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Synthesis & Fundamental Formation Mechanism Study of High Temperature & Ultrahigh Temperature Ceramics

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

SYNTHESIS & FUNDAMENTAL FORMATION MECHANISM STUDY OF HIGH
TEMPERATURE & ULTRAHIGH TEMPERATURE CERAMICS

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

MATERIALS SCIENCE AND ENGINEERING

by

Paniz Foroughi

2018

To: Dean John L. Volakis
College of Engineering and Computing

This dissertation, written by Paniz Foroughi and, entitled Synthesis & Fundamental Formation Mechanism Study of High Temperature & Ultrahigh Temperature Ceramics, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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Dean John L. Volakis
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Vice President for Research and Economic Development
and Dean of the University Graduate School

Florida International University, 2018

DEDICATION

I dedicate this thesis to my parents Negar Safizadeh Shabestari and Ata Foroughi. Without their patience, understanding, support, and most of all love, the completion of this work would not have been possible.

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ABSTRACT OF THE DISSERTATION

SYNTHESIS & FUNDAMENTAL FORMATION MECHANISM STUDY OF HIGH
TEMPERATURE & ULTRAHIGH TEMPERATURE CERAMICS

by

Paniz Foroughi

Florida International University, 2018

Miami, Florida

Professor Zhe Cheng, Major Professor

Borides and carbides of tantalum and hafnium are of great interest due to their ultrahigh temperature applications. Properties of these ceramics including oxidation resistance and mechanical properties might be further improved through solid solution/composite formation.

Synthesis of single-phase $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solution powders including nanopowders via carbothermal reduction (CTR) is complicated due to noticeable difference in reactivity of parent oxides with carbon, and also the low solubility of those oxides in each other. Moreover, for TaC-HfC system the solid solution may go through phase separation due to the presence of a miscibility gap at temperatures below 887°C.

In this study, a method of low-cost aqueous solution processing followed by CTR was used to synthesize $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solution powders. In fact, method was first used to synthesize boron carbide (B_4C) powders as it paves the way for a

detailed study on the synthesis of $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solutions powders considering the fact that B_4C contains both carbon and boron in its structure.

Particular emphasis was given to investigate the influences of starting compositions and processing conditions on phase separation during the formation of both carbide and boride phase(s). It was found that individual TaC - HfC and TaB_2 - HfB_2 phases always form quickly but separately during the CTR process (e.g., at 1600 °C within a few minutes). Those carbides and borides remain phase-separated unless heated to much higher temperatures for long time due to the slow inter-diffusion between them.

It was also found that for $Ta_xHf_{1-x}C$ applying a DC electric field through the use of spark plasma sintering (SPS) system significantly accelerates the inter-diffusion of Ta and Hf leading to formation of a single-phase $Ta_xHf_{1-x}C$ solid solution at 1600 °C for 15 minutes. On the other hand, for borides alkali metal reduction reaction (AMR) method appears to be an excellent alternative to CTR-based method for formation of a single-phase $Ta_xHf_{1-x}B_2$ solid solution. In this method, chlorides of tantalum and hafnium are directly reduced using sodium borohydride ($NaBH_4$) giving rise to formation of a single-phase $Ta_{0.5}Hf_{0.5}B_2$ solid solution nanopowders in one step at much lower temperatures (e.g., 700 °C) by avoiding the oxides formation and the associated phase separation of individual borides as observed in the CTR-based process.

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Chapter I: Introduction

Ultrahigh temperature ceramics (UHTCs) are a group of ceramics, which possess very high melting points (above 3000 °C). Transition metal carbides and borides of groups IV and V are both considered as UHTCs [1–4]. These ceramics have a unique combination of properties such as high hardness, high melting point, high electrical and thermal conductivity, which makes them promising materials for cutting tools and ultrahigh temperature applications such as critical parts for engines and hypersonic vehicles that may need to tolerate temperatures even above 2000 °C [5–10]. However, it has been noticed that conventional binary UHTCs are not sufficient for the oxidizing and rapid heating environments [9,10]. Previous studies show that, by controlling the composition via using alloying elements, ternary UHTC solid solutions/composites could provide better properties compared to binary systems such as higher oxidation resistance, higher melting point and enhanced mechanical properties [11,12]. In addition to composition, refining microstructure plays a significant role in improving the UHTCs properties such as hardness and toughness. Obtaining UHTC powders with reduced particle size will help achieving finer microstructure of the fabricated parts, and it also helps simplify the post synthesis processing such as milling/grinding and improves the sintering activity. All of these motivate the research on synthesis and processing of nano-scale ternary UHTC powders [13,14].

Among transition metal carbide UHTCs, hafnium carbide (HfC, $T_m=3900^\circ\text{C}$) and tantalum carbide (TaC, $T_m=3985^\circ\text{C}$) are of particular interest due to their very high melting points, high hardness (TaC: $\sim 19\text{GPa}$ and HfC: $\sim 20\text{GPa}$), high electrical and

thermal conductivity [1,2,5–10]. However, these properties could improve further through forming solid solutions and/or composites. It has been observed that compared to binary HfC and TaC, (Ta,Hf)C solid solutions provide better properties such as higher melting point (above 4000 °C), higher electrical resistivity and microhardness [15–17]. TaC and HfC can form continuous solid solutions in a broad composition range thanks to their similar crystal structure and also physical-chemical properties. Nevertheless, the solid solution may go through phase separation because of the presence of a miscibility gap at temperatures below 887 °C. Therefore, it is critical to understand how to control the synthesis process to avoid phase separation, which is an energetically favorable process under certain condition. There are a few studies on synthesis of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution powders using different approaches[18][16][19]. However, all these approaches suffer from certain drawbacks such as high cost of the starting materials (e.g., organometallic precursors, organic solvents), applying vacuum, long processing time, or introducing impurities. Moreover, the suggested methods are only used to synthesize a single composition of $\text{Ta}_{0.8}\text{Hf}_{0.2}\text{C}$ solid solution and there is no study on the synthesis of other compositions, which show even greater properties such as higher oxidation resistance and better mechanical properties [20]. Therefore all these bring the question of how to control the phase separation of TaC-HfC during the synthesis process using low-cost methods without any composition constraints.

Among refractory UHTC diborides hafnium diboride (HfB_2 , $T_m=3250^\circ\text{C}$) and zirconium diboride (ZrB_2 , $T_m=3000^\circ\text{C}$) are top candidates for thermal protection materials in both reentry and hypersonic vehicles due to their high melting point and superior oxidation resistance and thermal-mechanical properties [3,4]. Similar to UHTC carbides,

different properties of diborides such as oxidation resistance, toughness, mechanical and electrical properties could be improved using alloying elements [21–24]. For example, it has been observed that adding TaB₂ improves the oxidation resistance of HfB₂ noticeably. This is mainly because of the formation of tantalum pentoxide (Ta₂O₅, T_m=1880°C), which has lower melting point than hafnium oxide (HfO₂, T_m=2758°C). Hence, during the oxidation process Ta₂O₅ melts before HfO₂ and form a more dense oxide layer leading to less oxygen transport [25]. Up to now there is only one study by Xie et al. [26][27] on the synthesis of TaB₂-ZrB₂ composite powders. However, in addition to not being able to synthesize single phase Ta_xZr_{1-x}B₂ solid solution, their method suffers from several drawbacks such as high cost of the starting materials and issues with waste disposal. On the other hand, there is no study on the synthesis of Ta_xHf_{1-x}B₂ solid solution/composite powders, which could have even higher melting point than Ta_xZr_{1-x}B₂ composite/solid solution thanks to the higher melting point of HfB₂ when compared with ZrB₂. Additionally, there are several studies reporting rapid coarsening and abnormal grain growth during the synthesis of boron containing ceramics even at moderate temperatures [28][29][30][31]. All these bring the fundamental question of how to precisely control the phase and microstructure of Ta_xHf_{1-x}B₂ solid solution powders using low cost methods.

On the other hand, synthesis of high temperature ceramics (HTC) of boron carbide (B₄C, T_m=2763°C) powders was also of interest since it is closely related to the synthesis of both Ta_xHf_{1-x}C and Ta_xHf_{1-x}B₂ solid solutions considering the fact that B₄C contains both carbon and boron in its structure. Therefore, studying the synthesis of nano/submicron-sized B₄C with the emphasis on understanding the composition-processing-microstructure relationship is also very important as it will provide guidance

to low cost synthesis of other carbides and borides with controlled microstructure and properties.

Thus, the main objective of this work is to study the synthesis and formation mechanisms of nanocrystalline ternary $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solution powders with a focus on the interrelationships between composition, processing and microstructure. This is critical as it will provide better understanding about how to precisely control stoichiometry, phase, morphology and properties of the synthesized ternary UHTC materials. The secondary objective of this research is to synthesize nano/submicron-sized high temperature B_4C ceramic powders using a low-cost method, study the interrelationships between composition-processing-microstructure and develop understanding about the reaction kinetics and mechanisms of formation for such a highly applicable ceramic, which would help guide the synthesis of ternary UHTC carbides and borides.

This thesis will be organized into 6 chapters. Chapter 1 provides an introduction for B_4C and ternary carbide and boride UHTCs. Chapter 2 details the historic researches on the synthesis of nano B_4C and ternary UHTCs and their challenges with particularly focuses on the $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solutions/composites. Chapter 3 contains the materials, methods used for the synthesis of fine B_4C powders as well as the obtained results and detailed analysis of them. Materials, methods, results and detailed discussion for synthesis of $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solutions could be found in chapter 4 and 5, respectively. Summary of the major findings in this work and recommendations for future work are provided in Chapter 6.

Chapter II: Literature Review

2.1 Boron Carbide (B₄C)

Synthesis methods used to produce B₄C powders are reviewed below. Advantages and also disadvantages of each method are explained in details in order to provide a rationale for the synthesis approach used in this work. These methods are: elemental synthesis, magnesiothermic reduction reaction, vapor phase reaction (e.g., chemical vapor deposition) and carbothermal reduction reaction. Most of these approaches are not practical for synthesis of nano-scale boron carbide on a large industrial scale.

