



Ab initio investigations of the phase stability in tantalum carbides

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Abstract

Using a variable-composition ab initio evolutionary algorithm, the stability of various tantalum carbide compounds at ambient pressure and at 0 K was investigated. The results revealed that TaC, Ta₆C₅ and Ta₂C are the lowest energy configurations, with Ta₄C₃ and Ta₃C₂ having slightly higher energies. The vacancy ordered Ta₆C₅ phase had three energetically degenerate structures. A competition between the vacancy ordered and stacking fault variation of the phases was seen, with the latter becoming more favorable with lower carbon content. The close formation enthalpy of each stable and metastable phase appears to “frustrate” the carbide in the co-precipitation of multiple phases for substoichiometric compositions. Density functional theory calculations also provided the elastic constants for each of the stable and metastable phases. As the carbon content increased, the elastic constant values increased. This was associated with the change in metallic to more covalent bonding of the carbide from the density of states. The collective results of this computational work provide insight into why specific tantalum carbide phases form and the consequences they have on microstructure and properties.

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1. Introduction

Tantalum carbides, along with others in the group VB transition metal carbides, exhibit a range of high to ultra-high melting temperatures, microstructures controlled by the co-precipitation of metal-rich carbide phases and varied mechanical behaviors dependent on the phase content [1–6]. Consequently, these materials have been proposed for various applications, including thermal heat protection, automotive wear-resistant liners, and other types of thermo-mechanical loading [7–9]. Though these carbides may be classified as ceramics, which are often considered to be hard and brittle materials, some tantalum carbide phases exhibit significant plasticity that exceeds 30% at elevated temperatures [3,10]. Thus, the potential exists in this system to create multiphase carbides that exhibit varied

mechanical properties, providing unique opportunities to tailor their microstructure–mechanical property relationships. For example, it has been reported that a high volume fraction of Ta₄C₃ within a tantalum carbide matrix increases the room temperature K_{IC} to ~12–14 MPa \sqrt{m} [10,11], though the associated toughening mechanisms for this increase have not been fully elucidated but are likely linked to the material’s microstructure. These high fracture toughness microstructures consist of several co-precipitated nanoscale Ta₄C₃ laths, which are believed to contribute to extrinsic toughening. The precipitation and orientation relationship of the Ta₄C₃ phase is dictated by the close packed planes and directions of the parent material [1,12,13]. If the parent phase is TaC, with four {111} close-packed plane variants, a crisscross pattern of Ta₄C₃ laths forms in an equiaxed grain structure, Fig. 1a. In contrast, precipitation of Ta₄C₃ from a parent Ta₂C phase results in parallel lath formation because of Ta₂C’s single close packed basal plane [2], Fig. 1b. These grains also

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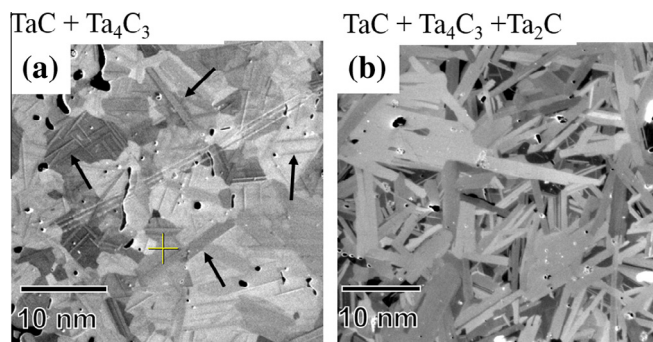


Fig. 1. (a) Micrograph of TaC_x with crisscross laths of Ta_4C_3 (indicated by arrows) for a 55Ta:45C sample. (b) Micrograph of $\text{TaC}_x + \text{Ta}_4\text{C}_3 + \text{Ta}_2\text{C}$ for a 63Ta:37C sample. The X-ray diffraction of these phases with these microstructures can be found in Ref. [1].

appear to be more acicular [2]. Unlike the group VB metal carbides, the group IVB metal carbides do not form these metal-rich phases [14], limiting the opportunities to tailor the microstructure, hence mechanical properties, through phase transformation routes. By understanding the phase equilibrium of the group VB metal carbides, insights can be gained that are crucial in tuning the microstructures and mechanical properties of these unique materials.

