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Ultrahigh Temperature Materials for Hypersonic Systems Readiness

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Monterey, California: Naval Postgraduate School

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NAVAL POSTGRADUATE SCHOOL

MONTEREY, CALIFORNIA

ULTRAHIGH TEMPERATURE MATERIALS FOR HYPERSONIC SYSTEMS

READINESS

by

Prof. Claudia C. Luhrs and Dr. Troy Ansell

July 2022

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14. ABSTRACT The goal of the study was to support the Hypersonics RDT&E efforts at the Strategic Systems Programs (SSP) by developing and validating materials that have potential to withstand the high temperatures encountered by systems used in hypersonic flight. Multilayered architectures that combine the high melting temperatures and oxidation resistance of ultrahigh temperature ceramics (UHTC) and graphitic composites were proposed along with the technical assessment of their performance.			
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I. INTRODUCTION

A. BACKGROUND FOR HYPERSONIC FLIGHT MATERIAL REQUIREMENTS

To achieve the strategic and operational goals required for the survivability of aircraft traveling at hypersonic speeds, it is imperative to develop new materials that will serve as thermal protection, capable of withstanding extreme heat, oxidative and ablative conditions. To understand such demanding material needs, it is convenient to revise the phenomena observed by an object moving at high velocities: When an object travels through the air, the molecules of the gas near the object are disturbed and move around it. At low speeds, (less than 250 mph) the density of the air remains the same. However, as the speed increases, some of the energy of the object goes into compressing the air and locally changing its density. The so called ‘compressibility effect’ can drastically change the resulting force of the moving object, affecting the lift and drag and generating shock waves as the speed increases [1]. When hypersonic speeds are reached (3000 mph and above), the friction between air and the high-speed object generate extremely high temperature regions (>2000 °C), high mechanical stresses and decreases the materials damage tolerance. Those severe conditions call for the use of a new type of highly engineered materials that can withstand not only high temperature, but also environments that tend to oxidize the components of the system passing through at those speeds.

B. MATERIAL SELECTION STATE OF THE ART

Ceramic tiles have traditionally been used for aircraft thermal protection; however, their brittleness, low damage resistance and high cost have limited their application [2]. Metallic thermal protection structures, super alloys, and intermetallic compounds [3-6] have also been considered, however, their melting temperatures and susceptibility to oxidation are drawbacks. Therefore, the search for ultrahigh temperature resistant materials is still a fertile area of research.

Some of the maximum service temperatures of diverse materials are illustrated in the graphs presented in figure 1. It is worth noting that only those denominated ultrahigh temperature ceramics (UHTC) are considered contenders for the extreme environments described above. UHTC tend to be non-oxide ceramics, such as carbides, borides, nitrides with melting or decomposition temperatures above 3000 °C. The list of the 10 materials with record high melting temperatures include substances such as tantalum hafnium carbide Ta_4HfC_5 (3983°C), graphite (3652 °C), diamond (3550 °C), tungsten (BCC 3380 °C), titanium boride TiB_2 (3225 °C), zirconium diboride ZrB_2 (3245 °C), rhenium (3186 °C), titanium carbide TiC (3100 °C), osmium (3045 °C) and silicon carbide SiC (2820 °C) [7]. Of those, our team got particularly interested on ZrB_2 and SiC due not only to their high melting temperatures, but the existence of reports of their good oxidation resistance [8]. Graphite and graphitic fibers are also of interest and will be employed in this study given their high thermal resistance, in combination with ZrB_2 or SiC .

