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Elastic and thermodynamic properties of Mo_2C polymorphs from first principles calculations

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Abstract

Transition metal carbides have unique physical and chemical properties and been widely used in engineering parts that need to work under high temperatures and pressures. o-Mo_2C, h-Mo_2C and t-Mo_2C are three critical molybdenum carbides polymorphs while remaining are largely unknown in their mechanical anisotropy, hardness and thermal properties. In this work, we investigated systematically the mechanical and thermodynamic properties of these three candidate carbides using first principles calculations based on density functional theory. Our results showed that the bonds in these compounds were mainly of metallic and covalent type. The Gibbs free energy analysis showed thermodynamically stable structures for all the three carbides. Their shear moduli were estimated to range from 149.1 to 153.4 GPa and hardnesses were expected to be less than 20 GPa. Young's moduli were analyzed to have more anisotropic features than bulk modulus for all the three compounds. In addition, heat capacities were calculated to predominate by phonon excitations at high temperature but electron excitations at low temperatures near 0 K. Published by Elsevier Ltd and Techna Group S.r.l.

Keywords: Ceramics; Molybdenum carbides; Thermal properties; Elastic modulus; Ab-initio calculations

1. Introduction

Transition metal carbides have attracted attention due to their remarkable physical and chemical properties such as good chemical stabilities, extreme hardness, high melting temperatures, outstanding thermal conductivities, and excellent corrosion and wear resistances. These unique properties enable them wide usages in cutting tools and wear resistance parts that need to work under high temperatures and pressures. Molybdenum semicarbide (Mo_2C), a member from group VI, is one of the most important transition metal carbides developed up to date. A unique superconducting transition temperature of 9.7 K was reported for Mo_2C in previous studies [1]. In addition, Mo_2C was reported to have huge application potential as diffusion barriers and electrical connections in microelectronics [2,3]. At temperatures above 1960°C, Mo_2C adopts a disordered, hexagonal L′3-type structure (space group P63/mmc, Z=1, h-Mo_2C), in which the molybdenum atoms form a hexagonal close packed array and the carbon atoms occupy one half of the octahedral interstitial sites in a random way [4,5]. Upon cooling, Mo_2C was observed to transition into ordered superstructures. At the temperature region between 1960 and 1350 °C, a ε-Fe_2N-type structure (space group P-3m1, Z=3, t-Mo_2C) was observed for Mo_2C metal. With further decreasing of temperature below 1350 °C, Mo_2C exhibited a ξ-Fe_2N-type structure (space group Pbcn, Z=4, o-Mo_2C).

In addition to morphological studies, temperature and pressure dependences of ceramic molybdenum semicarbide (o-Mo_2C) elastic properties were investigated using ultrasonic techniques as reported by Cankurtaran et al. [5]. Moreover, Young's moduli of o-Mo_2C along temperature range from 103 to 1373 K have been studied. Liu and co-workers [6] have probed the structural and electronic properties of o-Mo_2C and h-Mo_2C at

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zero-pressure. They pointed out o-Mo_2C is more easily formed than h-Mo_2C, and the bonds of o-Mo_2C and h-Mo_2C have both covalent and metallic properties. Kato et al. [7] have illustrated the surface electronic structure of α-Mo_2C (0001) by angle-resolved photoemission spectroscopy utilizing synchrotron radiation. Results indicated that surface state is formed on Mo_2C (0001) surface at 3.3 eV in normal-emission spectra. Further, the state includes substantial contribution of the 4d orbitals of Mo atoms in the second layer. Pistonesi et al. [8] have performed the adsorption and dissociation of methanol on β-Mo_2C (0 0 1) model surface using density functional theory calculations. They reported a Mo-Mo weakening upon adsorption and a strong H-Mo interaction after dissociation. Lin et al. [9] have discussed the effect of Mo_2C addition on the microstructure and fracture behavior of (W, Ti)C-based cemented carbides. They concluded that the grain size of cemented carbides decreased with the increase of Mo_2C content. The transverse rupture strength and fracture toughness also decreased when Mo_2C content more than 15 wt%. Chen et al. [10] synthesized the nano-structured Mo_2C thin films using metal-organic chemical vapor deposition. Moreover, anisotropic elastic and thermal properties of the double perovskite slab-rock salt layer $Ln_2SrAl_2O_7$ natural superlattice structure were studied in theoretical calculations [11].

