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Phase, hardness, and deformation slip behavior in mixed $Hf_xTa_{1-x}C$

Chase J. Smith [a], Xiao-Xiang Yu [a], Qianying Guo [a], Christopher R. Weinberger [b, c], Gregory B. Thompson [a, *]

[a] The University of Alabama, Department of Metallurgical and Materials Engineering, 401, 7th Avenue, 285 Hardaway Hall, Tuscaloosa, AL 35487, USA
[b] Colorado State University, Department of Mechanical Engineering, 1374 Campus Delivery, Fort Collins, CO 80523-1374, USA
[c] Colorado State University, School of Advanced Materials Discovery, Fort Collins, CO 80523-1374, USA

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ABSTRACT

A series of $Hf_xTa_{1-x}C$ atomic compositions, where x = 0.0, 0.13, 0.25, 0.50, 0.75, 0.83, and 1.0, were computationally and experimentally studied in terms of their phase, hardness, and dislocation emission behavior. Using an ab initio evolutionary algorithm, the B1 rocksalt structure was found to be the 0 K ground state phase for the binary carbides whereas the ternary compounds were a mixture of metal-site ordered monoclinic, trigonal, and cubic structures. However, all experimental carbides were found to exhibit a B1 structure, with two B1 phases forming for Hf-rich ternary compositions. A modest rise in the elastic constant computationally predicted hardness was found with experimental mean values showing a similar trend from nanoindentation tests. With the presence of Ta, even in small amounts, in the Hf-rich ternary compositions, <110>{111} slip was observed which is a change from the reported <110>{110} slip for HfC. This change is explained by the promotion of an intrinsic stacking fault in the {111} planes.

1. Introduction

While more than three hundred materials possess melting points above 2000 °C, approximately fifteen of those are greater than 3000 °C and comprise a special class of materials referred to as ultrahigh temperature ceramics (UHTCs). Within the UHTCs, the transition metal carbides (TMCs) TaC and HfC are the most refractory with the highest melting points of any binary compounds that approaches 4000 °C. Besides a high melting point, these TMCs also exhibit high hardness, strength, and wear resistance [1–3]. All of these properties are a consequence of their mixed covalent-metallic-ionic chemical bonding [4,5]. The covalent bonding has been noted as being the most dominant component in contributing to the high melting point and high elastic modulus for these TMCs [1,6].

The monocarbides in the group IVB and VB TMCs nominally adopt a B1 rocksalt structure that is composed of metal atoms occupying a face centered cubic (fcc) lattice with carbon atoms filling the octahedral sites. Though HfC and TaC share similar high melting points and equivalent lattice structures, suggesting similar bonding characteristics, at low temperatures their deformation slip is different [7]. HfC has been reported to slip as <110>{110} whereas TaC slips as <110>{111}. Consequently HfC displays less plastic flow and is more brittle than TaC [8,9]. Recently De Leon et al. [10] studied this slip deviation by implementing density functional theory (DFT) calculations to compute the generalized stacking fault energy (GSFE) for {110} and {111} planes in these TMCs. In both HfC and TaC, perfect slip was energetically more favorable on {110} than the {111}. However, if one considers the dissociation of a perfect dislocation into Shockley partials, an interesting observation was discovered. The TaC was found to have an intrinsic stacking fault (ISF) on the {111} planes which was absent in HfC. This ISF provided a lower energy pathway to promote {111} slip with a Peierls-Nabarro model further confirming the capability of partial dislocation disassociations in TaC on the {111} planes. This ISF energy has been suggested to be the prime indicator of slip control in the rocksalt TMCs [11].

At elevated temperatures, Kim et al. [12] also confirmed the presence of straight screw dislocations that slipped on TaC's {111} planes; to the authors' knowledge, there has not been any experimental studies of high temperature deformation slip in HfC. Yu et al. [13,14] expanded on this ISF work suggesting that it was also likely promoting the subtle phase changes between TaC and HfC with sub-stoichiometry. In TaC_x compounds, stacking fault phases of metal-rich TMCs are present [15–20] but are absent in HfC_x.

With two different slip systems being activated depending on the transition metal type, an opportunity to tailor deformation responses within the TMCs can now be perceived through mixing

* Corresponding author.
E-mail address: Gthompson@eng.ua.edu (G.B. Thompson).

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the metal species on the rocksalt lattice. In particular, the <110>{110} slip system does not satisfy the von Mises plasticity criterion by not having the requisite five independent slip systems. By activating additional slip systems by promoting <110>{111} via alloy, the mechanical responses could be tuned. Finally, with HfC and TaC sharing the same B1 crystal structure, the ability to provide this tuned deformation through solid solution mixing provides a processing advantage without the complicating aspects of solubility limits and secondary precipitation.

To date, most of the interest in mixing Hf-Ta-C has resided in increasing the melting point. The mixing of these carbides has been suggested to create stronger covalent and ionic bonds that adjust the Fermi level location between bands which then in turn has been suggested to increase the melting temperature [21]. To that end, the highest experimentally measured compound has been reported to be $Ta_{0.80}Hf_{0.20}C$ with a melting temperature as high as 3990 °C [22], while other researchers have suggested that this composition's melting temperature falls within the melting temperature range of TaC and HfC [23]. More recently, Hong et al. [21] has proposed a model $HfC_{0.56}N_{0.38}$ ternary which may even surpass the mixed TMC's melting temperature, but there has yet been substantial experimental development for this predication. Regardless of the exact melting temperature values, the mixing of TMCs has promise for bonding modification. These changes should not only effect melting but also the mechanical behavior.

