Studies on Characterizing Grain Geometries and Residual Strains of Ultra High Temperature Ceramic (UHTC) Carbides Using X-Ray Diffraction (XRD) and Raman Spectroscopy

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1. INTRODUCTION

The prospect of hypersonic aircrafts as a means of transport is reaching new heights in all realms of technological development, from production, to modelling, to testing, to integration, and so on. When it comes to the materials subrealm for achieving reusable hypersonic flight, scientists have engineered a variety of compounds that have the potential to withstand the extreme environments that flying greater than Mach 5 entails, including inclement climates, high temperatures and pressures, and harsh chemical and oxidizing environments [1].

Ultra high temperature ceramics (UHTCs) are a class of materials that are generally defined as nonoxide ceramics with melting temperatures above 3000°C, and chemical and structural stability above 2000°C [2, 3]. Most are binary compounds composed of a transition metal covalently bonded with either boron, carbon or nitrogen. This makes for a powerful combination, these materials exhibiting both metal-like and ceramic-like properties, namely high hardness, high stiffness, and high thermal conductivity as well as low thermal expansion at elevated temperatures. These material also have the ability to withstand extreme aerothermal environments, heat fluxes, chemically-aggressive environments, and mechanical loads that other structural materials tend to fail under [2, 4, 1].

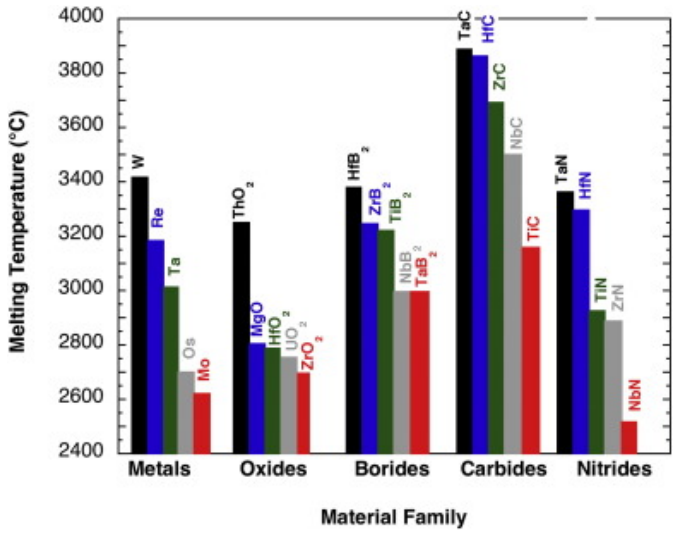

Figure 1. Melting temperatures of different materials [2].

When it comes to manufacturing critical components of hypersonic vehicles, such as propulsion systems and leading edges which undergo the brunt of these extreme environments, it is imperative to implement these refractory materials--with their formidable aerothermal and chemical responses--into the structure of these components as thermal barrier coatings (TBCs) and environmental barrier coatings (EBCs) to protect the bulk constituent metal substrate from degradation and subsequent failure [3, 5].

Tantalum carbide (TaC) and hafnium carbide (HfC) are candidate UHTCs that demonstrate a refractory top coat potential, showing much promise for surviving hypersonic, and more broadly, ultrahigh-temperature load-bearing environments. These compounds have melting temperatures reaching up to 3900°C, high hardness (18.9 GPa and 22.1 GPa, respectively), high room temperature elastic moduli (537 GPa and 461 GPa, respectively), and good resistance to chemical attack, oxidation, and thermal shock [2, 1, 6].

Table 1. Thermophysical properties of TaC and HfC [6].

	Tantalum carbide (TaC)	Hafnium carbide (HfC)
Melting point	3880 °C	3890 °C
Density	14.65 g/cm^3	12.8 g/cm^3
Crystal structure	FCC	FCC
Lattice parameters	4.44 Å	4.64 Å
Young's Modulus	486-560 GPa	423-500 GPa
Hardness	14.5-18 GPa	19 GPa
Fracture toughness	3.5-4.7 MPa.m$^{-0.5}$	2.5 MPa.m$^{-0.5}$

Manufacturing studies have demonstrated that it is difficult to fully densify carbide compounds due to their intrinsic covalent bonds and low self-diffusion coefficients [6, 1]. Pressure-aided methods, like field-assisted sintering (FAST)/spark plasma sintering (SPS), hot pressing, and hot isostatic pressing have been used to consolidate these materials into fine-grained structures, usually with the use of high temperatures or additives that may or may not be beneficial to the thermomechanical stability of the bulk carbide [1, 2, 6, 7]. Studies have demonstrated that HfC powder-turned-compacts reach near full densification (98-99%) using SPS at 2100–2200°C, a pressure of 65 MPa and a hold time of 3 minutes, though the process has shown to increase mean grain size as compared with the starting powdered grains (from 0.8 μm to 19 μm) [7]. TaC reached near full densification (97%) using SPS at 2400°C, a pressure of 35 MPa and a hold time of 5 minutes, also resulting in grain growth, though this phenomenon can be countered by using additives [7].

