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Phase stability, elastic, electronic, thermal and optical properties of $Ti_3Al_{1-x}Si_xC_2$ $(0 \le x \le 1)$: First principle study

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ABSTRACT

The structural parameters with stability upon Si incorporation and elastic, electronic, thermodynamic and optical properties of $Ti_3Al_{1-x}Si_xC_2$ $(0 \le x \le 1)$ are investigated systematically by the plane wave pseudopotential method based on the density functional theory (DFT). The increase of some elastic parameters with increasing Si-content renders the alloys to possess higher compressive and tensile strength. The Vickers hardness value obtained with the help of Mulliken population analysis increases as x is increased from 0 to 1. The solid solutions considered are all metallic with valence and conduction bands, which have a mainly Ti 3d character, crossing the Fermi level. The temperature and pressure dependences of bulk modulus, normalized volume, specific heats, thermal expansion coefficient, and Debye temperature are all obtained through the quasi-harmonic Debye model with phononic effects for $T=0-1000$ K and $P=0-50$ GPa. The obtained results are compared with other results available. Further an analysis of optical functions for two polarization vectors reveals that the reflectivity is high in the visible–ultraviolet region up to ~10.5 eV region showing promise as a good coating material.

1. Introduction

The ternary layered ceramic compound Ti_3AlC_2, a member of the well-known MAX phases, exhibits unique properties combining the merits of metals and ceramics. The compound is characterized by its high melting point, low density, excellent oxidation resistance, high strength at high temperatures, significant ductility, good electrical conductivity, having self-lubrication and good machinability [1–19]. These remarkable properties render Ti_3AlC_2 a technologically interesting material and hold promise in high temperature applications. As a result Ti_3AlC_2 and its isostructural counterpart Ti_3SiC_2 have been subjected to both experimental and theoretical investigations by many researchers [20–43] to highlight their characteristics. Some of these results are highlighted in two recent review works by Wang and Zhou [19] on layered machinable and electrically conductive Ti_2AlC and Ti_3AlC_2, and by Barsoum and Radovic [20] on the current understanding of the elastic and mechanical properties of bulk MAX phases.

The two MAX phases Ti_3AlC_2 and Ti_3SiC_2 are isostructural and hence these can form solid solutions that may possess properties of both these phases. Xu et al. [25] studied electronic and bonding properties of the solid solution $Ti_3Si_{1-x}Al_xC_2$ by first-principle calculations and the results demonstrated that as Al-content is increased, all the bonds weakened to a certain extent that lead to an unstable structure both energetically and geometrically. Wang and Zhou [32] carried out a first-principle study of $Ti_3Si_{0.75}Al_{0.25}C_2$ solid solution to investigate the changes in the equilibrium properties and electronic structure of Ti_3SiC_2. Previous theoretical and experimental works show that it is possible to increase the hardness and strength of Ti_3AlC_2 by alloying. Zhou et al. [18] synthesized a series of $Ti_3Al_{1-x}Si_xC_2$ $(x \le 0.25)$ solid solutions using an in situ hot pressing/solid–liquid reaction method. They observed a significant strengthening of Ti_3AlC_2 by incorporation of Si to form $Ti_3Al_{1-x}Si_xC_2$ solid solutions. However they limited their study on the strengthening aspects only for $x \le 0.25$.

We know that many macroscopic properties of MAX phases are closely related to the electronic structure of the compound. Investigation of the electronic structure and bonding properties is thus essential for understanding the various properties of Ti_3AlC_2. Zhou et al. [21] calculated the electronic structure of Ti_3AlC_2 using the ab initio total-energy pseudopotential method based on the density functional theory, and analyzed its chemical bonding properties. It is necessary to see the effects of the influence of incorporation of different amounts of Si on the physico-chemical and electronic properties for the entire range. It is well-known that the thermodynamic properties are the basis of solid state science and industrial applications since they reveal the specific behavior of materials under high pressure and high temperature environments. Thus knowledge of the heat capacity of a substance not only provides essential insight into its vibrational

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properties but also is necessary for many applications. Although some thermodynamic properties of Ti_3AlC_2 have been studied theoretically [31] and experimentally [30], a thorough theoretical investigation for the entire stoichiometric range will be useful to provide a deep understanding of their thermodynamic properties.