In this paper, we explore the stability and structure of the tantalum carbide phase diagram using electronic structure density functional theory calculations. To date, there has not been a comprehensive and inclusive computational investigation of the different phases that comprise the tantalum carbon system [15]. In contrast, there has been some limited computational investigations into the group VB niobium and vanadium carbides [16,17]. According to the phase diagram of the Ta–C system provided by Gusev et al. [18,19], there are four compounds in the tantalum-rich portion of the diagram: TaC, Ta_6C_5 , Ta_4C_3 and Ta_2C . The structure, space group and lattice parameter for these phases are given in Table 1. The monocarbide phase of TaC forms the B1 or rock salt crystal structure and, similar to other group VB metal carbides, is not a line compound. It can accommodate the loss of some carbon, creating several site-occupancy defects [20] with an accompanying change in lattice parameter [18]. For substoichiometric TaC_{1-x} at temperatures lower than ~ 1500 K, a Ta_6C_5 phase can precipitate. This phase's experimental presence is very uncommon and has been suggested to require a very low cooling rate (~ 0.15 K min^{-1}) to form [19]. Consequently, it is not even shown on the Ta–C phase diagram by Frisk [21]. Gusev et al. [14,18] proposed that this phase is derived from cubic TaC_{1-x} where the vacancies create a vacancy ordered structure that is either monoclinic or trigonal. Unlike the tantalum carbides, this Me_6C_5 phase (where Me is a metal) is more frequently observed in the niobium and vanadium carbides [18], which are also group VB metal carbides. The phase stability between the sub-stoichiometric TaC_{1-x} structure and these yet to be definitively determined Ta_6C_5 structures provides clear motivation for further computational investigation.

Unlike the Ta_6C_5 phase, the rhombohedral ζ - Ta_4C_3 phase has been experimentally observed by several groups [19,22–24]. Similar to the Ta_6C_5 phase, there has been some debate on its thermodynamic stability. In their pioneering work, Rudy et al. [12] noted that the Ta_4C_3 phase formed under compressive stresses by epitaxially growing off the TaC_{1-x} phase when the temperature was too low to phase transform directly into Ta_2C . After 400 h at 1700°C , Ta_4C_3 decomposed, suggesting to them that the Ta_4C_3 phase was metastable. Considering this phase's significant effect on tantalum carbide's mechanical behavior as noted above [11], understanding its thermodynamic stability is essential. This phase has also been shown to experimentally co-exist in the presence of TaC and Ta_2C ; yet thermodynamics dictates that only two phases should exist in binary systems, providing a yet further need to elucidate the phase equilibrium between all of these phases.

Further reduction in carbon will stabilize the Ta_2C phase where the metal atoms form a hexagonal closed-packed arrangement. This stoichiometric ratio compound exhibits an order–disorder transition with temperature. At temperatures less than ~ 1800 K, the α - Ta_2C 's carbon sublattice is ordered, occupying every other plane of octahedral interstices, while at elevated temperatures this sublattice disorders [25]. Further loss in carbon does not result in any additional carbide compounds. The metallic body centered cubic Ta phase exhibits negligible carbon solubility except at temperature near 3000 K [19].

Tantalum carbides represent a rich collection of phases where the stability and microstructure are still not completely understood. The clear links of phase content with microstructure formations and mechanical properties dictate the need for a definitive equilibrium investigation. This work aims to clarify the energetics associated within the tantalum carbide compounds to better understand their intrinsic stability.

2. Computational methodology

The stoichiometric compounds and their crystal structures were predicted by using the evolutionary algorithm implemented in the USPEX code [26,27]. This approach features global optimization with real-space representation and flexible physically motivated variation operators. For each candidate structure generated by USPEX, the density functional theory (DFT) calculations were performed at 0 K by application of the Vienna Ab initio Simulation Package (VASP) [28,29]. The compounds in the Ta–C system explored in this work contained up to 30 atoms in the unit cell. The initial generation consisted of 50 structures produced randomly. All the subsequent generations contained 40 structures; of these, 40% of the new structures were produced by heredity, 20% produced by soft mutation, another 20% produced by transmutation and the final 20% produced randomly. Thermodynamically stable structures were determined by a convex hull construction; a phase was stable if its decomposition enthalpy into any

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