2.1.1 Elemental Synthesis

There are some studies on the synthesis of B₄C powders via elemental synthesis method. For example, Chang et al. [32] synthesized submicron-sized B₄C powders (~ 350 nm) through heat treating a mixture of amorphous boron and carbon powders at 1550 °C for 4 hours under argon flow. Wei et al. [33] synthesized B₄C nanorods through mixing the carbon nanotubes (CNT) with amorphous boron (B) powders followed by heat treating at 1150 °C for 2 hours under flowing of argon gas. However, synthesis of B₄C powders using elemental synthesis method is not economically preferred for industrial production due to the high cost of the elemental boron.

2.1.2 Magnesiothermic Reduction Reaction

B₄C powders can also be synthesized via magnesiothermic reduction reaction. Equation below shows the formation of B₄C using magnesium as the reducing agent:[34]

However, the above reaction does not occur in a single step but they rather in two subsequent steps see equations below:

Nevertheless, the B_4C powders synthesized by this method always contain residual magnesium compounds. Although hot acids could be applied to purify the synthesized powders, those impurity compounds would not be removed completely. Moreover, the high cost of magnesium and the need for treating the waste acid make this method less favorable to be implemented for industrial scale synthesis of B_4C . There has been a report by Singh et al. [35], which describes the synthesis of uniform B_4C nanoparticles by one step reduction of boric acid using activated magnesium at very low temperatures (800°C) for 20 hours. However, that method utilized a specially designed high pressure autoclave, which is expensive and has safety and productivity concerns.

2.1.3 Vapor Phase Reaction

Vapor phase reaction method has been widely used to synthesize B_4C powders, thin film coatings, and whiskers[36][37][38][39]. In this method, the boron containing gaseous species such as boron trichloride (BCl_3) and boron triiodide (BI_3) will be reduced by carbon containing gaseous species such as carbon tetrachloride (CCl_4) and hydrocarbon gases (e.g., CH_4) to form B_4C [34,40]. The equation below refers to the formation of B_4C through the reduction of gaseous BCl_3 with CH_4 :

It should be noted that in this method, hydrogen (H₂) gas must be added to CH₄ during the whole process in order to convert the chlorine to hydrogen chloride (HCl). Although this method leads to formation of B₄C products with high purity, it is not ideal for synthesis of B₄C nano powders on large scale due to the high cost of gaseous materials and equipment. As a result, it is not appropriate for large industrial B₄C powders production.

2.1.4 Carbothermal Reduction Reaction

Among all the methods mentioned earlier, carbothermal reduction reaction (CTR) is most commonly carried out since it is an inexpensive method that uses low cost starting materials such as boron trioxide (B₂O₃) and carbon and relative simple equipment. In fact, it is used for industrial production of B₄C (e.g., via the Acheson process). Eq. 2.5 shows the overall reaction for boron carbide synthesis through CTR [40]:

Researchers have made numerous reports on the synthesis of B₄C powders based on CTR process. For example, Weimer et al. [40,41] has synthesized uniform and fine B₄C particles (~100 nm) at 2000 °C for a few seconds in a graphite transport reactor using rapid CTR reaction of B₂O₃ and carbon from cornstarch. Miler et al. [42] also has synthesized submicron B₄C particles (~0.4µm) through rapid CTR reaction of B₂O₃ and carbon lamp black at 1750 °C in a specially designed graphite furnace. Gao et al. [43,44] has also synthesized submicron B₄C particles (~0.35µm) using an aqueous solution of boric acid and carbon as precursors followed by pyrolysis (to remove the low molecule

species such as excess water) and rapid CTR at 1850 °C. Kakiage et al. [45] synthesized micron-sized B₄C particles (~5 µm) using PVA and boric acid through conventional CTR at a low temperature of 1100°C. Najafi et al. [46,47] synthesized a mixture of nano B₄C particles and whiskers using sol-gel process of phenolic resin and boron alkoxide followed by pyrolysis and conventional CTR reaction at 1270 °C. However, despite the successful synthesis of B₄C powders via CTR method there are still some issues that need to be addressed, especially in terms of product microstructure.

In spite of CTR advantages over other B₄C synthesis methods, there are not enough studies on a detailed examination of interrelationships between composition-processing-microstructure and there is still a significant lack of a systematic study on the effect of different parameters (e.g., CTR processing conditions and precursors) on final morphology and as a result properties of B₄C. For example, Alizadeh et al.[28]reported the formation of highly non-uniform B₄C powders via CTR reaction between boric acid and carbon (see Figure 2.1).

Figure 2.1: SEM image of the B₄C powders synthesized by Alizadeh et al.[28]

Ma et al. [48] reported formation of B_4C nanowires through CTR of $B_2O_3/B/C$ mixture without adding any catalyst. On the other hand, Weimer et al. [40][41] reports the synthesis of highly uniform B_4C powders via CTR method using essentially the same kinds of starting materials. All these bring questions of:

1- What causes such large variations in B_4C powder microstructure?

2-How to better control the B_4C product morphology?

Study aimed at revealing the interrelationships between composition-processing-microstructure for synthesis of nano/submicron-sized B_4C powders via CTR method will help answer those questions and also influence the scaling up of the synthesis process to industrial production for fine B_4C powders.

2.2 UHTC Carbides and Borides Synthesis

All the methods used to synthesize UHTC carbides and borides along with their advantages and disadvantages are discussed in the following section.

2.2.1 Direct Reaction Using Elemental Metals

In this method, the elemental transition metal powders react with boron or carbon powders in order to form UHTC borides and carbides, respectively. There are several studies on the synthesis of UHTC borides and carbides using this method [49–51]. For example, Matsudaira et al. [49] synthesized a mixture of niobium diboride (NbB_2) and niobium boride (NbB) with particle size of $\sim 5\text{--}10\text{ }\mu\text{m}$ at $1000\text{ }^\circ\text{C}$ for 1 hour using elemental niobium metal and amorphous boron powder. However, as earlier explained in section 2.1.1, elemental synthesis suffers from several drawbacks including high cost of the elemental precursors. On the other hand, the use of coarse starting materials (in

particular transition metal powders) along with the relatively high reaction temperatures leads to a noticeable grain growth.

Moreover, there are also several studies on the synthesis of UHTC borides and carbides from the elements using self-propagating-high-temperature synthesis (SHS) method [50,51][52]. However, the obtained products from the SHS process may have non-uniform morphology due to the temperature non-uniformities during the synthesis procedure (see Figure 2.2). In other words, there would be almost no control on the microstructure of the synthesized powder via SHS process due to the very fast reactions with high transient reaction temperature ($\sim 2000\text{ }^{\circ}\text{C}$)[27]. All these make the elemental synthesis an unfavorable process to produce nanocrystalline UHTCs.

Figure 2.2: SEM image of synthesized ZrB_2+SiC composite via SHS method [50].

2.2.2 Vapor Phase Reaction

Both carbides and borides of transition metals could be synthesized via vapor-phase reaction method [53–55]. Eq. 2.6 shows the reduction of the gaseous transition metal chloride and boron trichloride with hydrogen gas.

Eq. 2.7 shows the formation of transition metal carbides through the reaction between the gaseous transition metal chlorides with gaseous hydrocarbons (e.g., propene).

However, as earlier mentioned in section 2.1.3 this method suffers from some disadvantages such as high cost of the gaseous precursors and equipment and also safety concerns with using such flammable gases (e.g., CH_4) and the byproduct of highly corrosive HCl.

2.2.3 Carbothermal and Borochemical Reduction Reactions

Carbothermal reduction reaction (CTR) is commonly used for commercial production of the UHTC carbides and borides. Compared with the methods explained previously, CTR reaction is low cost, scalable and environmentally friendly.

Example CTR reactions for formation of carbides and borides could be written as follows, assuming product of MC and MB_2 :

The transition metal oxides need to react with carbon and carbon plus boron trioxide to form UHTC carbides and borides, respectively.

Borothermal reduction reaction (BTR) is another method used to synthesize UHTC borides. In this method the transition metal oxide reacts with B to form boride as shown below [56][57]:

The reaction temperature for Eq. 2.10 could further decrease by adding carbon to help reducing the metal oxide[57]:

B₄C can also be used instead of elemental boron in the above reaction [31] However, similar to elemental boron, B₄C is also expensive especially for the ones with smaller particle size. In comparison B₂O₃ is much less expensive and could be used as B source for the synthesis of UHTC borides via CTR reaction (see Eq. 2.9).

In conventional CTR processing method used for synthesis of UHTC carbides and borides, very high temperature and long holding times on the order of several hours are required due to the non-homogenous mixture of coarse reactants, which result in formation of micron-sized particles instead of uniform UHTC nanopowders. On the other hand, CTR reaction can use soluble precursor materials that can offer intimate, molecular mixing of reactants. This would result in lower CTR temperatures and shorter dwell time giving rise to formation of UHTC powders with smaller particle size. Moreover, more uniform powders would form via solution processing followed by CTR thanks to the homogeneous distribution of all reactants at molecular level.

It should also be mentioned that there would be a large choices of precursors and processing conditions for CTR, which offers the flexibility to have better control on the

morphology and stoichiometry of the synthesized powders, and is not applicable in the earlier mentioned methods.

2.2.4 Alkali Metal Reduction

Alkali metal reduction reaction (AMR) method has been used for the synthesis of UHTC diborides before. In this approach, the alkali metals or their active compounds such as sodium borohydride (NaBH_4) are used to react with transition metal chlorides in order to form UHTC diborides. The overall AMR reaction is written as below [58,59]

The reaction above occurs at low temperatures, while at higher temperatures ($>500^\circ\text{C}$) NaBH_4 starts to decompose (see Eq. 2.13) and the metal chlorides will react with decomposition products of NaBH_4 sodium hydride (NaH) and boron hydride (BH_3) in order to form metal diborides (see Eq. 2.14).