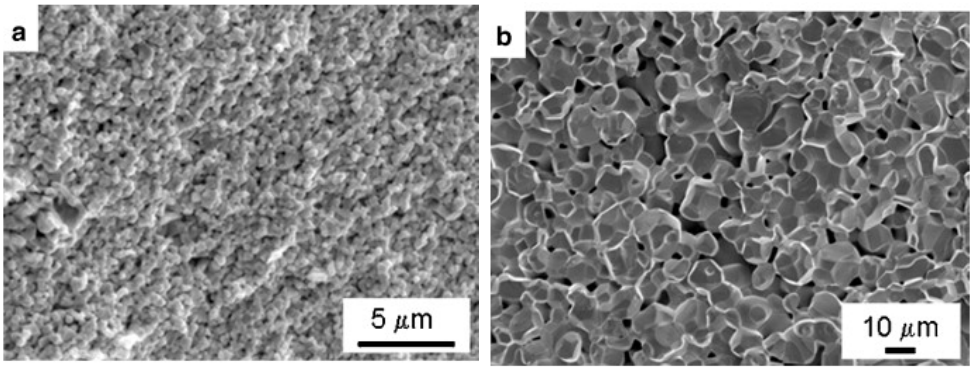

Figure 2. SEM micro images of TaC fracture surface samples prepared by SPS at a pressure of 60 MPa and (a) 1800 °C, and (b) 2200 °C [7].

The purpose of this study is to both qualify and quantify the effect of different SPS manufacturing parameters (temperature and hold time) on the carbides' relative density and grain geometry. The residual micro-strains that arise from manufacturing will also be studied in order to better understand the structural integrity of these prospective protective top coats.

Residual stresses are stresses that remain in a system, even after external forces from mechanical loadings and thermal gradients are removed [8]. They arise in every step of processing, manufacturing, and testing, on both a macroscopic and microscopic level, and give rise to residual strains. It is crucial to quantify these hidden strains within a material and qualitatively analyze whether or not they are beneficial or detrimental to the structural integrity of a material.

2. MATERIALS AND METHODS

2.1. Manufacturing

TaC and HfC powders were densified using field-assisted sintering (FAST) on varying thermomechanical and hold time cycles, as illustrated in Table 1, and machined into nine ≈5mm x 5 mm x 225μm (length x height x width) samples of the pure carbides, as well as a solid solution consisting of both carbides. The samples were manufactured and supplied by the Applied Research Laboratory at PennState University.

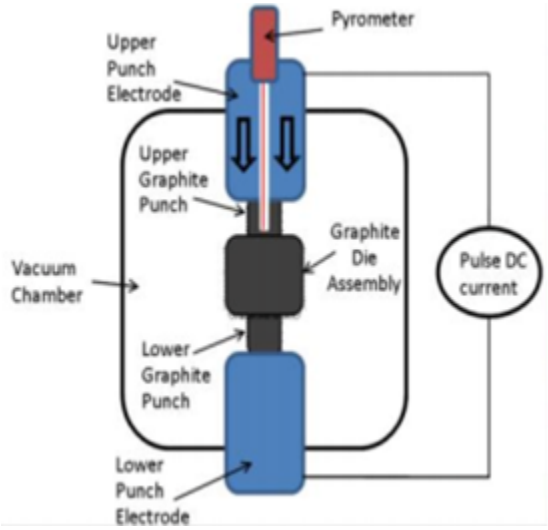

Figure 3. Schematic representation of FAST system [11]

Table 2. FAST parameters of the ten carbide samples.

Sample	Sintering temp. (°C) Cycle 1/cycle 2	Sintering pressure (MPa) Cycle 1/cycle 2	Sintering hold time (min) Cycle 1/cycle 2	Relative density(%)
TaC	2300	55	10	97.1
TaC	2300	55	20	98.8
TaC	2300	55	30	99.4
TaC	2300	55	40	99.7
TaC	2300	55	50	99.8

HfC	2050/2400	55/30	30/20	98.4
HfC	2100/2400	55/30	30/20	99.0
HfC	2150/2400	55/30	30/20	99.2
HfC	2200/2400	55/30	30/20	99.5
TaC+10%volHfC	2100/2400	55/30	30/20	95.8

2.2. Characterization

Mean grain sizes, lattice parameters, and residual strains will be examined using x-ray diffraction (XRD). XRD is a nondestructive characterization technique in which incident x-rays hit electrons in the atoms of a sample which then re-emit x-rays with the same energy. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles (2θ) from each set of lattice planes in a sample. This method provides information on structures, phases, preferred crystal orientations, average grain size, crystallinity, strain, and crystal defects [10].

For the carbide samples, 71 keV of power will be used with a sample-to-detector distance of 2.5 meters. Diffraction peaks will be fit using a Gaussian model. 2D lattice parameters will be calculated using Bragg's Law, where λ is the X-ray wavelength, d is the lattice parameter, and θ is the incident angle. This value will be compared with values found in other literature, as well as Raman measurements. Residual strains will be found by comparing the lattice parameters of the carbide powders with that of the manufactured samples. Grain size, τ, will be calculated using the Scherrer equation, where β is the width (full-width at half-maximum, FWHM) of the X-ray diffraction peak in radians, and k is assumed to have a value of 0.9 [9].

Bragg's Law $$n\lambda = 2dsin\theta$$

(1) Residual Strain $$\epsilon = \frac{\Delta d}{d} \quad (2)$$

Scherrer Equation $$\tau = \frac{k\lambda}{\beta cos\boldsymbol{\theta}} \quad (3)$$

Both grain sizes and residual strains will be validated using Raman spectroscopy on a Raman microscope. Raman spectroscopy is also a nondestructive material characterization technique where a photon of radiation interacts with chemical bonds within a material and a phonon of greater or lower energy is given off depending on the vibrational state of the molecule. The observed Raman shift of the Stokes and anti-Stokes features are a direct measure of the vibrational energies of the molecule. Raman spectroscopy provides information about chemical structure, phase and polymorphy, crystallinity, stress and strain, and molecular interactions.

Samples were placed under a Renishaw Raman microscope under 532 nm with an integration time of 1 second, resolution of 50x and an 1800 g/mm grating. Residual strain calculations are still being worked out.

3. RESULTS AND DISCUSSION

TBD

4. CONCLUSIONS

TBD

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