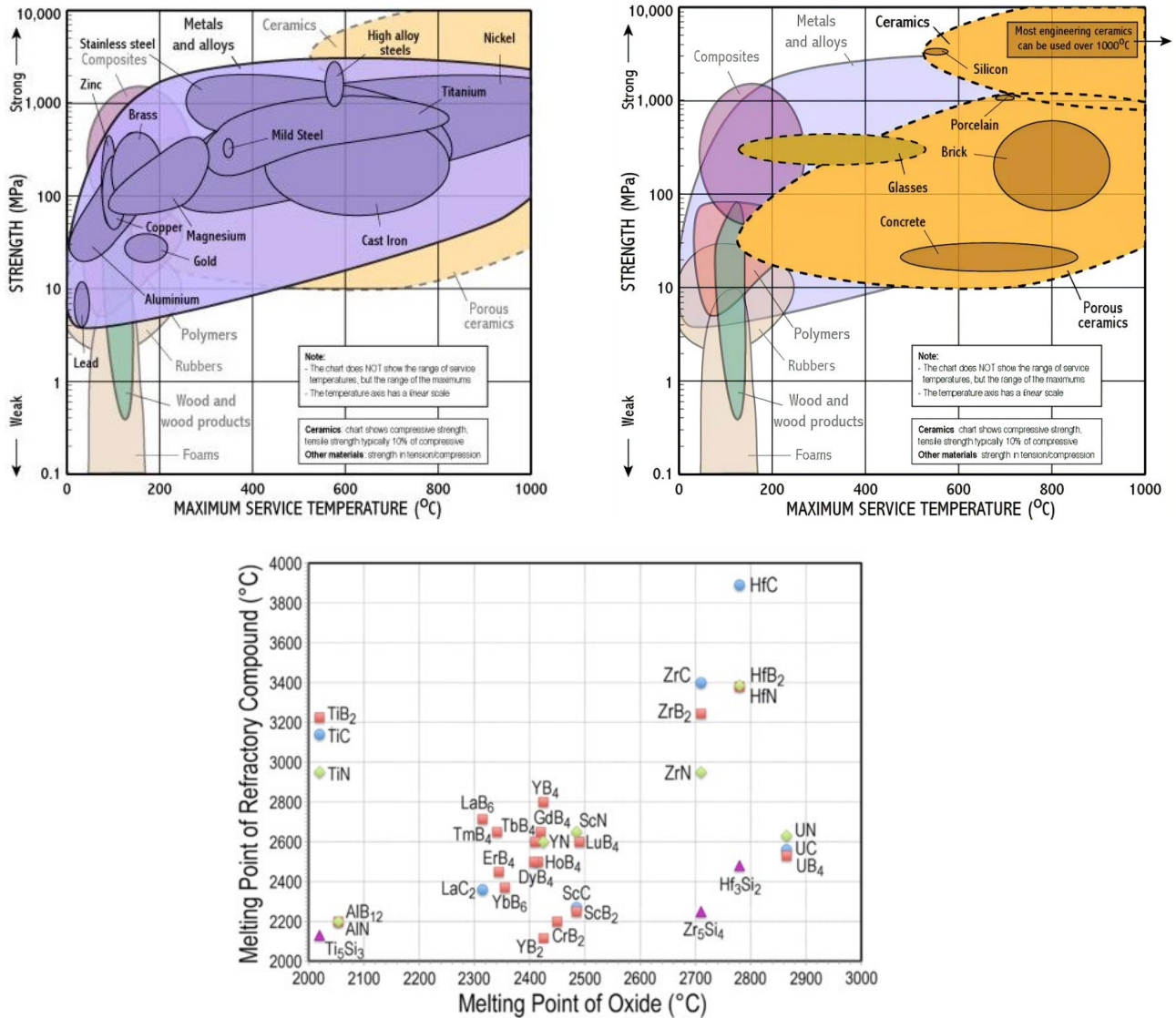


Figure 1. Top Left: Material resistance to failure, given by the applied stress, vs. maximum service temperatures of common metals and alloys. Top right: Material resistance to failure vs maximum service temperatures for ceramic materials of common use [9]. Bottom: Melting points of UHTC candidate materials and the melting point of the corresponding oxides [10].

The development and study of non-oxide UHTC has not advanced at the same pace as oxide ceramics because the non-oxides are rarely found in nature [11]. Thus, the research undertaken as part of this NRP study included the exploration of routes to produce ZrB₂ and SiC, which were selected based on the availability of precursors when compared to other ceramics seen in figure 1. The overall research objectives of the effort are outlined in the following sections.

C. FABRICATION ROUTES FOR ZIRCONIUM DIBORIDE AND SILICON CARBIDE

Transition metals (TM) are known to form a wide variety of borides, presenting stoichiometries that will be unusual for elements in the representative groups, to a great extent, due to

their ability to exist in multiple oxidation states. Moreover, transition metal borides can exist in a complicated mix of bonds, conferring them ceramic-like and metal-like properties [12]. Structures where the transition metal occupies the position A in the formula A_1B_2 (with B being boron) present a structure that consists of layers of close-packed metal atoms, that alternate with boron in graphite-like sheets. The metallic bond in ZrB_2 results in high electrical and thermal conductivities, while the covalent bond in the B layers confers its high hardness [13-16]. The same characteristics that produce those remarkable properties make it challenging to fabricate high purity and dense monoliths of the material. The typical reactions employed for their fabrication start from the transition metal oxides or chloride, as seen in figure 2. The graph of standard free energy ΔG for the diverse reduction reactions that produce ZrB_2 from ZrO_2 illustrates the need for temperatures above 1300 °C to produce the conditions that will allow the formation of the transition metal boride, to be thermodynamically viable.

