

Oxidation resistance of tantalum carbide-hafnium carbide solid solutions under the extreme conditions of a plasma jet



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ABSTRACT

The oxidation behaviors of tantalum carbide (TaC)- hafnium carbide (HfC) solid solutions with five different compositions, pure HfC, HfC-20 vol% TaC (T20H80), HfC- 50 vol% TaC (T50H50), HfC- 80 vol% TaC (T80H20), and pure TaC have been investigated by exposing to a plasma torch which has a temperature of approximately 2800 °C with a gas flow speed greater than 300 m/s for 60 s, 180 s, and 300 s, respectively. The solid solution samples showed significantly improved oxidation resistance compared to the pure carbide samples, and the T50H50 samples exhibited the best oxidation resistance of all samples. The thickness of the oxide scales in T50H50 was reduced more than 90% compared to the pure TaC samples, and more than 85% compared to the pure HfC samples after 300 s oxidation tests. A new Ta₂Hf₆O₁₇ phase was found to be responsible for the improved oxidation performance exhibited by solid solutions. The oxide scale constitutes of a scaffold-like structure consisting of HfO₂ and Ta₂Hf₆O₁₇ filled with Ta₂O₅ which was beneficial to the oxidation resistance by limiting the availability of oxygen.

1. Introduction

Hafnium carbide (HfC) and tantalum carbide (TaC) both are considered ultrahigh temperature ceramics (UHTCs) [1–3]. Applications of these materials include rocket nozzles and leading edges for hypersonic vehicles due to their extremely high melting points (~ 3900 °C) [4]. Even with such high melting points, the adoption of TaC and HfC have still been obstructed due to the unsatisfying oxidation resistance of these two carbides, and the oxidation mechanisms are yet to be fully understood.

Early studies have been carried out to understand the oxidation behaviors of TaC and HfC, respectively. In general, HfC is considered a superior oxidation resistance material due to a three-layer oxide structure observed in previous isothermal oxidation experiments. The oxidized structure consisted of an outer layer that is fully oxidized HfO₂, an inner layer of un-oxidized carbides, and a partially oxidized, oxy-carbide layer sandwiched in between [5]. The oxy-carbide layer can act as oxygen diffusion barrier and protect the underlying carbides. The formed HfO₂ has a high melting point around 2900 °C, and it has a very low vapor pressure (10⁻⁴ Torr at 2500 °C [7]), which makes it one of the least volatile oxides [6]. However, during the oxidation of HfC, gaseous products like CO and CO₂ leave a porous HfO₂ oxide scale, which can be detrimental to the mechanical integrity [8].

One solution to enhance the integrity of a porous exterior oxide

layer is to seal the cracks and pores with a liquid phase material, resulting in a solid scaffold and liquid phase structure. An example of this structure can be seen during the oxidation of HfB₂-SiC [9–11]. Previous results have demonstrated that HfO₂ provides a stable solid scaffold for the mechanical rigidity of the resultant oxide layers to withstand the harsh environment and borosilicate glass melts and seals the cracks in the HfO₂, leading to a fully dense oxide layer. While the mechanisms are demonstrated in this system, this specific borosilicate glass begins to evaporate around 1400 °C, limiting the peak application temperature of the HfB₂-SiC system. Mimicking this structure with higher temperature materials could lead to improved oxidation resistant UHTCs with enhanced mechanical rigidity. As a scaffold material, the enhanced mechanical properties of the UHTC carbide systems have the potential to form a stronger scaffold-liquid structure. Candidates for the liquid sealing phase should have a melt temperature below the application temperature (~ 2000 °C) to ensure liquid phase formation and flow but have a boiling point much higher than the application temperature to prevent the evaporation (seen in Hf₂B-SiC). In this study, HfC can provide a stable HfO₂ solid scaffold, similar to HfB₂, while the and the main oxidation product of TaC, Ta₂O₅ that has a relatively low melting point of 1872 °C, [12] can be the perfect candidate to provide liquid phase during the oxidation of HfC while maintaining stability.

Recently, few studies on the synthesis of TaC-HfC solid solutions

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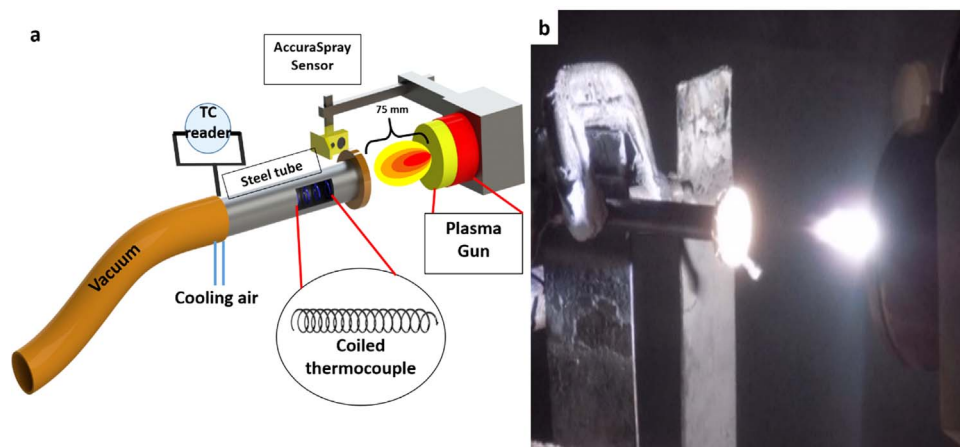


