulk modulus (B) and shear modulus (G) were obtained. The other mechanical properties were also calculated with respect to elastic constants. Finally, the partial density of states (PDOS) and Mulliken population were used to compare and analyze the mechanical strength of compounds.

3. Results and discussion

3.1. Crystal structure of Ti_7TMN_8

The crystal structure of TiN is cubic B1, which normally keeps the same structure when doped with other elements. In this part, the effect of dopant element on the structural properties of Ti_7TMN_8 is studied (Table 1). In the studied supercell (Fig. 1), there are 16 atoms, which 8, 7 and 1 atoms are assigned to N, Ti, and the doped one, respectively. Owing to symmetric constraints, the crystal structure changes to tetragonal P4/MMC with two independent lattice constants; a and c. Because the solid solution compound is cubic, the lattice constant of that was estimated from the volume of the tetragonal modeled structure. The volume of the unit cell (or lattice constant) is proportionally influenced by the atomic radius of the dopant elements (Fig. 2) except for Mn and Os. Although the radius of manganese is smaller than vanadium and chromium, the lattice constant of Ti_7MnN_8 is larger than Ti_7CrN_8 and Ti_7VN_8. This effect can be originated from the polarized spins of manganese in the structure. In order to investigate the effect of spins polarization in Ti_7MnN_8, the calculation was also carried out with unpolarized spins in which the lattice parameter, as normally expected, became smaller than Ti_7CrN_8 and Ti_7VN_8.

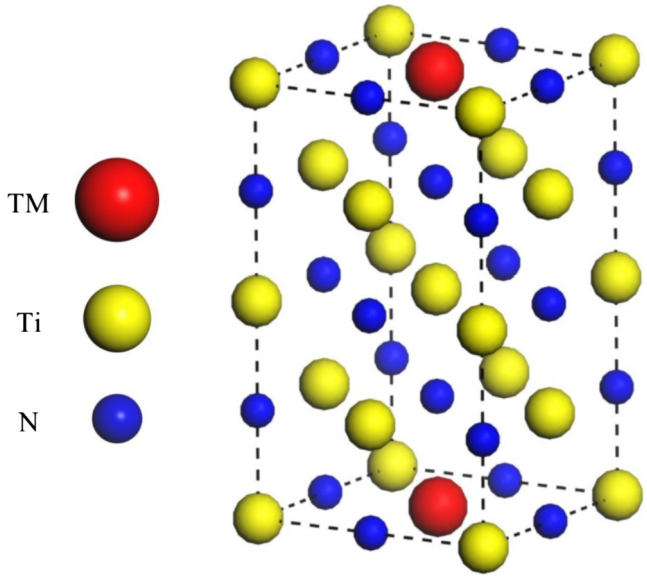

Fig. 1. The supercell of Ti_7TMN_8 where TM = V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re and Os.

The lattice constant becomes very important when multilayer coating design is considered. As seen in Fig. 2, the lattice constants of Ta and Zr-doped titanium nitrides are very close to each other, leading to coherent interface between Ti_7ZrN_8 and Ti_7TaN_8. Although the nature of chemical bonds within the interface influences the hardness of multilayer coatings, the interface coherency is also of significance in enhancing the mechanical strength [34,35]. The bonding character of the interface is not studied here and only properties of the monolithic layer (one component) are examined.

3.2. Thermodynamic stability

Chemical stability of solid solution Ti_7TMN_8 can be studied by cohesive energy and enthalpy of formation [36] with the following equations [37]:

$$E_{coh} = \frac{E_{tot} - \sum N_i E^i_{atom}}{\sum N_i} \quad (1)$$

$$\Delta H_f = \frac{E_{tot} - \sum N_i E^i_{solid}}{\sum N_i} \quad (2)$$

here E_{coh} is the cohesive energy, ΔH_f is the enthalpy of formation, E_{tot} is the total energy of the unit cell, N_i is the number of i atom in the unit cell, E^i_{atom} is the energies of the isolated i atom and E^i_{solid} shows the total energy per atom of pure element in its ground state.

Because the cohesive energy is associated with the binding force among the atoms of a solid, it can be used to evaluate the chemical stability of a structure. The negative value of cohesive energy indicates that the phase is thermodynamically stable [38]. The cohesive energy and enthalpy of formation are listed in Table 2. As it is seen, the cohesive energy and formation enthalpy are negative and very close to those of TiN, showing all compounds are thermodynamically stable. The cohesive energy of V, Cr and Mn (the fourth row of the periodic table) doped compounds increases by moving toward the right of the periodic table. However, in the fourth and fifth row, the cohesive energy reaches a minimum and then increases. Ti_7NbN_8 is the most stable phase between doped compounds. It shows that the binding energy between the atoms of $Ti_7Nb_1N_8$ is greater than TiN and other Ti_7TMN_8.

3.3. Mechanical properties of Ti_7TMN_8

Estimation of mechanical properties of such doped-TiN, which is strongly related to their elastic constants, is of huge prominence because it helps to select the more appropriate materials (coatings) for industrial applications. Owing to the modeled supercell (Fig. 1),