This method provides some advantages such as lower reaction temperature ($<1000^\circ\text{C}$), which would help obtaining very small crystallite size in range of few nanometers. However, there are also a few difficulties associated with this approach. For example, alkali borohydrides, which are used as the reducing agent as well as the boron source, may bring safety concerns. Moreover, both transition metal chlorides and alkali borohydride are sensitive to air/moisture. Therefore, rigorous atmosphere control is required in order to prevent their reaction with air/moisture, otherwise the product of the

AMR reaction might contain metal oxides instead of pure borides. Additionally, as can be seen in Eq. 2.14 alkali halides are the byproduct of the AMR reaction, which need to get removed by washing the products via water.

2.3 Synthesis of Ternary UHTCs

Preparing solid solutions and composites of UHTC carbides and borides enable flexibility in tuning the composition and properties such as mechanical, thermal and chemical properties [9,60][24]. The solid solutions and/or composites of UHTC borides and carbides often show the potential to be used for certain aerospace applications thanks to the improved mechanical or chemical properties [24][61]. For example, Mroz [61] reported that (Ti,Zr)C and (Ti,Zr)B₂ solid solutions show better mechanical properties (e.g., higher hardness) compared with the end members for each system (see Figure 2.3).

Figure 2.3: Hardness of single-phase TaZrB₂ solid solution with different compositions[61]

For thermal properties, Andrievskii et al. [15] studied the melting points for different compositions of (Ta,Hf)C solid solutions. It was found that Ta_{0.8}Hf_{0.2}C has higher melting point (~4010 °C) than both pure HfC and TaC. Additionally, Monteverde

et al.[62] reported that addition of 10 vol.% HfB_2 into ZrB_2 +15vol.%SiC enhanced the thermal shock resistance of the sintered ceramic from 385 °C to 475 °C through formation of $(\text{Zr,Hf})\text{B}_2$ solid solution during the consolidation process. For chemical property, Zhang et al. [20] performed oxidation tests on sintered $(\text{Ta,Hf})\text{C}$ solid solutions with different compositions such as $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ using a plasma gun. The oxidation test results showed that the formed oxide layer on the surface of the sintered $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ sample is noticeably thinner than those formed on the surfaces of the sintered pure TaC and HfC, suggesting better oxidation resistance for the system of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ under certain testing condition.

Table 2.1: The thickness of oxide layers formed at ~2720 °C after different times [20]

Unit: μm	PT	T8H2	T5H5	T2H8	PH
1 min	35.99 $\pm$ 2.33	19.74 $\pm$ 1.00	9.00 $\pm$ 0.44	20.30 $\pm$ 2.29	57.28 $\pm$ 3.44
3 min	73.36 $\pm$ 6.64	29.18 $\pm$ 1.43	15.73 $\pm$ 1.09	50.54 $\pm$ 3.43	151.05 $\pm$ 2.86
5 min	305.20 $\pm$ 11.47	39.64 $\pm$ 1.91	28.46 $\pm$ 1.41	101.04 $\pm$ 2.36	189.78 $\pm$ 2.72

PT: Pure TaC

T8H2: $\text{Ta}_{80}\text{Hf}_{20}\text{C}$ solid solution

T5H5: $\text{Ta}_{50}\text{Hf}_{50}\text{C}$ solid solution

T2H8: $\text{Ta}_{20}\text{Hf}_{80}\text{C}$ solid solution

PH: Pure HfC

In another example, Talmy et al. [63] observed that addition of TaB₂ to ZrB₂-SiC composite would improve the oxidation resistance at temperatures up to 1400 °C. All these motivate the research on synthesis and processing of ternary UHTCs.

2.3.1 Previous Study on Synthesis of Ternary UHTC Carbides and Borides

As discussed earlier, synthesis of binary UHTC powders has been extensively studied. However, there have not been many studies on the synthesis of ternary UHTC carbides and borides powders. It should be noted that there are some studies on synthesis of bulk UHTC solid solutions and/or composites from binary carbides and borides using high temperature and/or high pressure processes. For example, Valvoda et al. [64] synthesized (Ta,Hf)C solid solution by annealing the TaC and HfC cold pressed powder mixture for 200 hours at 1900 °C. Ghaffari et al. [65] fabricated bulk Ta_{0.8}Hf_{0.2}C in the presence of molybdenum disilicide (MoSi₂) sintering aid by pressureless sintering at 2000 °C for 1 hour using a micron-sized mixture of TaC-HfC ceramic powders. Ghaffari et al. [66] also fabricated bulk TaC-HfC solid solution at 1650 °C for 5 minutes under pressure of 30 MPa using the spark plasma sintering (SPS) method.

However, these methods could only produce bulk ceramic materials with relatively coarse scale of mixing. On the other hand, as mentioned before, obtaining UHTC powders with reduced particle size will help achieving finer microstructure of the fabricated parts, and it also helps simplify the post synthesis processing such as milling/grinding and improves the sintering activity. Additionally, powders enable flexibility for different applications such as input materials for coatings via plasma spray.

There are some limited studies on synthesis of ternary UHTC carbides and borides powders. For example, Patsera et al. [52] produce (Ta,Zr)C solid solution using self-propagating high temperature synthesis (SHS) of mechanically activated Ta-Zr-C mixture. However, this method suffers from some drawbacks such as long ball milling process and introduction of impurities. Moreover, there would be no control on the morphology of the synthesized powders, which is not favorable. Gaballa et al. [19,67] has synthesized $Ta_{0.8}Hf_{0.2}C$ ceramic powders with particle size of $\sim 1\mu$ via ball milling 4TaC-HfC mixture for 18 hours. However, in addition to not achieving nano-sized (Ta,Hf)C solid solution, long milling procedure and introduction of impurities make this method less industrial desirable for adoption. Simoneko et al. [16] has successfully synthesized highly dispersed $Ta_{0.8}Hf_{0.2}C$ solid solutions using sol-gel method followed by carbothermal reduction reaction (sol-gel/CTR), that produces homogenous mixture of metal oxides and carbon precursors. The gel is pyrolyzed in an inert atmosphere to remove hydrogen and water to produce finely mixed oxide-carbon, which was finally heat treated at higher temperatures (e.g., 1500 °C) for CTR to happen. During CTR, carbon reduces the Hf-Ta oxides and $Ta_{0.8}Hf_{0.2}C$ ternary solid solution powders were obtained. However, the use of vacuum ($\sim 10^{-6}$ MPa) as well as expensive organometallic precursors makes their method less attractive. Recently Jiang et al. [18] has synthesized nano-sized $Ta_{0.8}Hf_{0.2}C$ solid solution powders via solvothermal treatment followed by CTR using inorganic precursors. Nonetheless, the use of non-aqueous solvents, the high cost of autoclave instrument, and the safety concern with autoclave operation make this method less economically favorable.

The synthesis of ternary UHTC borides powders has not been investigated as much as ternary UHTC carbides. Mroz [61] has synthesized $(\text{Ti,Zr})\text{B}_2$ solid solution powders (7-10 μm) from a mixture of the metal oxides and boron in a continuous graphite furnace at 1975 °C. Nevertheless, apart from not achieving uniform nano/submicron-sized solid solution powders, the use of very high BTR temperature of 1975 °C is not desirable. Xie et al. [26] has studied the $\text{TaB}_2\text{-ZrB}_2$ synthesis via sol-gel/CTR method. However, despite the use of the expensive organometallic precursors and non-aqueous solvents, only a $\text{TaB}_2\text{-ZrB}_2$ two-phase composite powder was obtained despite temperature as high as 1800 °C.

2.3.2 Challenges with Synthesis of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ and $\text{Ta}_x\text{Hf}_{1-x}\text{B}_2$ Solid Solution Powders via Aqueous Solution Processing/CTR Method

Compared with other methods to synthesize ternary nano-sized UHTCs, the aqueous solution processing/CTR method has several advantages. First, solution processing offers ability to achieve uniform molecular mixture of precursors, which increases reactivity of precursors and the possibility to produce high purity products due to avoidance of mechanical milling that introduces impurities. Moreover, aqueous solution processing is cheap and does not have safety concerns with waste disposal as non-aqueous solution processing does. As described before, aqueous solution processing will be followed with subsequent heat treatment of pyrolysis and CTR. The advantages of using CTR over other methods have been discussed in details in section 2.2.3. However, although aqueous solution processing/CTR has noticeable advantages over other

methods, there are several challenges for synthesis of ternary $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ and $\text{Ta}_x\text{Hf}_{1-x}\text{B}_2$ solid solution powders using this method.

2.3.2.1 Phase Separation of TaC-HfC

Both HfC and TaC have NaCl-type crystal structure (B1, $\text{Fm}\bar{3}\text{m}$), in which the carbon atoms are accommodated into the octahedral interstitial sites (see Figure 2.4). In addition to their identical crystal structure, these carbides have a very similar lattice parameters ($a_{\text{HfC}}=4.46\text{\AA}$ and $a_{\text{TaC}}=4.44\text{\AA}$). Therefore, theoretically they can form continuous solid solutions at elevated temperatures thanks to their similar crystal structure and lattice parameters.

Figure 2.4: NaCl-type crystal structure

However, according to the TaC-HfC phase diagram (see Figure 2.5), there is a miscibility gap at temperatures below 887 °C, which suggests that at lower temperatures a composite of TaC-HfC would be energetically more stable than the uniform solid solution for a large composition range (e.g., at room temperature x is between ~0.05 and

~0.98). Hence, it is critical to control the synthesis processing to avoid the phase separation from uniform solid solution, which is a thermodynamically favorable process at lower temperatures.

Figure 2.5: Phase diagram of TaC-HfC system [68]

On the other hand, during the CTR process, hafnium oxide (HfO_2) and tantalum pentoxide (Ta_2O_5) should react with carbon to form $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solutions. However, formation of a single-phase $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution via CTR is complicated due to noticeable differences in reactivity of HfO_2 and Ta_2O_5 with carbon, which is also related to the low solubility of those two oxides in each other. Such a difference always leads to the formation of individual TaC and HfC powders. For example, Simoneko et al. [16] has shown that under the same $p\text{CO}$ of 10^{-5} MPa, TaC could form at ~1000K, while the temperature for HfC to form in similar atmosphere is ~1400K (see Figure 2.6). Therefore

during the CTR process TaC can form at much lower temperature than HfC leading to formation of phase-separated TaC-HfC composite instead of single-phase $Ta_xHf_{1-x}C$ solid solution powders. It should be mentioned that the difference between the reactivity of the HfO_2 and Ta_2O_5 with carbon decreases by reducing the pCO . This is why Simoneko et al. [16] applied vacuum during the CTR process for the synthesis of $Ta_{0.8}Hf_{0.2}C$ solid solution powders. However, as already discussed applying vacuum is not favorable for industry production. Moreover, despite the use of vacuum during the CTR process, they were not successful to prevent the phase separation when the CTR heating rate was too slow (< 100 K/min).