Unfortunately, most of these previous studies focused their view at morphological, thermal and electrical aspect of Mo_2C transition metal carbides. When it comes to the mechanical anisotropy, hardness and thermal properties of o-Mo_2C, h-Mo_2C and t-Mo_2C transition metal carbides, however, there is never enough data and solid conclusion obtained. These properties of the carbides are critical for further research and application explorations. Here in this article, we applied first principles calculations in systematically investigation of mechanical and thermodynamic properties of o-Mo_2C, h-Mo_2C and t-Mo_2C. Results were analyzed in comparison with available theoretical and experimental data.

2. Methods and details

Mechanical and thermodynamic properties of o-Mo_2C, h-Mo_2C and t-Mo_2C were investigated using first principles calculations based on the density functional theory (DFT) [12], implemented as Cambridge Serial Total Energy Package (CASTEP) code [13]. The interactions between ionic cores and valence electrons were represented by ultrasoft pseudo potentials. The exchange-correlation energy was evaluated with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) approach [14]. The total energy changes during the optimization process were finally converged to 1.0×10^{-6} eV and the forces per atom were reduced to 0.02 eV/Å. The valence electron configurations in this calculation have included $4s^2 4p^6 4d^5 5s^1$ for Mo and $2s^2 2p^2$ for C, respectively. The BFGS (Broyden-Fletcher-Goldfard-Shannon) optimized method was performed to obtain the equilibrium crystal structures for carbides. The minimization process of electron energy was calculated by Pulay density mixing scheme. A special k-point sampling method was used for the integration by setting parameter as 10 × 10 × 10 for all carbides with Monkhorst-Pack scheme in the first irreducible Brillouin zone [15]. A kinetic energy cut-off value was set of 450 eV for plane wave expansions.

It is noticed that in disordered hexagonal phase h-Mo_2C unit cell, the carbon atoms randomly occupy one-half of all octahedral interstices in the molybdenum sublattice. Accordingly, supercell method was used in this study considering h-Mo_2C structure as the uniform alternation of vacancies and carbon atoms along [0 0 1] crystal direction. The crystal structures of o-Mo_2C, h-Mo_2C and t-Mo_2C are shown in Fig. 1. The elastic constants

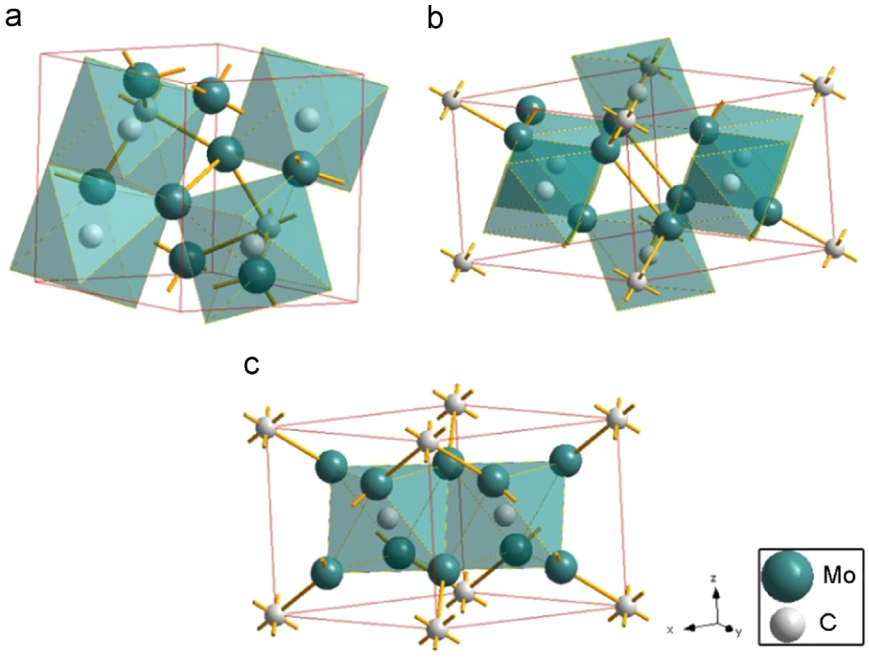

Fig. 1. The crystal structures of (a) o-Mo_2C, (b) h-Mo_2C, and (c) t-Mo_2C, respectively.