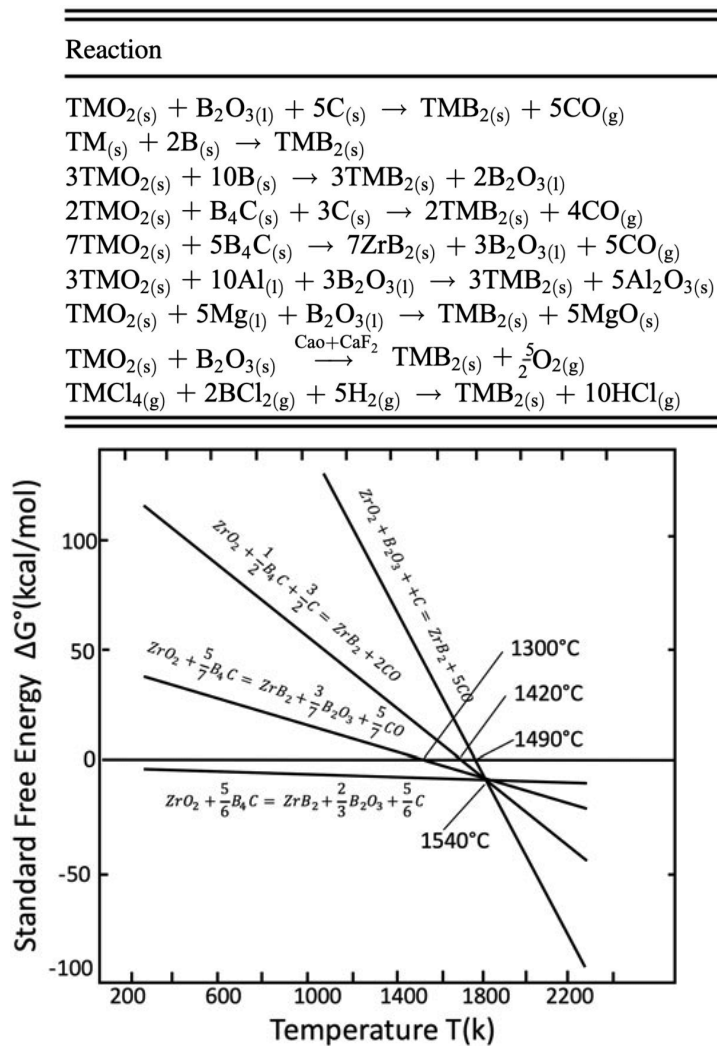


Figure 2. Top: Reactions used to generate transition metal (TM) diborides. Bottom: Standard free energy ΔG for the diverse reduction reactions that produce ZrB_2 from ZrO_2 . From [17]

D. RESEARCH OBJECTIVES

The proposed study aimed to support the Hypersonics RDT&E efforts at the Strategic Systems Programs (SSP) by:

- a) Validating the use of diverse fabrication routes as an operational alternative to generate the ultrahigh temperature ceramics ZrB_2 and SiC ,
- b) Integrating the UHTC of the previous step as the surface layer of a composite containing graphitic fibers and a carbonaceous matrix,
- c) Performing a technical assessment to determine if the newly achieved composite material has the chemical makeup and microstructural characteristics desired, and
- d) Evaluating the potential of the composite to withstand oxidative and ablative conditions that simulate those encountered by systems used in hypersonic flight.

E. REPORT OUTLINE

Chapter II of this report describes the experimental techniques employed for the fabrication of the materials of interest and set of conditions in which the instruments were operated. The chapter also mentioned the apparatus used to collect data regarding the microstructural features, such as shape, size of the particulates in the products obtained, their crystal structure before and after high temperature treatments and particulars of the high temperature tests.

Chapter III presents a summary of the findings illustrated with X-ray diffraction analysis, scanning electron microscope and briefly discusses the significance of the materials observed behavior.

Chapter IV provides a condense list of milestones and achievements regarding the technical outcome of the project and suggest possible next steps if the work was to be continued.

References to the work cited are located at the end of the report.

II. EXPERIMENTAL METHODS

A. MATERIALS AND METHODS EMPLOYED FOR THE SYNTHESIS OF UHTC

As previously mentioned, the typical routes employed to generate ZrB_2 are centered in the carbothermal reduction of ZrO_2 employing B_4C and C or B_2O_3 and C [17]. In here, two main approaches were used to attempt the production of ZrB_2 , an atmospheric plasma (ATP) and carbothermal reduction in a furnace. Section 1 of this chapter is devoted to present the principles of operation of the ATP and other experimental variables employed to produce ZrB_2 .

SiC has been traditionally added to UHTC composites because at temperatures more than $1500\text{ }^\circ\text{C}$ it tends to form a protective amorphous borosilicate coating [11]. The precursor and thermal procedure used for SiC generation is described in section 2.

1. Fabrication of ZrB_2

1.1 Atmospheric Plasma System

A plasma torch is employed here to generate a plasma discharge, producing very high temperatures when a gas is partially ionized by a microwave generator. The plasma gas is typically an inert gas such as argon and the hot zone of the discharge is known to reach temperatures between $2000\text{-}3000\text{ }^\circ\text{C}$. The plasma torch can, however, use other gasses such as neon and xenon. The high temperatures of the discharge or hot zone can be used to induce chemical reactions or simply melt the precursor particles to create self-standing products. The schematic representation of the system is presented in figure 3.

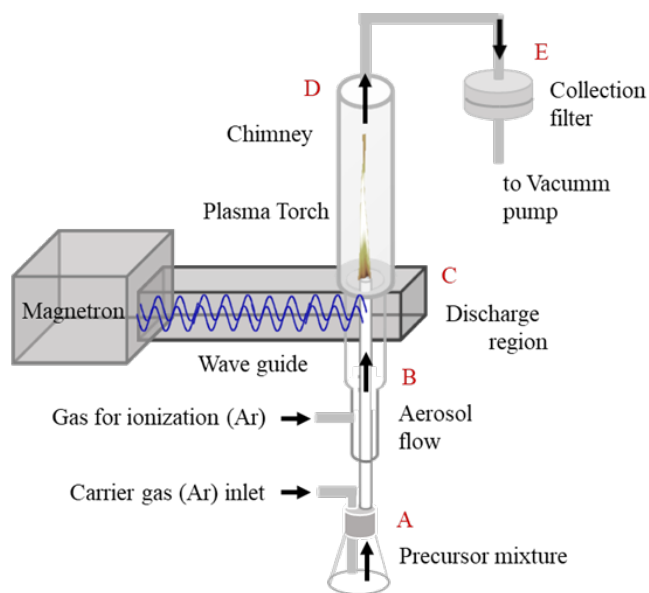


Figure 3. Microwave plasma.

Precursor particles are initially placed in a beaker (point A) and carried using a gas stream, as an aerosol (point B) into the discharge region or hot zone of the microwave plasma discharge (point C). The byproducts of the experiment are collected downstream from the chimney (point D), employing a filter (point E).

The precursors used as the raw powders for the plasma experiments were ZrO₂ nanoparticles as a source of zirconium, B₄C or B as source of boron and carbon black, as the compound that was to aid the carbothermal reduction. All raw materials were supplied by Sigma-Aldrich and had a purity above 99%. Carbon black was acquired as the product Vulcan XC 72R from Cabot corporation. Diverse stoichiometries were employed under diverse plasma and aerosol gas flows. The microwave generator was set at 900 W, the argon supplied as the argon plasma gas set to 3.5 standard liters per minute.