Figure 2.6: Equilibrium temperatures of TaC and HfC formation via CTR under different pressures[16]

2.3.2.2 Phase Separation of TaB₂-HfB₂

Continuous solid solutions can form among diborides of group IV and V at higher temperatures ($> \sim 1400$ °C) due to several reasons: First, there is a small difference between their atomic radii ($< 10\%$), second, the borides of group IV and V have the same crystal structure (AlB₂-type (hexagonal, P6/mmm)) and similar lattice parameters (e.g., $a_{\text{HfC}} = 3.141 \text{ \AA}$ and $a_{\text{TaC}} = 3.088 \text{ \AA}$). (Please see Figure 2.7 that shows the AlB₂-type crystal structure with P6/mmm symmetry for the majority of transition metal diborides such as TaB₂, HfB₂, ZrB₂, TiB₂, NbB₂.) However, although these borides should form continuous solid solution, phase separation was observed for the boride previously. For example, Xie et al. [26,27] studied the synthesis of TaB₂-ZrB₂ powder via sol-gel/CTR method and observed obvious phase separation of two individual binary diborides despite the carefully adopted sol-gel reaction route involving organometallic precursors and non-aqueous solvents: Instead of a uniform single phase Ta_{0.25}Zr_{0.75}B₂ solid solution powder, only a TaB₂-ZrB₂ two-phase composite powder was obtained at temperature as high as 1800 °C. Therefore, phase separation, which was noted in (Ta,Zr)B₂ system might also be encountered in the (Ta,Hf)B₂ system due to the very similar physical-chemical properties of Zr and Hf.

Figure 2.7: AlB_2 crystal structure showing $P6/mmm$ symmetry.[24]

2.3.2.3 Microstructural Non-uniformity in UHTC Borides

As already discussed, for synthesis of boron-containing ceramics such as UHTC borides using CTR method, B_2O_3 is the favorable boron precursor as it is much less expensive when compared with elemental boron. However, rapid coarsening of boron containing high temperature ceramics such as B_4C is reported to happen due to the liquid B_2O_3 , which remains in the system even at moderate temperatures [69]. Moreover, due to rapid evaporation of boron trioxide at temperatures above 1100°C , excess amount of B_2O_3 is often added to compensate for boron loss during the synthesis process. This excess liquid B_2O_3 presents at elevated temperatures facilitates mass transport leading to excessive grain growth. However, observation of morphological non-uniformity during the synthesis of boron-containing ceramics including UHTC borides are not limited to the synthesis methods in which B_2O_3 is used as the boron source. For example, Zhang et al. [31] synthesized TaB_2 powders using Ta_2O_5 , B_4C and graphite at 1600°C . However, they also observed a significant non-uniformity in TaB_2 product morphology including both

needle-like (5 μm) and round particles (0.4 μm). Guo et al. [70] has synthesized ZrB_2 powders via BTR method at 1550 °C using ZrO_2 and B as the zirconium and boron sources. However, despite the use of boron instead of B_2O_3 , they also observed noticeable coarsening of the synthesized ZrB_2 powders (~2-3 μm). These observations could be explained by considering the side reactions that might occur during the synthesis process of these borides. For example, for the synthesis of ZrB_2 via the BTR method, it has been shown that ZrO_2 could react with elemental boron to form liquid B_2O_3 phase at temperatures below 1200°C based on the following reaction:

Therefore, the formation of liquid B_2O_3 during the BTR process seems inevitable. To deal with this, Guo et al. proposed a two-step BTR route, in which the sample was washed with hot water after 2 hours of BTR reaction at 1000 °C to remove the excess B_2O_3 . The residual B_2O_3 was further eliminated by heat treating the sample at higher temperature of 1550 °C for one hour to remove the remained residual B_2O_3 . Compared with the sample synthesized in a single step BTR at 1550 °C for one hour, this sample contains smaller particles (0.4-0.7 μm vs 2-3 μm). However, this method still could not lead to synthesis of nanocrystalline ZrB_2 due to the further annealing at higher temperature of 1550 °C.

For the synthesis of TaB_2 using Ta_2O_5 , B_4C and graphite the reaction might happen via two different routes:

single-step route:

two-step route:

Eq. 2.16 is thermodynamically favorable at temperatures above 1064 °C when $p_{\text{CO}}=1\text{atm}$, while ΔG° for the Eq. 2.17 is negative at all temperatures, which makes this reaction thermodynamically favorable at all temperatures. Therefore, B_2O_3 would always form during the synthesis procedure despite the use of B_4C as the boron source.

All these observations confirm that B_2O_3 (as a boron precursor or reaction byproduct) is the main factor responsible for the abnormal grain growth of the UHTC borides during the synthesis process.

Chapter III: Morphological Variation in the Formation of B₄C via CTR

This chapter details the study on synthesis and understanding the morphological variation of B₄C during the CTR process.

3.1 Introduction

Boron carbide (B₄C) is considered as one of the hardest materials known after diamond and cubic boron nitride (c-BN). Possessing this interesting quality paves the way for use of B₄C in different applications, such as abrasive materials for polishing, lapping, cutting tools and ceramic armor for protecting civilian and armed forces [29,44]. Reducing B₄C particle size to the submicron range is desirable as it helps improve mechanical properties of the sintered ceramics. For example, Moshtaghioun et al. [71] showed that by reducing the B₄C grain size from 17.2 μm to 690 nm, the experimentally measured hardness increased from 29 ± 2 to 34 ± 2 GPa, which is consistent with the Hall-Petch equation. Reducing B₄C particle size is also beneficial because it helps simplify the post-synthesis processing such as milling/grinding, and improve the sintering activity.

Different methods, such as elemental synthesis [34,72,73], magnesiothermic reduction, carbothermal reduction (CTR) [40,41], chemical vapor deposition (CVD) [34,72], have been used to synthesize fine submicron and even nano B₄C powders. Among them, elemental synthesis is not economically favorable for industrial manufacturing due to the high cost of elemental boron and high synthesis temperature (1800-2200°C)[73]. For magnesiothermic reduction method, the final synthesized powders are generally contaminated with magnesium compounds, which cannot be easily

removed even by applying hot acids[35,40,72,74,75]. CVD method also is not suitable due to the high cost of gaseous materials and complex equipment [34].

Among all these methods, CTR is most commonly carried out due to its cost-effectiveness and uncomplicated equipment. Additionally, the CTR method provides the greatest flexibility to modify the starting materials and processing conditions to control the product microstructure (e.g., particle size and uniformity) and composition. Eq. 3.1 is the general reaction for the synthesis of B₄C using the CTR method:

Synthesis of B₄C submicron and nanoparticles using CTR method has been studied for some time [40,41,43,47,76]. Weimer et al. [40,41] have synthesized fine uniform B₄C particles (~50nm) at 1900°C in a graphite transport reactor using rapid CTR reaction of B₂O₃ and cornstarch. Miler et al. [42] also have synthesized submicron B₄C particles (~0.4µm) through rapid CTR reaction of boric acid and carbon black at 1750°C in a specially-designed graphite furnace. Yet, Kakiage et al. [45] synthesized micron-sized B₄C powders using PVA and boric acid through conventional CTR at a low temperature of 1250°C.

However, there are not enough studies on in-depth examinations of the interrelationships between composition-processing-microstructure for B₄C formation via CTR. For example, large variation exists in the literature concerning B₄C synthesis condition via CTR: B₄C powder with fine particle size of ~50nm was synthesized at a very high temperature of 1900°C [40,41], whereas coarse ~5µm B₄C powder was synthesized at a very modest temperature of 1250°C [45] using essentially the same kinds of starting materials. How to explain such seemingly counter-intuitive observation was

unclear. Another example is related to the large variability in the morphology of synthesized B_4C powders: different size and shaped particles from tens of micron-sized elongated platelets to micron/submicron-sized polyhedral particles and even nano uniaxial particles all appeared in a relatively pure B_4C product synthesized at $1450^\circ C$ from homogenous precursors, as reported in our previous work [74]. Such an observation also seems to occur in some other studies on the synthesis of B_4C powders [28,30,69,77], but how to explain such variation in the product morphology was also unclear.

Hence, understanding all these is critical to improve control of B_4C production with desired particle size and morphology for industrial applications. In this study, the effects of CTR processing conditions (i.e., temperature, time and heating rate), atmosphere (i.e., argon flow rate), B_2O_3 : C molar ratio, precursors type and moisture absorption of pyrolyzed powders are investigated. The most critical factors influencing the uniformity and morphology of B_4C powders are identified. The variation in morphology development is explained according to considerations from CTR reaction kinetics, and the most favorable condition to obtain uniform-sized fine B_4C powders is recommended based on observations in this study.

3.2 Experimental

For B_4C synthesis, the method follows typical solution processing [43,45–47,74,76] Boric acid (99.99%, Alfa Aesar # 36771) was used as a boron source. For the carbon precursor, sucrose (99.5%, SIGMA # S9378) and polyvinyl alcohol (PVA, 98-99%, Alfa Aesar # 41243) were used as low and high molecular weight carbon sources, respectively. Table 3.1 shows the weight ratio of boric acid, sucrose/PVA and expected B_2O_3 : C molar ratios for all recipes.