We note that despite comprehensive knowledge on the properties of the stoichiometric compound, less information is available for the solid solution $Ti_3Al_{1-x}Si_xC_2$. In the present work, the focus will be on areas where little or no work has been carried out, particularly for the solid solution in the entire doping range. The phase stability, change of structural parameters (e.g., lattice parameters), mechanical and electronic properties with Si content in $Ti_3Al_{1-x}Si_xC_2$ $(0 \le x \le 1)$ will be investigated. The Vickers hardness will be estimated for $x=0$, 1 and discussed. We will also carry out a comparative study on the thermodynamic properties of $Ti_3Al_{1-x}Si_xC_2$ $(0 \le x \le 1)$ using the quasi-harmonic approximation within the density functional theory (DFT). Further the parameters of optical properties (dielectric function, absorption spectrum, conductivity, energy-loss spectrum and reflectivity) will be calculated and discussed.

2. Computational methods

The zero-temperature energy calculations have been performed using the CASTEP code [44] which utilizes the plane-wave pseudopotential based on the density functional theory (DFT). The electronic exchange-correlation energy is treated under the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [45]. The interactions between ion and electron are represented by ultrasoft Vanderbilt-type pseudopotentials for Ti, Al, Si and C atoms [46]. The crystal models of solid solution $Ti_3Al_{1-x}Si_xC_2$ ($x=0$, 0.25, 0.5, 0.75, 1) have been built using the supercell method based on the structure of Ti_3AlC_2. The 24-atom supercells are built as two times the unit cell of Ti_3AlC_2 for the case $x=0.5$ and four times for $x=0.25$, 0.75 (48-atom supercell). The calculations use a plane-wave cutoff energy 500 eV for all cases. For the sampling of the Brillouin zone, $10 \times 10 \times 2$ k-point grids generated according to the Monkhorst–Pack scheme [47] are utilized. These parameters are found to be sufficient to lead to convergence of total energy and geometrical configuration. Geometry optimization is achieved using convergence thresholds of 5×10^{-6} eV/atom for the total energy, 0.01 eV/Å for the maximum force, 0.02 GPa for the maximum stress and 5×10^{-4} Å for maximum displacement. Integrations in the reciprocal space were performed by using the tetrahedron method with a k-mesh of 54 k-points in the irreducible wedge of the Brillouin zone (BZ). The total energy is converged to within 0.1 mRy/unit cell during the self-consistency cycle.

To investigate the thermodynamic properties, we employed the quasi-harmonic Debye model, the detailed description of which can be found in the literatures [48,49]. Through this model, one could calculate the thermodynamic parameters, including the bulk modulus, thermal expansion coefficient, specific heats, Debye temperature, etc. at any temperatures and pressures using the DFT calculated E–V data at $T=0$ K, $P=0$ GPa and the third-order Birch–Murnaghan EOS [50].

3. Results and discussion

3.1. Structural parameters and stability upon Si incorporation

Ti_3AlC_2 has two polymorphs in α- and β-form, but the former has a lower total energy (-0.22 eV/f.u.) than the latter-type and is energetically more favorable. We will thus consider the α-polymorph