1.2 Use of furnace

A furnace with the capability of heating up to 1550 °C was used to react the same mixtures that were used in the plasma experiments. The largest difference between the two methods (plasma vs furnace) was the heating rates that the precursors experienced. While the particulates travel through the plasma in fractions of a second, the particulates reacted in the furnace were heated at a rate of 2 °C/min up to 1450 °C, where the samples dwell for 2 hours before being allowed to cool. All the steps of the experiments were conducted under an argon atmosphere.

2. Production of SiC

The material selected for the generation of SiC was SMP-10, from Starfire systems [18]. According to the manufacturer “StarPCSTM SMP-10 is the only commercially available one-component liquid precursor to silicon carbide (SiC) ceramics. It facilitates the manufacture of ceramic matrix composites, monolithic parts created from ceramic powders, high-temperature silicon carbide coatings, and joined silicon carbide materials”.

Commercial SiC (from Sigma-Aldrich) was used in some of the samples to compare the stability and behavior with the SiC produce from SMP10. Some of the experiments employed graphite (Sigma-Aldrich less than 10-micron particle size) or carbon nanotubes (CNT), acquired from Nanocomp Inc.

B. MATERIALS CHARACTERIZATION

This research employed a simultaneous thermal analyzer (STA 449 from Netzsch Corporation) to identify the mass changes and the heat flow signal of producing ZrB₂ and SiC. A Neon 40 Zeiss Scanning Electron Microscope (SEM) was employed for the microstructural analysis of the products and the evaluation of morphological features before and after exposure to an oxygen acetylene torch. A Rigaku benchtop X-ray diffractometer (XRD) was used to collect the patterns of the samples after fabrication and after exposure to high temperatures.

C. HIGH TEMPERATURE TESTING

Given the lack of a standard method to test UHTC, this project employed an oxygen acetylene torch to reach the desired extreme temperatures. The initial idea was to test densified monoliths of ZrB₂, SiC from SMP10 and commercial, Graphite, CNT and their combinations at diverse loadings. However, given a malfunction in the high temperature furnace, the samples were only studied in their powder form.

An oxygen acetylene torch can produce neutral, carburizing or oxidizing flames. Neutral flames have an approximate temperature of 3000 °C while oxidizing ones can reach 3480°C. A neutral flame is produced when the ratio of oxygen to acetylene, in the mixture leaving the torch, is almost exactly one-to-one. It is named neutral because it will usually have no chemical effect on the samples being treated. The carburizing (or reducing) flame is created when the proportion of acetylene in the mixture is higher than that required to produce the neutral flame, that is, the flame is in a fuel rich mixture. The oxidizing flame, in contrast, has a higher amount of oxygen than acetylene and was the one selected for the tests.

A reducing, carburizing or oxidizing flames can be recognized by the profile and contours that exist between the inner cone and the outer envelope of the flame. The image of the torch and flame employed in thus study are presented in figure 4 below.



Figure 4. Oxygen acetylene torch.

III. RESULTS AND DISCUSSION

A. FABRICATION OF SAMPLES

All synthetic approaches followed the carbothermal reduction of ZrO_2 employing B_4C or B and C. Multiple stoichiometries were attempted. Given that this technical report is only meant to convey the major findings, it does not contain the complete XRD, SEM, TG data of all the precursor mixtures employed or the products generated. We selected the most representative results to provide an idea of how the work was conducted and a sample of the observations.

1. ATP synthesis and oven synthesis of ZrB_2

All the experimental conditions employed in the atmospheric plasma system were insufficient to fully reduce the zirconium oxide and only large excess B and C were able to produce small amounts of ZrB_2 . It is believed that the short residence times inherent of the plasma instrument, in which the particulates only spend fractions of a second in the hot glow/discharge zone, were responsible for the partial reduction. Figure 5. Presents a picture of the chimney while the jet of precursor particles is observed (left) and the X-ray diffraction pattern of a sample produced in the ATP starting with a mixture with a stoichiometry of $2\text{ZrO}_2 + \text{B}_4\text{C} + 3\text{C}$ (right). The stoichiometry used to mix some of the precursors was previously reported by [17].

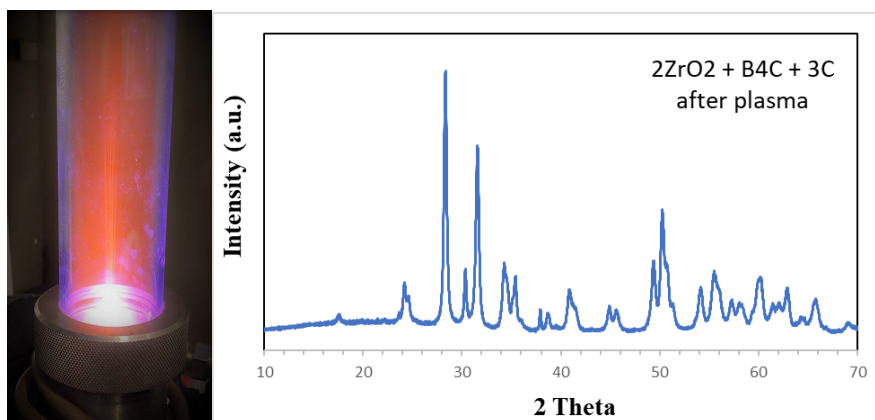


Figure 5. Left: Plasma chimney showing the discharge zone in the lower region and the jet of particles that emerge from it and travel towards the filter located downstream. Right: XRD pattern showing that the higher intensity peaks correspond to unreacted zirconium oxide.