Table 3.1: Weight ratio of boric acid, sucrose /PVA for three different recipes

Recipe #	$\text{H}_3\text{BO}_3 : \text{C}_{12}\text{H}_{22}\text{O}_{11}$ weight ratio	Expected $\text{B}_2\text{O}_3 : \text{C}$ molar ratio ^a
R4	1 : 0.81 :	2 : 7 ^b
R16	1 : 1.2	1.33 : 7 ^c
	<hr/> $\text{H}_3\text{BO}_3 : \text{PVA}$ weight ratio <hr/>	
RP1	1 : 3.1	1.77 : 7

a. Expected $\text{B}_2\text{O}_3 : \text{C}$ molar ratio before CTR assuming no C and B_2O_3 loss in pyrolysis.

b. The molar ratio is stoichiometric according to reaction (1)

c. R16 is carbon rich according to reaction (1)

Boric acid and sucrose/PVA were dissolved in deionized hot water and dried at temperatures up to 200°C in air. The dried boric acid-sucrose and boric acid-PVA gel were then pyrolyzed following our previous work [74] and Kakiage et al. [45], respectively, to remove water and other volatile species and produce finely mixed B_2O_3 -C. CTR of pyrolyzed powders was carried out at temperatures in the range of 1150°C to 1750°C for different holding times in flowing argon atmosphere in a tube furnace. The typical heating rate was 10°C/min and typical argon flow rate was 80cc/min. Moreover, a higher argon flow rate of 800cc/min was also applied to study the effect of argon flow rate on B_4C product morphology. Due to limited heating/cooling capability for the tube furnace used, a ceramic micro-reactor set up was designed to realize CTR with a very fast heating rate (measured up to ~400°C/min, named rapid heating rate CTR hereafter). Figure 3.1 shows the schematic of the set up. The set up consists of 6.35mm OD one-end closed alumina tube to carry the pyrolyzed powders. The open end of the alumina tube was hinged to a T-connector to provide gas inlet and outlet (through another 3.18mm OD alumina tube). The tube furnace was preheated to 1750°C and the micro-reactor set up

was pushed into the hot zone to achieve a very high heating rate. The sample was held in the hot zone of the furnace for 3 minutes and withdrawn. Table 3.2 shows the summary of all experimental conditions conducted in this work.

Figure 3.1: Schematic (a) and exploded view (b) of the set-up (micro-reactor) for rapid heating rate CTR experiment.

Table 3.2: Summary of the experimental conditions in this work

Sampl e #	Recipe	CTR temperature	CTR holding time	CTR heating rate	Ar flow rate
1	R4	1750°C	3mins	400°C/min	80cc/min
2	R4	1450°C	2hrs	10°C/min	80cc/min
3	R4	1450°C	2hrs	10°C/min	800cc/min
4	R4	1450°C	20mins	10°C/min	80cc/min
5	R4	1350°C	2hrs	10°C/min	80cc/min
6	R4	1350°C	20mins	10°C/min	80cc/min
7	R4	1250°C	5hrs	10°C/min	80cc/min
8	R4	1150°C	24hrs	10°C/min	80cc/min
9	R16	1450°C	2hrs	10°C/min	80cc/min
10	R16	1250°C	2hrs	10°C/min	80cc/min
11	RP1	1300°C	5hrs	10°C/min	80cc/min

CTR reaction products were characterized by X-ray diffraction (Siemens D5000) for phase identification. The kinetic data for the formation of B_4C powder was obtained following the method reported by Weimer et al. [41] based on composition information, which was obtained by applying the Rietveld profile analysis method using Maud software (version 2.0, University of Trento, Lutterotti et al. [78]) This method is a whole pattern fitting approach and the refinement occurs by modifying the parameters, such as lattice constants, atomic position, scale factor (to modify the peaks intensities) ,etc. [79] It is assumed in this study that carbon is either released as carbon monoxide (CO) or reacts to form B_4C or remains as residual carbon. Having said that, the fractional carbon conversion (α) can be calculated from the relative amount of B_4C and carbon as obtained from quantitative analysis (an example of fractional carbon conversion calculation is Supplementary Materials (1)). In addition, Raman micro-spectroscopy on post CTR samples was also carried out for phase identification in local regions (down to $\sim 10\mu m$ diameter range) using an Ar ion laser (Spectra Physics, model 177G02) with a wave length of 514.5nm. The morphology and particle size of the synthesized powders were studied by a scanning electron microscope (SEM JEOL JSM-6330F). To further investigate the microstructural evolution during the CTR process, a focused ion beam (FIB, JOEL JIB 4500 multibeam) was used to prepare cross sections on the B_4C micron-sized polyhedral particles in the partially reacted sample, followed by SEM analysis.

3.3 Results

3.3.1 Impacts of CTR Temperature and Time

Figure 3.2 shows the SEM images of synthesized B_4C powders from the same batch using recipe R4 via CTR at $1450^\circ C$ for 2 hours. The XRD pattern confirms the

high purity of this sample (see Figure 3.3). On the other hand, as reported before [74] significant non-uniformity in B_4C product morphology including 10 to 30 micron-sized elongated platelets (see Figure 3.2 (b)), submicron-sized ($<1\mu m$) polyhedral particles (see Figure 3.2 (c)), and also nanoparticles ($\sim 50\text{-}80\text{nm}$, see Figure 3.2(d)) can all be observed in this sample.

Figure 3.2: SEM micrographs of synthesized B_4C powders via CTR at 1450°C for 2 hours from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) showing significant non-uniformity in morphology such as micron sized elongated platelets (a and b), sized particles (c), and nanoparticles (d).

Figure 3.3: XRD patterns of synthesized B_4C powders via CTR at 1450°C and 1750°C for holding time of 2 hours and 3 minutes respectively from recipe R4 (starting boric acid : sucrose molar ratio = 1: 0.81).

Figure 3.4 shows the SEM images of the reaction product obtained from the same recipe R4 after CTR at 1450°C for only 20 minutes, which is partially reacted based on XRD. On the other hand, for a short CTR holding time of 20 minutes, significant non-uniformity in morphology is already prevalent and all types of morphologies, including elongated platelets, can be observed, as shown in Figure 3.4 (a-c).

Figure 3.4: SEM micrographs of synthesized B_4C powders via CTR at $1450^{\circ}C$ for 20 minutes from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) showing significant non-uniformity in morphology including micron sized elongated platelets (a), micron and nano-sized polyhedral particles (b), and nanoparticles (c).

Figure 3.5 shows the SEM images of the reaction product using recipe R4 via CTR at $1250^{\circ}C$ for 2 hours. Contrary to conventional expectation of smaller particle size at lower temperature, the results show the formation of micron-sized B_4C particles on the surface of unreacted pyrolyzed powders decorated with nanobelts and nanowires. Additionally, none of the uniaxial nanoparticles as observed before in Figure 3.2(d) were noticed anywhere in this sample. Generally, as a high level of overview, significant non-uniformity in B_4C product morphology (as shown in Figure 3.2-Figure 3.4) has been observed by the authors for a broad range of CTR temperatures (~ 1150 - $1625^{\circ}C$) and holding times (~ 10 minutes-24 hours), and such non-uniformity in product morphology also seems to occur in other studies [28,30].

Figure 3.5: SEM micrographs of CTR product at 1250°C for 2 hours from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) showing heterogeneous nucleation of B_4C particles on the surface of a pyrolyzed particle (a), and nucleated micron-sized B_4C polyhedral particle decorated with nanobelts and nanowires (b).

Figure 3.6 shows SEM images of the rapid heating rate CTR product obtained at 1750°C for 3 minutes from the same pyrolyzed material using the micro-reactor described in the experimental section. The product shows uniform B_4C powders without any large irregular thin elongated platelets or uniaxial nanoparticles. The particle size of the synthesized B_4C powder is around 400nm (estimated from SEM image). The XRD for this sample is given in Figure 3.3, showing primarily B_4C with a trace of unreacted carbon. Diffraction peaks corresponding to line compound of tetra aluminum diboron oxide ($Al_4B_2O_9$) with JCPDS No. 98-002-7010 were also observed as a contaminant due to side reaction between alumina (from micro-reactor wall) and B_2O_3 .

Figure 3.6: SEM micrographs of synthesized B₄C via rapid heating rate CTR at 1750°C for 3 minutes from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81).

3.3.2 Impacts of Atmosphere (Ar flow rate)

Figure 3.7 (a) and Figure 3.7 (b) show low-magnification SEM images of the B₄C powders synthesized via CTR at 1450°C for 2 hours in argon flow rates of 80cc/min and 800cc/min respectively. As can be seen, micron-sized thin elongated platelets and polyhedral particles still can be observed in the B₄C product morphology synthesized in high argon flow rate of 800cc/min. However, compared to 80cc/min, this sample shows better uniformity and contains, on average, smaller particles.

Figure 3.7: SEM micrographs of synthesized B_4C powders via CTR at $1450^\circ C$ for 2 hours from recipe R4 (boric acid: sucrose weight ratio 1 : 0.81) under argon flow rate of 80cc/min (a), and 800 cc/min (b).

3.3.3 Impacts of B_2O_3 : C Molar Ratio

Figure 3.8 (a) and Figure 3.8 (b) show the SEM images of the B_4C powders synthesized via CTR at $1450^\circ C$ for 2 hours using recipes R4 and R16 (lower B_2O_3 : C molar ratio) respectively. Although the CTR process for both recipes was carried out at the same temperature and time, the sample with the lower B_2O_3 : C molar ratio (i.e., carbon rich sample) contains smaller particles with more uniformity. However, the X-ray pattern showed that the lower B_2O_3 : C molar ratio results in significant residual carbon in the final B_4C product [74]

Figure 3.8: SEM micrographs of synthesized B_4C via CTR at $1450^{\circ}C$ for 2 hours from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) (a), and recipe R16 (boric acid : sucrose weight ratio 1 : 1.2) (b).

3.3.4 Impacts of Carbon Precursor Type

Figure 3.9 shows the SEM image of the synthesized B_4C powders via CTR at $1300^{\circ}C$ for 5 hours using boric acid-PVA as boron and carbon sources in which PVA as a polymer has higher molecular weight of 11000-31000g/mol, compared to sucrose (molecular weight of 342g/mol). XRD suggests the sample is only partially converted. Nevertheless, the morphology is still highly non-uniform and *similar* to the synthesized B_4C powders after CTR at $1250^{\circ}C$ for 2 hours using recipe R4 with sucrose as the carbon precursor: micron-sized ($\sim 5\mu m$) B_4C polyhedral particles along with smaller ones ($\sim 0.5-1\mu m$) were formed heterogeneously on the surface of pyrolyzed powders and no B_4C nanoparticles were detected.