Fig. 1. The oxidation testing setup. (a) A detailed schematic of oxidation testing, (b) snapshot of high-temperature oxidation testing.

have emerged [13–15]. In a recent study, we were able to synthesize compacts of TaC-HfC solid solutions using spark plasma sintering (SPS) [13]. Five compositions were chosen, pure TaC (PT), TaC-20 vol % HfC (T80H20), TaC-50 vol% HfC (T50H50), TaC-80 vol% HfC (T20H80), and pure HfC (PH) to explore a range of compositions. The formation of a solid solution was achieved in each composition. The literature on the oxidation behavior of TaC-HfC solid solutions is very scarce [16,17]. Coutright et al. synthesized HfC and HfC-25 wt% TaC solid solution by hot pressing. The oxidation behaviors of HfC and HfC-TaC solid solutions were performed by thermogravimetric method from 1200 to 1530 °C and defocused CO₂ laser for 1800–2200 °C. The results showed the microstructure of the oxides of HfC and HfC-TaC were similar, but with severe cracking in HfC-TaC samples. Ghaffari et al. studied Ta_{0.8}HfC_{0.2} solid solution with 24 vol% MoSi₂ as sintering aid consolidated using pressureless sintering. The oxidation behavior was evaluated by oxidized flame at 3000 °C. The results suggested the formation of double protective oxide layers during the oxidation. None of these two studies provided a clear verdict on the effect of solid solution formation on oxidation behavior of TaC-HfC based UHTCs. Moreover, these studies [16,17] were limited to only a couple of compositions. Our study is the first systematic study to evaluate oxidation behavior of large spectrum of TaC-HfC solid solution compositions. Moreover, oxidation is carried out in a high speed plasma jet with temperatures exceeding 2000 °C making our study unique.

The simulation of the application conditions of UHTCs, a temperature above 2000 °C with airflow at sonic speed, is difficult in a laboratory environment. What is more challenging is how to hold the samples under the extreme conditions without introducing stress concentration. Normally the specimens are physically held in place with fixtures, and these fixtures become stress concentrations that lead to premature cracking during the oxidation testing due to the thermal expansion of the specimens. These cracks provide the pathways for oxygen to penetrate and cloud the true oxidation behaviors of the studying subjects. A new fixture has been developed in the current work and described in Section 2.2. The specimens are held by vacuum so that the stress concentration will be eliminated. The oxidation behavior of TaC-HfC solid solutions samples is evaluated by exposing to a high-temperature plasma torch that used in plasma spray. The plasma torch can provide up to 5000 K temperature with airflow with sonic speed, which is an improved tool to mimic the extreme conditions in the real world applications. The samples are subjected to the plasma exposure for 60 s, 180 s, and 300 s. Detailed characterization of the oxidized samples have been carried out, and the oxidation mechanisms have been proposed in the current work.

2. Experimental procedure

2.1. Materials

Oxidation testing was conducted on each composition of the spark plasma sintered pellets. Each pellet was twenty (20) mm in diameter and approximately 4–5 mm in thickness. The details of the sintering conditions can be found in our previous work [13]. The pellets were ground using 15 μm diamond paper to remove the graphite foils from the sintering as well as provide relative flat surfaces.

2.2. Oxidation testing

The oxidation tests were conducted by a plasma flow generated from a Praxair SG-100 DC plasma gun. The input power was 30 kW and the exposure time was 60 s, 180 s, and 300 s for all the samples. A 75 mm standoff distance was measured from the plasma gun and sample front surface. A significant standoff distance ensured the ample air (oxygen) exposure. Primary argon gas flowed at 56 slpm, and secondary helium gas flowed at 60 slpm to form a plasma. The front side temperature and gas flow velocity were evaluated by an accurate spray in-flight particle diagnostic sensor (Tecnar Automation Ltd., QC, Canada). The sensor head was mounted 75 mm from the plasma gun, and AIO-101 (Praxair Surface Technologies, Inc. Indianapolis, IN, USA.) powder was used as spraying powder for the temperature and velocity measurement. The temperature at the surface was measured above 2700 °C with a velocity of 330 m/s. With these simulated testing conditions, samples would experience both oxidation and ablation similar to the ones that space vehicles would face upon reentry. The setup of the newly designed fixture for oxidation tests is schematically described in Fig. 1a. It consists of a steel tube which is connected to the vacuum. SPS sample is held by the vacuum instead of clamps and eliminates stress concentration produced by mechanical forces. Moreover, entire disk shaped sample is exposed to plasma (see Fig. 1b) and not masked by the clamps. A thermocouple was inserted into the steel tube to measure the samples' back side temperature. It was swirled into a coil shape to make sure proper contact throughout oxidation testing.

2.3. Post-oxidation characterization

The phases after the oxidation tests were identified by X-ray diffraction (XRD) (Siemens D-5000) using Cu Kα radiation at a scan rate of 2 °/min. The operating voltage and current were set at 40 kV and 35 mA, respectively. The relative oxide contents were computed using the area under the peaks. The oxidized pellets were then cut from

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