High hardness in TMCs is attributed to bonding states between metal and nonmetal orbitals of a particular band that heavily resists shear strain [24]. Subsequently TMCs have been found to possess high Peierls stresses and GSFEs [25,26]. Wu et al. [5] performed a theoretical study into the elasticity and electronic structure of transition metal carbo-nitrides and TMCs where they hypothesized that a Hf-Ta-C could possess the largest shear modulus in the materials they considered. Their calculations assumed a B1 rocksalt structure, but, as pointed out by Gusev [27] and the authors here [13], lower ground state structures could exist with metal atom ordering within the B1 lattice. Experimentally, the hardness of various mixed Hf-Ta-C have ranged between approximately 15.0 to 21.0 GPa, with the differences associated with composition and possibly processing as some fabrication methods were less prone to residual porosity [28–30]. For example, Gaballa et al. [28] reported that hot pressed $Ta_{0.80}Hf_{0.20}C$ has a micro-hardness of 21.4 GPa whereas Ghaffari et al. [29] reported micro-hardness between 15.0 and 18.2 GPa for SPS processed Hf-Ta-C. None of these current studies investigated and/or quantified the slip mechanisms that are responsible for their reported hardness. Being aware that each individual binary carbide – HfC and TaC - has a preferred slip system, which slip system dominates in mixing has yet to be determined. Through this computational and experimental study, we aim to address how mixed metal species within the B1 TMCs alter mechanical properties and the active slip systems.

2. Methods

2.1. Computational details

To determine the potential ground state phases for mixing Hf-Ta-C, an evolutionary algorithm was implemented via USPEX code to predict the $Hf_xTa_{1-x}C$ crystal structures [31,32]. DFT calculations were performed via Vienna ab initio simulation package (VASP) for each USPEX generated structure [33,34]. A convex hull construction was used to identify thermodynamically stable crystal structures [35]. Stability was determined if the lowest enthalpy of formation energy at 0 K structure did not change after 10 generations. These convergent results were established through the plane wave basis set with a 600 eV cutoff energy and $2\pi \times 0.03$ Å^{-1} k-point mesh resolution in reciprocal space. For elastic constants and density of states (DOS) calculations, denser k-point meshes with resolution of $2\pi \times 0.02$ Å^{-1} in reciprocal space were implemented. Phonon spectra calculations were obtained by Phonopy code coupled with the force constants previously calculated [36].

2.2. Fabrication

To verify and validate the computational predictions, $Hf_xTa_{1-x}C$ samples were fabricated by hot isostatic pressing (HIP) commercial HfC (H.C. Stark, <1.3 μm, 99.5%) and TaC (H.C. Stark, <1.0 μm, 99.5%) powder blends to obtain targeted compositions that ranged $x = 0.0$, 0.13, 0.25, 0.50, 0.75, 0.83, and 1.0 to match the thermodynamically stable phases predicted from Section 2.1. Single TMC and mixed TMC powders were pressed into tantalum canisters in an inert gas environment inside a glove box. The cans were outgassed under a heating plate while being evacuated and then subsequently hermetically sealed by welding the canister closed and He leak checked prior to HIP. The cans were then HIP'ed under an argon atmosphere for 1 h at the parameters listed in Table 1. Variations in parameters are from the use of two different HIP units for fabrication. The very minor differences in parameters are not believed to be sufficient enough to affect the final product based on previous processing experience of the authors. The cans were then allowed to furnace cool in the HIP to room temperature. A representative image of a HIP canister pre and post HIP is shown in Fig. 1. The extent of densification was measured by the Archimedes principle to the ideal density of the targeted composition. These results are also tabulated in Table 1.

2.3. Characterization

The starting HfC and TaC powders were imaged in a JOEL 7000 FE scanning electron microscope (SEM) to determine initial particle size. Post HIP, the samples were removed from the tantalum canisters using a diamond cutting saw. The interior carbide was then cut and mounted in cross-section and mechanically polished up to 1200 grit followed by another polish using 0.04 μm diamond suspension. A final vibratory polish was implemented to provide a mirror surface using a 0.02 μm colloidal silica suspension. The samples were then imaged in the SEM which included secondary, backscattered, and electron backscatter diffraction (EBSD) to quantify grain size, grain orientation, and phase.

X-ray diffraction (XRD) analysis was also performed for phase identification using a Bruker D8 diffractometer equipped with a Co K_α source operated at 40 keV and 35 mA. The reflections were identified using either the crystallographic data provided by the International Center for Diffraction Data and/or the computational structures generated in Section 2.1.

Hardness testing was performed using an Agilent Nano Indenter G200 equipped with a Berkovich diamond tip indenter in single cycle testing mode. Tests were not initiated until a drift rate of ≤0.05 nm/s was reached or the thermal drift time of 1 h was exceeded. Indentations were made to a depth of 500 nm with test loads ranging from 90 to 134 mN where the maximum load was held for 1 s. This was done to provide an indent impression that was on the size of a single grain which would be more comparable to the forthcoming computational predictions of hardness based on elastic constants. Microindentation hardness tests would sample multiple grains and be more susceptible to microstructure contributions to the hardness. The measured nanoindent hardness values were converted to Vickers Hardness using ISO 14577–1:2015 [37]. A mean hardness value was computed from each sample that comprised between 22 and 52 indents. Each indent was imaged in the SEM and if an indent was found to be on or near a porous