The same multitude of stoichiometries that ran through the microwave plasma system were placed in the furnace that heated them to $1450\text{ }^\circ\text{C}$ for 2 hours. Of those, the one with a ratio $\text{ZrO}_2:\text{B}:\text{C}$ of 1:4:4, with boron and carbon black in excess, produced an XRD pattern with only ZrB_2 peaks. Thus, the in-situ characterization of carbothermal reduction of ZrO_2 was analyzed in the STA instrument, shown in figure 6.

2. Fabrication of SiC

Also shown in figure 6, the thermal decomposition of SMP10 was studied by thermogravimetry and it was determined that it occurred in 3 major steps, which correspond to temperatures of approximately 160, 420 and 800 °C.

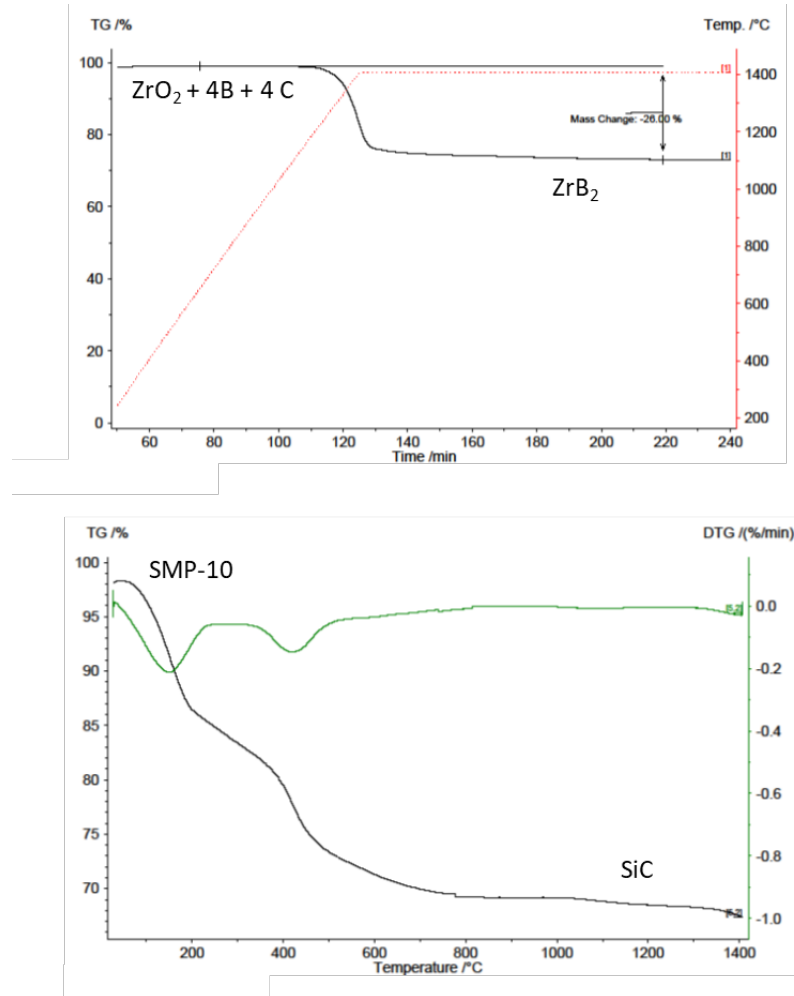


Figure 6. Thermogravimetric analysis of the mixture ZrO_2 :B:C of 1:4:4 under argon environment (top) and thermal decomposition of SMP10 (bottom).

The X-ray diffraction patterns presented in figure 7 show the pristine ZrB_4 produced from the 1:4:4 mixture (top), the SiC polymorphs generated from SMP10 (middle) and the SiC acquired commercially (bottom). It is worth noting the significant differences between the SiC samples (middle and bottom). The SiC crystalline phases identified in the samples produced from SMP10 were α -SiC, moissanite 15R and 4H, which differences lay in the stacking arrangement of the atoms in their crystal structures. Alpha silicon carbide is the most common encountered polymorph, it has a hexagonal crystal structure similar to wurtzite and was the only phase encountered in the commercial sample.