Figure 3.9: SEM micrographs of CTR product at 1300°C for 5 hours from recipe RP1 using PVA as carbon precursor (boric acid : PVA weight ratio 1 : 3.1).

3.3.5 Impacts of Aging after CTR (For Partially Reacted Sample that Still Contains B_2O_3)

Figure 3.10 (a) is the SEM image of the partially reacted sample heat treated at 1350°C for 20 minutes showing unreacted pyrolyzed powders decorated with some layered structures. In comparison, Figure 3.10 (b) shows the SEM image of this sample after aging for 6 months. After aging, the morphology changed dramatically: the powder surface became decorated with highly crystalline ~5-10 micron-sized particles. To find out what these crystals are, Raman micro-spectrometry measurement was done by focusing the laser on one of the formed crystals (see Figure 3.11). Two Raman peaks were detected at peak shifts of ~ 500 and 880cm^{-1} which match with the strongest Raman peaks for boric acid [80].

Figure 3.10: SEM micrographs of synthesized B_4C after CTR at $1350^\circ C$ for 20 minutes from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) before aging (a), and after aging for 6 months (b).

Figure 3.11: Raman spectra of the formed crystal in post CTR sample at $1350^\circ C$ for 20 minutes from recipe R4 ((boric acid : sucrose weight ratio 1 : 0.81).

3.4 Discussion

To explain such non-uniformity in the formation of B_4C powders via CTR and quest for better control of product morphology, some understanding about kinetics and mechanism of B_4C formation via CTR reaction is essential. During the CTR process,

at temperatures above the melting point of B_2O_3 ($\sim 450^\circ C$), carbon particles are dispersed into the liquid B_2O_3 and depending on CTR temperature, the reaction could occur through the liquid-solid, gas-liquid-solid, or even gas-solid phase by nucleation and later growth of nuclei. The generalized mathematical formula for nucleation and growth model is given by Erofeyev et al. [81]:

$$\ln(1 - \alpha) = -(kt)^m \quad \text{Eq. 3.2}$$

Where α is the fraction of conversion, k is the reaction rate constant, t is the reaction time and m is the exponent parameter, which can accept values of 1-4 depending on the nucleation rate, growth geometry, and the nature of the reaction rate limiting step [82,83].

Due to the presence of liquid B_2O_3 during the CTR process, the diffusion rate of reactants to the favorable reaction sites could be assumed to be fast enough and the CTR reaction for the formation of B_4C would be interface-controlled, i.e., the arrangement of B-C atoms to form B_4C at the B_2O_3 -C interface would be the rate limiting step. Based on Hulbert et al. [83] when the reaction is interface-controlled, m could accept values of 3-4 for 3D growth (e.g., sphere) depending on nucleation rate: m is considered as 4 when the nucleation rate is constant and 3 when the nucleation rate is zero, i.e., instant nucleation at the beginning and saturation of active sites.

Figure 3.12 shows the plot of the reaction rate constant (k) in natural log versus inverse temperature compiled from different groups, including the present study [28,30,41]. The reaction rate constant k was estimated by fitting the kinetic data, in particular, fraction of conversion α into Eq. 3.2 for the case of $m=4$ assuming constant nucleation rate. The data for fraction of conversion α were either calculated based on

the Rietveld QXRD method (see supplementary materials (1)) or taken directly from the original papers [28,30].

Figure 3.12: Plot of natural log of fitted reaction rate constant k (in unit of sec^{-1}), $\ln(k)$, versus inverse temperature for formation of B_4C via CTR for different data in the literature (i.e., Weimer (1992) [41], Alizadeh et al. (2004) [28], Bigdeloo et al. (2009) [30]), and the current study

Such assumption of $m=4$ is reasonable, especially at low to intermediate temperatures, since partially reacted CTR samples do not appear to have instant nucleation/saturation of fine, nano B_4C throughout (e.g., see Figure 3.5). On the other hand, B_4C nanoparticles were observed in both samples that were heat treated at 1450°C for a short holding time of 20 minutes and long holding time of 2 hours. This strongly suggests constant nucleation under that reaction condition (see Figure 3.2 (d) and 3.4(c)).

It is noted that for the kinetic data by Weimer et al. [30] rate constants are calculated for both the case of $m = 4$ assuming constant nucleation rate, as well as the case for $m = 3$, which assumes instant nucleation/site saturation. The later ($m=3$) was adopted by Weimer et al.[30]based on the high reaction temperature used and short reaction time within minutes or even seconds. However, the present authors feel that $m = 4$ probably better describes the CTR reaction kinetics, especially at temperature $< \sim 1800^{\circ}\text{C}$ with partial reaction and gradual formation of nuclei even after minutes or longer of reaction time. Based on

Figure 3.12 all available kinetic data, including the present study, are in good agreement with each other [28,30,41] regardless of what type of starting precursors or the reaction temperature/time was used. Such consistency suggests the same underlying reaction mechanism dominating in a wide temperature range from ~ 1100 - 1800°C . Similar to the observation by Weimer et al. [41] the slope for the natural log of rate constant versus inverse temperature seems to show an abrupt change from above $\sim 1800^{\circ}\text{C}$: the estimated activation energy above $\sim 1800^{\circ}\text{C}$ is $\sim 820\text{kJ/mol}$ [41] , while below is 327kJ/mol using all data available. The fundamental reason behind this change is not exactly clear at this moment [41].

Nevertheless, as explained, within a large processing window, the reaction appears to follow the same mechanism containing nucleation and growth. Eq. 3.3 shows the nucleation rate based on classical nucleation theory [84].

$$I = I_0 N_s \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{Eq. 3.3}$$

where I_0 is frequency of adding one more atom to a nucleus, N_s is the available nucleation site density and ΔG^* is the nucleation barrier. Different from the

solidification/precipitation-types of phase transformation in which undercooling is required for the formation of the new phase, the CTR reaction is highly endothermic, i.e., the enthalpy change is positive. Therefore, the driving force for the CTR reaction becomes larger (ΔG becomes more negative) by increasing the temperature. Simple analysis of this case suggests that the nucleation barrier (ΔG^*) would decrease with increasing temperature (see Supplementary Materials (1)). On the other hand, by assuming that the available nucleation site density is constant for all samples (i.e., N_s is fixed), it can be concluded from equation (3.3) that the nucleation rate would increase with increasing the CTR temperature. Hence, at low CTR temperatures, a small amount of B_4C nuclei will form at the favorable reaction sites since the nucleation rate is very slow. After nucleation, CTR proceeds via growth, i.e., attachment of B-C atoms to favorable sites of existing B_4C nuclei, sometimes leading to one-dimensional growth, as observed for nanowires (see Figure 3.5(b)).

Figure 3.13 shows a schematic illustrating the CTR reaction limited by slow nucleation at low temperatures from the liquid B_2O_3 -solid carbon intimate mixture. The schematic is supported by actual observation of samples after partial CTR reaction. For example,

Figure 3.13(d) shows the SEM image of the reaction product after CTR at 1150°C for 24 hours ($\alpha=0.026$) from R4. It illustrates the spread out of individual ~5-10 micron-sized B_4C crystals embedded and emerging out from the surface of pyrolyzed materials. Further examination of these micron-sized B_4C crystals was done by preparing a cross section and analyzing the junction between pyrolyzed materials and

the formed B_4C polyhedral particle using FIB, as shown in Figure 3.14. This image together with Figure 3.13 clearly suggests that during CTR, B_4C crystals preferably form on the surface of pyrolyzed materials and they grow along certain orientation(s) (as shown by the flat interfaces between B_4C crystal and surrounding pyrolyzed material). At the same time, the pyrolyzed material nearby gets consumed and recedes.

Figure 3.13: Schematic of nucleation and growth process via CTR at low CTR temperature (e.g., $1150^{\circ}C$, which favors growth due to very slow nucleation and results in formation of huge micron-sized B_4C particles) (a), intermediate CTR temperature (e.g., $1450^{\circ}C$ when nucleation and growth rates are comparable, resulting in formation of huge B_4C micron-sized particles accompanied with nanoparticles) (b), very high CTR temperature (e.g., $> 1800^{\circ}C$ which favors nucleation and results in formation of uniform-sized fine B_4C particles) (c), and SEM micrograph of the CTR product at $1150^{\circ}C$ for 24 hours from recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) showing micron-sized heterogeneously distributed B_4C particles emerging from the surrounding pyrolyzed materials (d)

Figure 3.14: FIB micrograph of the junction between pyrolyzed materials and synthesized micron-sized B_4C polyhedral particle at 1150°C for 24 hours.

When the temperature increases to the intermediate range (e.g., 1450°C) the nucleation barrier will decrease (see Supplementary Materials (1)) and, as a result, the nucleation rate will increase. Hence, the B_4C particles become spaced closer to each other, and in some regions even very fine and uniform nanoparticles are formed due to continuous nucleation. However, the nucleation rate is not high enough to form all the nuclei in the early stage of reaction. Therefore, similar to lower CTR temperatures, CTR also proceeds via growth of formed nuclei, still leading to the formation of micron-sized faceted particles and even elongated platelets (see Figure 2(a-b)). Overall, because the CTR reaction proceeds via both new nucleation and growth of existing ones, the product displays a large variation in morphology, as shown before for the 1450°C/20 minutes and 1450°C/2 hours samples.

When the CTR temperature increases further, such as for the sample after CTR at 1750°C for 3 minutes, nucleation will be fast due to high reaction temperature and it occurs throughout the pyrolyzed material, as illustrated in the schematic in Figure 3.13. As a result, the sample contains uniform-sized B₄C powders, while the short, yet still 3-minute reaction time, probably explains why the particles are submicron instead of nano-size. Therefore, to obtain uniform nanoparticles while maintaining complete reaction, the synthesis condition of even higher CTR temperatures but shorter CTR holding times needs to be adopted. In fact, Weimer et al. [40] successfully synthesized very fine uniform ~50nm particles via CTR at 1900°C and above for less than 3 seconds.