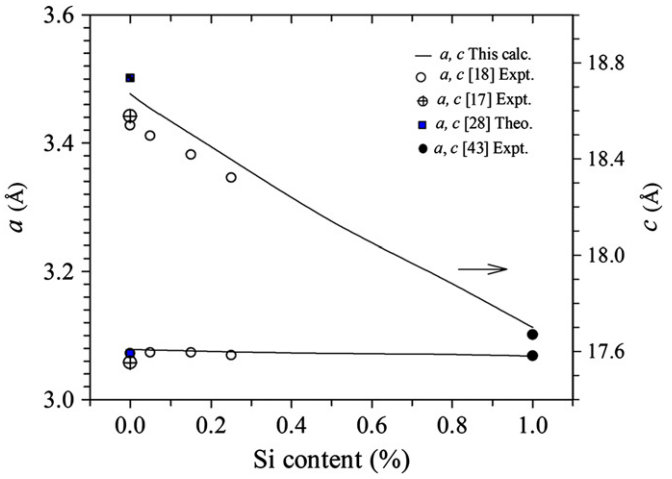

Fig. 1. Lattice parameters a and c as a function of Si-content in $Ti_3Al_{1-x}Si_xC_2$.

Ti_3AlC_2 which crystallizes in a hexagonal structure with a space group of $P6_3/mmc$, with Ti(1) atoms in position 2a, Ti(2) atoms in 4f ($z=0.129$), Al atoms in 2b, and C atoms in 4f ($z=0.570$). There are two formula units per unit cell. The phase stability of the energetically favorable α-Ti_3SiC_2 has also been studied [22] and the estimate shows that $\alpha \rightarrow \beta$ transition will take place at $P \sim 380$–400 GPa. To investigate the ground-state properties of $Ti_3Al_{1-x}Si_xC_2$ we obtained the structural configurations that reached the energy and force convergence. The calculated fully relaxed equilibrium values of the structural parameters of $Ti_3Al_{1-x}Si_xC_2$ $(0 \le x \le 1)$ are presented in Fig. 1 together with other available data [17,18,28,43]. It is evident from the figure that the lattice parameters change as Si is incorporated in Ti_3AlC_2. The dramatic decrease of lattice parameter c as a function of Si content is borne out satisfactorily by the available measured values for $x \le 0.25$ and $x=1$ [17,18,43]. On the other hand theoretical a, in excellent agreement with the available measured values [17,18,43], remained almost unchanged for the entire ranges of x studied. The volume of the solid solution decreases linearly with increasing x. From the average nearest-neighbor bond lengths of Ti–C, Ti–Si, and Ti–Al, it is seen that the change in bond length of Ti–C and Ti–Si ($x=1$) bonds is small whereas the bond length of Ti–Al ($x=0$) decreases with increasing Si content, in total by ~ 0.2 Å. However, the hexagonal structure of the material is retained.

Previous study showed that the solid solution can be formed in the Ti_3AlC_2–Ti_3SiC_2 system, with experimental observations of strong indications of Si substituting for Al for $x \le 0.25$ [18]. It may be useful to discuss here the phase equilibria of the solid solutions $Ti_3Al_{1-x}Si_xC_2$. The strength of the forces that bind atoms together in the solid state is measured by its cohesive energy which is relevant in studying the phase equilibrium. The cohesive energy of $Ti_3Al_{1-x}Si_xC_2$ per atom is defined as the total energy of the constituent atoms at infinite separation minus the total energy of the compound (per f.u.) at equilibrium configuration [32,51]. The cohesive energy of Ti_3AlC_2 is found to be close but less than that of Ti_3SiC_2 i.e. $E_{coh}^{x=0} < E_{coh}^{x=1}$. The calculated cohesive energies of $Ti_3Al_{1-x}Si_xC_2$ for $x=0.25$, 0.5, and 0.75 are all between those of the two end members. This indicates that the solid solutions $Ti_3Al_{1-x}Si_xC_2$ can be formed from the viewpoint of energy favorability.

3.2. Elastic properties

It is now well established that first principle studies based on the density-functional theory can be used to obtain reliable elastic properties of inorganic compounds. The elastic constant tensor of $Ti_3Al_{1-x}Si_xC_2$ ($x=0$–1.0) is reported in Table 1 along