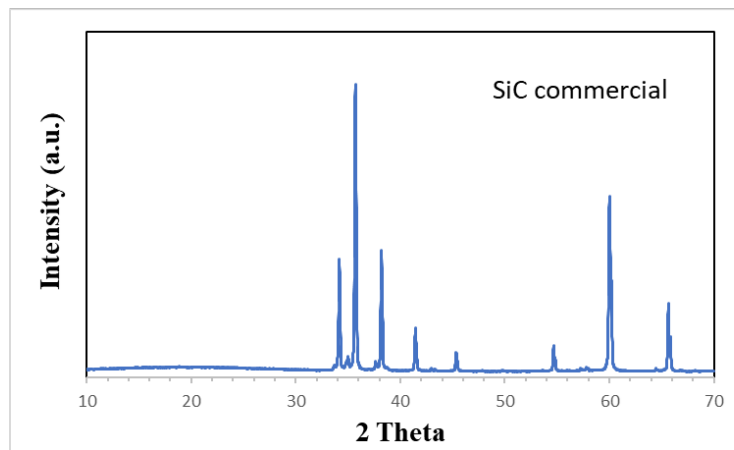
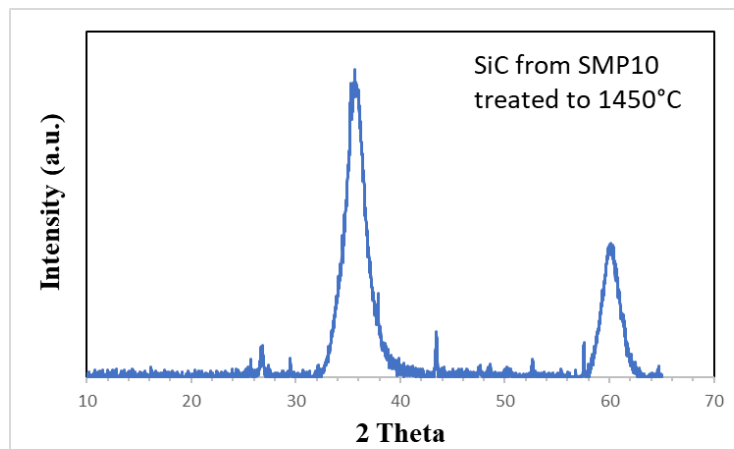
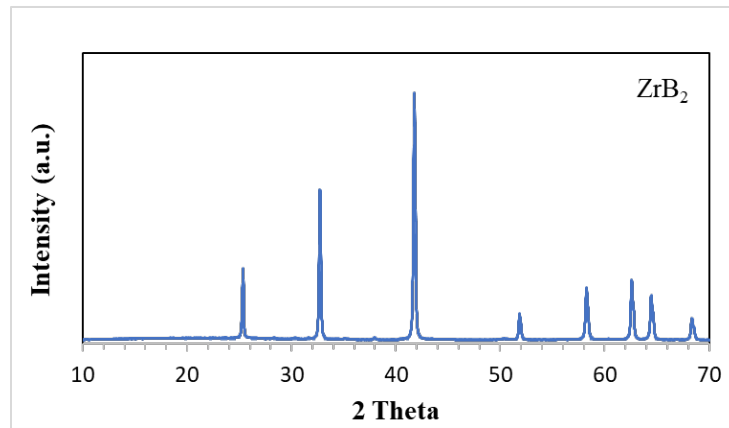


Figure 7. XRD patterns of ZrB_2 (top), SiC fabricated from SMP10 precursor (middle) and commercial SiC (bottom).

B. CHARACTERIZATION BEFORE AND AFTER ULTRAHIGH TEMPERATURE TREATMENTS.

The images of the mixtures of some ZrB_2 and SiC samples by themselves or with carbonaceous components during the exposure to the temperatures generated by an oxygen acetylene torch and after the treatment are presented in figure 8. The profile of colors during the experiment varied by sample and some presented white or orange deposits on top after. The white deposits were associated with small amounts of oxides and the orange with the presence of iron oxides contained in the CNT samples as a byproduct of the iron used as catalyst in their production.

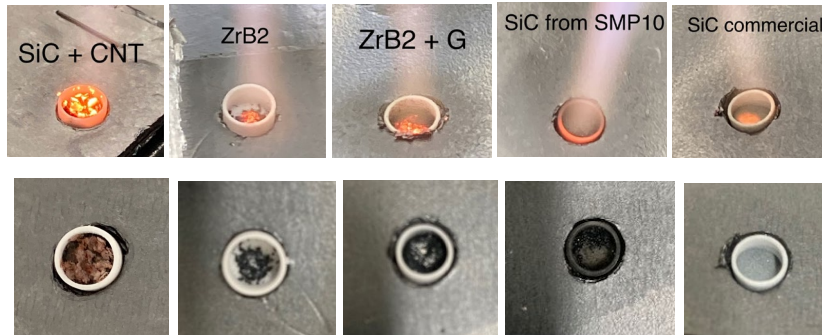


Figure 8. Samples contained in sintered alumina crucibles during the exposure to high temperatures (top) and images of their appearance after the treatment (bottom).

ZrB_2 and its mixture with graphite did not present significant morphological changes after exposure to ultrahigh temperatures, see figure 9. The zirconium boride samples produced in the oven contained excess carbon as a byproduct of their synthesis (particles with approximate sizes of 5 nm), mixed with columnar particles that reached sizes in the micron scale, a large contrast with the particle shapes and sizes located in the raw mixture. The same columnar cylindrical particulates are observed after the high temperature treatment.



Figure 9. Mixture of precursors denominated 1:4:4 (left), after fabrication of ZrB_2 (middle) and after torch treatment (right).

ZrO₂ peaks of reduced intensity were detected in the XRD pattern after torch treatment of the samples 1:4:4 ZrB₂ and the one that had graphite added. Figures 10 and 11 show that the addition of graphite reduces the intensity of the oxide peaks with respect of the peaks of ZrB₂ when compared to the XRD of the boride by itself, which still dominate the pattern. The excess carbon particles (Vulcan carbon black) do not seem to generate any peaks before or after heat application, however, the presence of graphite generates the typical G peaks, which are evident in both patterns (before and after test), although with a reduction in intensity after torch treatment.