The above discussion shows CTR reaction temperature and associated total reaction time have a dominating role on the product morphology, including uniformity and it can be understood well from the kinetics point of view.

For the influence of Argon flow rate, the calculated free energy change of reaction (1) for different hypothetical carbon monoxide partial pressures using data from JANAF Thermochemical Tables [85] (see Figure S1.3 in Supplementary Materials (1)) shows that, by reducing pCO, the driving force at the same CTR temperature becomes larger (ΔG becomes more negative). It can be easily seen from equation S1.2 in Supplementary Materials (1) that, at a fixed CTR reaction temperature, with increasing driving force via lowering pCO, the nucleation barrier ΔG^* would decrease. Hence, according to equation 3.3, the nucleation rate would increase. This explains the experimental observation, as shown for Figure 3.7: with higher Argon flow rate of 800cc/min versus 80cc/min, the effective CO partial pressure was decreased. As a result, the nucleation rate become

faster accompanied by less growth, leading to much smaller and more uniformly shaped B_4C powders.

For the influence of B_2O_3 : C molar ratio, the observation of finer and more uniform B_4C for lower B_2O_3 : C ratio (see Figure 3.8(b)) could be explained by the existence of B_2O_3 as a liquid during the CTR reaction. Liquid B_2O_3 greatly facilitates the mass transfer during CTR via the growth mechanism, leading to the formation of huge, tens of micron-sized elongated platelets. On the other hand, B_2O_3 may also function as a flux that promotes coarsening of B_4C particles [45] (i.e., smaller B_4C particles merge together into larger B_4C particles). That lower amount of B_2O_3 leading to uniform and smaller B_4C particles is noticeable at low CTR temperatures. Figure 3.15 shows the SEM image of synthesized B_4C at 1250°C for 5 hours using recipe R16. For this sample a significant portion of the B_4C product contains uniform submicron-sized particles (~200nm). On the other hand for the sample synthesized using the B_2O_3 -rich recipe of R4 at the same CTR temperature (1250°C), no nano/submicron particles were noticed (see Figure 3.5).

Figure 3.15: SEM micrographs of CTR product at 1250°C for 5 hours from recipe R16 (boric acid : sucrose weight ratio 1 : 1.2) showing heterogeneous nucleation of submicron and micron B_4C particles on the surface of pyrolyzed material (a), and uniform submicron B_4C particles (b).

For the carbon precursor type, as shown before, even by using the high molecular weight PVA polymer as a carbon source, the CTR products still show the formation of heterogeneously distributed B_4C crystals with micron-sized particles, similar to the sucrose-boric acid mixture, despite the differences in CTR temperature and precursors. Fundamentally, the morphology of synthesized B_4C powders is still primarily determined by the temperature-time effect. This in fact is consistent with the observation by Miller et al. [42]: even with the powder mixture of boric acid and carbon black, uniform submicron B_4C particles were obtained after CTR at $1750^{\circ}C$ for 2 minutes.

Finally, for the moisture effect, Figure 3.10(b) and Figure 3.11 show that for partially reacted samples, product morphology would change dramatically, accompanied by the formation of boric acid during aging. This leads to an experiment in which a few grams of pyrolyzed powder from recipe R4 were exposed to the air for 15 days. Figure 3.16 shows almost 12% weight gain for the pyrolyzed powders after 15 days of aging. Figure 3.17 shows the XRD pattern for the pyrolyzed powders before and after aging. As can be seen in Figure 3.17, the sample contains significant amount of crystalline boric acid after the 15-day exposure, while no trace of boric acid peaks were detected earlier before aging.

Figure 3.16: Weight gain of pyrolyzed recipe R4 versus time after exposure to the air for 15 days.

Figure 3.17: Figure.17. XRD pattern of pyrolyzed powders from recipe R4 (starting boric acid : sucrose molar ratio = 1: 0.81) before and after 15 days of aging.

Figure 3.18 shows SEM images for the sample before and after 15 days of aging in the air. These results indicate that the pyrolyzed sample containing amorphous B_2O_3 and C obtained from solution processing and subsequent pyrolysis heat-treatment readily absorbs moisture to form boric acid and gains weight, leading to global *segregation* of B_2O_3 and C. Therefore, there is a need for greater care to control the moisture adsorption when studying the B_4C formation process due to the dramatic effect on reaction yield and scale of mixing.

Figure 3.18: SEM micrographs of pyrolyzed recipe R4 (boric acid : sucrose weight ratio 1 : 0.81) before aging (a), and after aging (b).

3.5 Conclusion

Uniform submicron-sized B_4C powders have been synthesized via a rapid heating rate carbothermal reduction reaction of the B_2O_3 -C mixture obtained from water-soluble boric acid and sucrose. The morphology of B_4C product powders is determined primarily by reaction kinetics. At low CTR temperatures, due to low nucleation rate, CTR reaction proceeds primarily via growth at favorable sites leading to significant non-uniformity, including nanobelts and micron-sized particles. At very high CTR temperatures ($> \sim 1750^\circ C$) reaction proceeds primarily via nucleation leading to uniform

particles. At intermediate CTR temperatures, mixed mechanism of both nucleation and growth leads to variety of morphologies. Very high CTR temperatures ($> \sim 1750^{\circ}\text{C}$) with very short holding time (within minutes) appears to be the most effective condition in producing uniform nano/submicron sized B_4C particles. Other factors, such as CTR atmosphere and composition, also have effects on the product morphology: higher Ar flow rate lowers pCO and leads to faster nucleation rate and better product uniformity. On the other hand, lower boric acid: sucrose weight ratio limits coarsening, which helps yield more uniform product but at the expense of increased residual carbon. Finally, B_2O_3 in both the pyrolyzed material and partially reacted products readily absorb moisture to form boric acid that not only causes weight change but also dramatically influences the micromorphology. This needs to be managed carefully in order to produce B_4C or to study its formation process.

3.6 Supplementary Materials(1)

3.6.1 Example Showing Definition of the (carbon) Fractional Conversion (α)

The (carbon) fractional conversion (α) was calculated following Weimar et al. (1992) [8]:

$$\alpha = \frac{[\text{B}_4\text{C}]}{[\text{B}_4\text{C}] + \frac{1}{7}[\text{C}]}$$

Take the example for the sample after CTR at 1350°C for 2 hours:

Rietveld analysis, using Maud software gave the relative weight fraction of B_4C and carbon to be:

$$\frac{\text{Wt}\% \text{B}_4\text{C}}{\text{Wt}\% \text{C}} = 63/37$$

B₄C molar weight is 55.25g/mole and carbon molar weight is 12.01g/mole →

Fractional conversion is calculated as:

$$\alpha = \frac{[^{63}/_{55.25}]}{[^{63}/_{55.25}] + \frac{1}{7}[^{37}/_{12.01}]}$$

$$= \sim 72\%$$

The calculated α for all samples in this study are summarized in Table S1.1:

Table S1.1: Kinetic Results for recipe R4 (boric acid : sucrose weight ratio 1 : 0.81)

Temperature (°C)	Time (s)	Carbon conversion (α)
1150	36000	0.026
1250	18000	0.890
1350	7200	0.722
1450	7200	0.993
1450	1200	0.500
1750	180	0.985

3.6.2 Critical Nucleus Size and Free Energy Change for the Formation of B₄C from B₂O₃-C Mixture

The following provides a quick analysis of the critical nucleus size and nucleation barrier for the formation of B₄C nucleus from a fine mixture of B₂O₃ and carbon. Figure S1.1(a) shows liquid B₂O₃ region in close contact with carbon at the surface, as in pyrolyzed sample, before nucleation. Figure S1.1(b) shows a small B₄C nucleus formed at the interface between liquid B₂O₃ and carbon on the pyrolyzed particle surface. (The assumption of nucleation at the surface is supported by the SEM observations for

partially converted samples as shown before for Figures 13(b) and 14 and associated discussion.)

Figure S1.1: Schematic for the formation of B_4C nucleus at the interface of B_2O_3 and C near the surface of the pyrolyzed material

Define the following parameters:

V_{B_4C} is the volume of the B_4C nucleus

d_{B_4C} is the depth of the B_4C nucleus

ΔG_V is the volume free energy change for the CTR reaction to form B_4C

$\gamma_{\alpha/\beta}$ is the interfacial energy between phase α and phase β

t_{B_4C} is the thickness of the B_4C nucleus

w_{B_4C} is the length of the interface between B_2O_3 and C

T_{eq} is the equilibrium reaction temperature , i.e., the temperature at which the free energy change for CTR reaction is zero for a given fixed CO partial pressure (pCO)

The free energy change in nucleation process will be:

$$\Delta G = \Delta G_v V_{B_4C} + d_{B_4C} \cdot w_{B_4C} \cdot (\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C})$$

Because during B_4C nucleation, new interfaces of B_2O_3/B_4C and B_4C/C are created while the original interface of B_2O_3/C is eliminated locally, as assumed in the schematic.

To derive the critical nucleus size, it is also assumed that:

There is a linear relationship between nucleus depth (d_{B_4C}) and nucleus width (t_{B_4C}) , i.e., $t_{B_4C} = c \cdot d_{B_4C}$ which is rational considering that the CTR has to happen near the B_2O_3/C interface and the release of CO through the pyrolyzed material.

$$\Delta G = \Delta G_v \cdot d_{B_4C} \cdot w_{B_4C} \cdot t_{B_4C} + d_{B_4C} \cdot w_{B_4C} \cdot (\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C})$$

$$\Delta G = c \cdot w_{B_4C} \cdot \Delta G_v (d_{B_4C})^2 \cdot + (\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C}) \cdot w_{B_4C} \cdot d_{B_4C}$$

To find the critical condition:

$$\frac{d\Delta G}{d(d_{B_4C})} = 2c \cdot w_{B_4C} \cdot \Delta G_v \cdot d_{B_4C} + w_{B_4C} \cdot (\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C}) = 0$$

$$-(\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C}) = \Delta\gamma \rightarrow$$

$$d_{B_4C}^* = -\frac{(\gamma_{B_2O_3/B_4C} + \gamma_{B_4C/C} - \gamma_{B_2O_3/C})}{2c \cdot \Delta G_v}$$

$$d_{B_4C}^* = \frac{\Delta\gamma}{2c \cdot \Delta G_v} \quad (S1.1)$$

As a result:

$$\Delta G^* = -\frac{\Delta \gamma^2}{4c \cdot \Delta G_v} \cdot w_{B_4C} \quad (S1.2)$$

On the other hand, as can be seen in Figure S2.2, ΔG_v is a function of ΔT ($\Delta G_v \propto \Delta T$)

Figure.S1.2.Volume free energy change as a function of temperature. The temperature at which $\Delta G_f = 0$ is considered as the equilibrium temperature (T_{eq}).