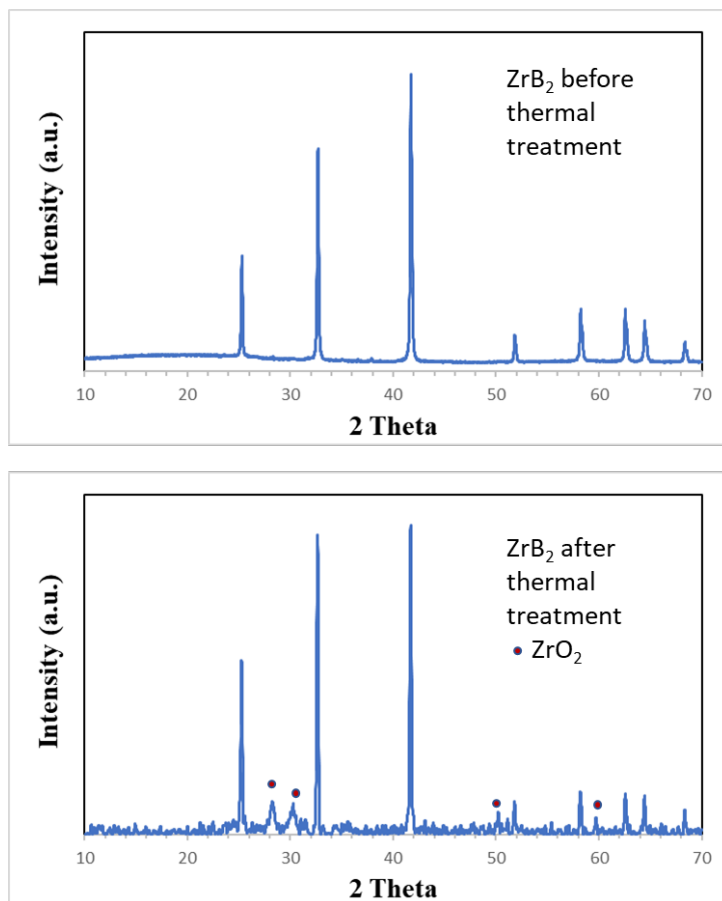


Figure 10. XRD pattern of ZrB₂ samples before (top) and after (bottom) high temperature treatment.

Literature in the field suggests that the presence of carbon during the high temperature exposure of ZrB₂ to oxidative/ablative conditions produces ZrC, preventing the boride to revert to its oxidized form [17].

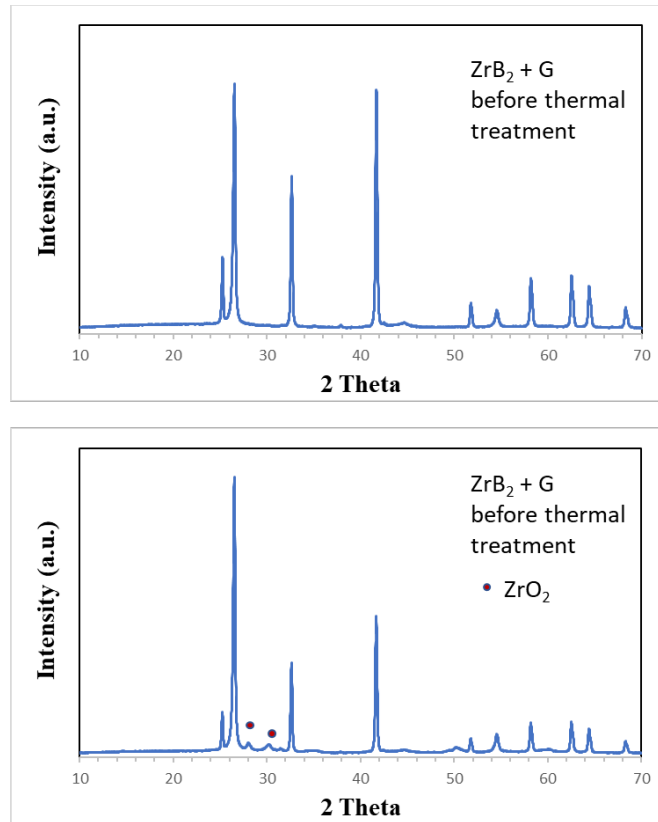


Figure 11. XRD pattern of ZrB₂ + graphite samples before (top) and after (bottom) high temperature treatment.

SiC from SMP 10 produced a glassy sintered byproduct, similar to the one reported by [11], a drastic morphological change from the submicron particle size observed in samples of SMP10 that were decomposed in argon by the treatment at 1450°C before exposure to the temperatures of the oxygen acetylene torch. See figure 12. The high temperature treatment of that sample also had the effect to reduce the number of peaks of one of the SiC polymorphs, see figure 13. No oxidation was detected in the pattern. In contrast with the SEM observations described for SiC from SMP10, the commercial SiC did not suffer any changes on its XRD pattern or SEM profile.

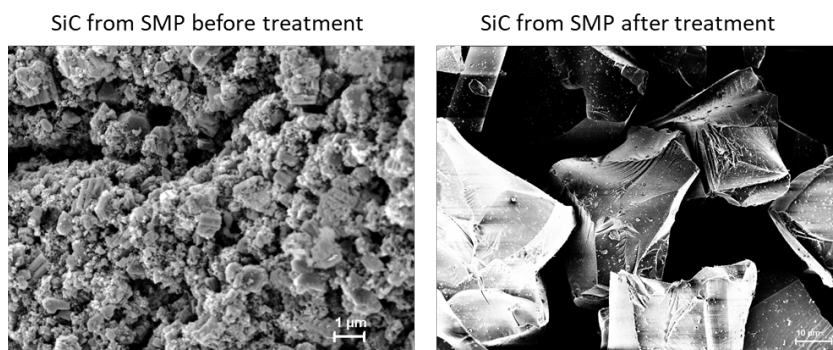


Figure 12. SiC before (left) and after (right) high temperature exposure.

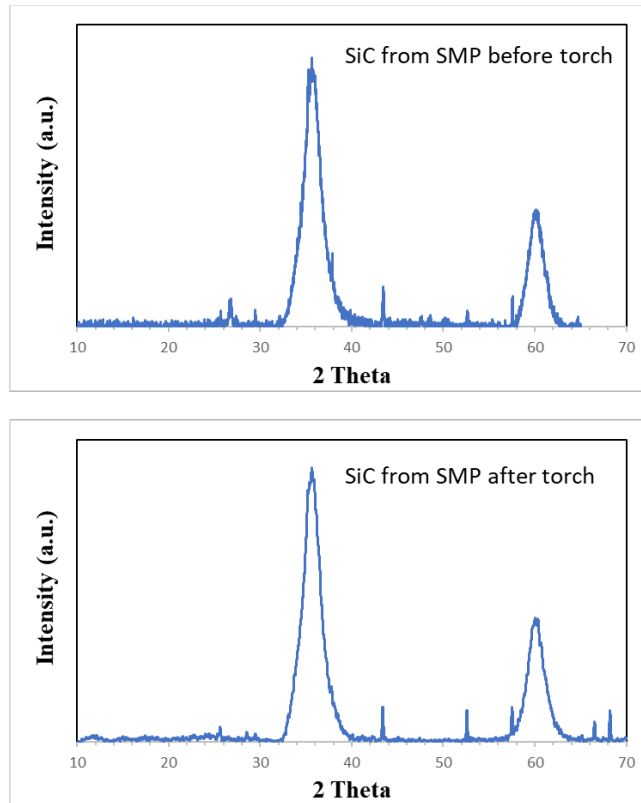


Figure 13. XRD pattern of SiC produced from SMP10 before (top) and after (bottom) high temperature treatment.

CNT mixtures presented the largest levels of oxidation due to the presence of Fe catalyst particles, which turned into FeO and Fe₂O₃, depending on the nanotube location in the mixture, internal or superficial, respectively. The graphite peaks in the sample before treatment disappeared or largely reduced their profiles after the oxygen acetylene treatments. See figure 14 below.

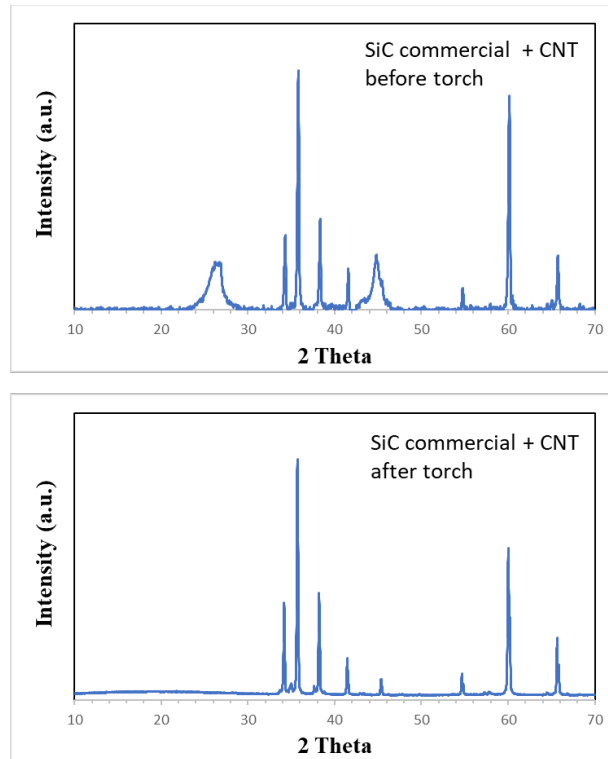


Figure 14. XRD pattern of SiC + CNT specimen produced using commercial SiC before (top) and after (bottom) high temperature treatment.

IV. CONCLUSIONS

Carbothermal reduction of zirconium oxide employing boron and carbon black as precursors, at temperatures in excess of 1450 °C, rendered a higher purity ZrB₂ than the specimens generated by atmospheric plasma fabrication approaches and based on the data collected by this study, is the most indicated method to produce zirconium boride.

The use of a one-component liquid precursor (SMP10) successfully produced diverse polymorphs of silicon carbide (SiC). The precursor decomposition takes place in three stages and can be readily mixed with ZrB₂ without promoting its oxidation, once that the samples have undergone the initial decomposition step at 160°C.

There are no standard methods to test UHTC, if the use of an oxygen acetylene torch is to be continued, an in-situ temperature monitoring system or probe should be employed to accurately determine treatment conditions and their effects. The use of high-power lasers should also be considered.

ZrB₂ and its mixture with graphite did not present significant morphological changes after exposure to ultrahigh temperatures, however, ZrO₂ peaks of reduced intensity were detected in their XRD patterns, with those containing graphite being smaller than the bare ZrB₂. Zirconium diboride, thus, has the potential to withstand extreme environments, as initially hypothesized. SiC from SMP 10 produced a glassy sintered byproduct, while commercial SiC did not suffer any changes. CNT mixtures presented the largest levels of oxidation due to the presence of Fe catalyst, which turned into FeO and Fe₂O₃, depending on the nanotube location in the mixture, internal or superficial, respectively.

Next steps should include assessment of mechanical properties of sintered monoliths of diverse zirconium boride, silicon carbide, and carbonaceous combinations.

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