Hence, ΔG^* is inversely proportional to ΔT :

$$\Delta G^* \propto \frac{1}{\Delta G_v} \rightarrow \Delta G^* \propto \frac{1}{\Delta T} = \frac{1}{T - T_{eq}} \quad (S1.3)$$

3.6.3 Change of Free Energy of Formation for the CTR Reaction Eq. 3.1

Figure S1.3: Change of free energy of formation for the CTR reaction Eq. 3.1 with temperature at different p_{CO} .

Chapter IV: Controlling Phase Separation of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ Solid Solution Nano-powders during Synthesis via CTR

This chapter details the study on synthesis and controlling the phase separation of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution powders during the CTR process.

4.1 Introduction

Among all ultrahigh temperature ceramics (UHTCs), hafnium carbide (HfC , $T_m=3900\text{ }^\circ\text{C}$) and tantalum carbide (TaC , $T_m=3880\text{ }^\circ\text{C}$) are of particular interest due to their extremely high melting points, high hardness (TaC : $\sim 19\text{ GPa}$ and HfC : $\sim 20\text{ GPa}$), and high electrical and thermal conductivity and are promising candidates for many important applications that may need to tolerate temperatures above $2000\text{ }^\circ\text{C}$ [86][6][7][8][9]. Previous studies show that by tailoring the composition (e.g., via using alloying elements), ternary UHTC solid solutions and related composites could provide even better properties than simple binary UHTCs, such as further improved oxidation resistance and/or mechanical properties[9][65][87][15][16]. In addition to optimizing the composition, reducing the particle size of these materials from micron to submicron or nanometer range ($\sim 100\text{ nm}$) provides additional benefits in terms of simplified post-synthesis processing and improved mechanical properties [86][88][14]. All these motivate the research on the synthesis of nano-scale $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ ($0 < x < 1$) ternary solid solution and related composite powders.

Although the synthesis of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution/composite powders has been studied for some time, the methods reported in the literature all suffer from some drawbacks, such as high cost, inferior product quality and/or concerns with process

safety[16][67][18][19]. In addition, it is noted that all powder syntheses reported in the literature are performed on a single, Ta-rich composition of $\text{Ta}_{0.8}\text{Hf}_{0.2}\text{C}$, while there is no study on the synthesis of Hf richer compositions such as $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$, which sometimes shows even better mechanical properties [89] and oxidation resistance[20]. Because of these, there is a need for better synthesis methods to produce nanocrystalline $\text{Ta}_{1-x}\text{Hf}_x\text{C}$ powders, especially for those with alternative compositions.

However, examination of the TaC-HfC system suggests some challenges regarding controlling the exact phase(s) that would be obtained: The TaC-HfC phase diagram available shows that the two individual carbides would form a continuous solid solution at high temperature[67]. However, there is also a wide miscibility gap with critical temperatures of $\sim 887^\circ\text{C}$, which suggests that at a lower temperature a TaC-HfC two-phase composite would be energetically more stable than the uniform solid solution over a large composition range for $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ (e.g., at room temperature x is between ~ 0.05 to ~ 0.98). This means uniform, single-phase $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution powder, even after it is formed at a higher temperature, would have a tendency to go through phase separation under certain conditions such as slow cooling to room temperature. Because solid solution and related two-phase composite often offer different properties [90], understanding when and how the phase separation would occur and learning to control it during the synthesis of $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ nano powders is expected to bring significant new insights to the general field of nano science and engineering and help understand other related systems [91][92].

In this paper, the authors report a low-cost synthesis method to produce nano-sized $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution and related nanocomposite powders through aqueous

solution-based processing starting from inorganic metal salts of tantalum pentachloride (TaCl_5) and hafnium tetrachloride (HfCl_4) and soluble hydrocarbon (e.g., sucrose) as the metal and carbon precursors, respectively. The simple equipment and cost-effectiveness of the CTR reaction are preserved in this method to convert the metal and carbon precursors into metal carbide(s). In addition, the precursors and processing conditions could also be easily modified for CTR reaction, which enables better control of product morphology, composition, and phase. For the current system, the initial step of solution processing would yield a fine, even nano-scale mixture of Ta-Hf oxide(s) and carbon, which would then go through the CTR reaction in which oxides of tantalum and hafnium are reduced by carbon to form carbide(s), and the overall CTR reaction (assuming formation of a single-phase solid solution) can be written as below:

As mentioned before, due to the presence of a miscibility gap in the TaC-HfC system, the ternary $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ powder may exist as a uniform solid solution, a nanocomposite of individual carbide phases, or their mixture. Therefore, particular focus was given to revealing the effects of various factors from starting composition to processing conditions on promoting/inhibiting phase separation in the TaC-HfC system, and the fundamental understanding generated is expected to guide synthesizing nanopowders for other multi-component materials.

4.2 Experimental

For $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ powder synthesis, the starting metal precursors used are tantalum pentachloride (TaCl_5 , 99.8%, Alfa Aesar # 14164) and hafnium tetrachloride (HfCl_4 , 98+%, Alfa Aesar # 11834). Sucrose (99.5%, SIGMA # S9378) and phenolic resin

(Plenco, 14353, R5420) were used as carbon sources for the aqueous and non-aqueous systems, respectively. Totally, five recipes were adopted, as summarized in Table. For recipes R6, R7, R11, and R13 that are aqueous-based, TaCl₅ and HfCl₄ were hydrolyzed separately in DI water giving fine white tantalum oxychloride (TaOCl₃) precipitate and colorless water-soluble hafnium oxychloride (HfOCl₂). The aqueous solution and suspension were mixed, and then sucrose was added. For recipe R10 that is organic solvent-based, TaCl₅ and HfCl₄ were dissolved together into 1-pentanol (99+%, Alfa Aesar # 30898) at room temperature forming a translucent solution, followed by addition of phenolic resin, which was pre-dissolved in a co-solvent of ethanol (99.5+%, Acros Organics #61509-0020) at concentration of 0.02 g/ml.

Table 4.1: weight ratio of TaCl₅, HfCl₄ and sucrose (C₁₂H₂₂O₁₁) or phenolic resin ((C₆H₆O·CH₂O)_x) and expected Ta : Hf : C molar ratio used in this study

Recipe #	Solvent	TaCl ₅ : HfCl ₄ : C ₁₂ H ₂₂ O ₁₁ : H ₂ O weight ratio	Expected Ta : Hf : C ^a molar ratio before CTR
R6	DI water	4.47 : 1 : 3.54 : 93.66	4 : 1 : 17
R7	DI water	1.11 : 1 : 1.35 : 19.70	1 : 1 : 6.50
R11	DI water	1.11 : 1 : 1.01 : 19.70	1 : 1 : 4.87
R13	DI water	4.47 : 1 : 2.65 : 93.66	4 : 1 : 12.75
TaCl ₅ : HfCl ₄ : (C ₆ H ₆ O·CH ₂ O) _x : 1-Pentanol : Ethanol weight ratio			
R10	1-Pentanol & Ethanol	1.11 : 1 : 2.18 : 197.16 : 81.57	1 : 1 : 6.50

a: The carbon yield in pyrolysis at 700 °C is considered as 18% for sucrose and 35% for phenolic resin, respectively, based on TGA results.

For all recipes, the obtained mixed solution/suspension was stirred continuously on a hot plate set at 300 °C (the solution temperature was ~100 °C) using a magnetic stir bar until they were completely dried. Then, the dried precursor's mixtures were pyrolyzed at 700 °C for 1 hour in argon (UHP grade, Airgas) with a flow rate of 80 cc/min in a tube furnace with an inner diameter of 40 mm. During the pyrolysis process, precursors lose low molecular weight species (e.g., water, carbon monoxide, and hydrogen chloride) to yield uniform amorphous (as shown later) Ta₂O₅-HfO₂-C fine mixtures. Most of the subsequent CTR heat treatments were performed isothermally in a tube furnace at 1500-1700 °C for different holding times in flowing argon atmosphere. Due to the limited heating/cooling capability for the tube furnace used (up to 10 °C/min), in some cases, a graphite rope was connected to a graphite boat containing the pyrolyzed powders and extended to the exhaust end of the tube furnace. The graphite rope was used to quickly pull the sample into and, later, out of the hot zone of the tube furnace preheated to CTR reaction temperature (e.g., 1600 °C) to investigate the effect of high heating/cooling rate (measured up to ~500 °C/min) during the CTR process, as illustrated in the schematic in Figures S2.1(a) and S2.1(b) (see supplementray materials(2)). Additionally, in order to study the effect of electric field on the formation of Ta_{0.5}Hf_{0.5}C solid solution/nanocomposite powders, CTR of the pyrolyzed powder from recipe R7 was also performed in a spark plasma sintering (SPS) system (Thermal Technologies, Model 10-4, Santa Rosa, CA, USA) under vacuum (base pressure of 2×10⁻² torr) at 1600 °C with a low applied pressure of 5 MPa in a 20 mm diameter graphite die set. To investigate the impact of the pressure alone on the phase formation/separation of Ta_{0.5}Hf_{0.5}C powder, CTR of the R7 pyrolyzed powder was also carried out in the same SPS system but with

two boron nitride (BN) disks touching the graphite die punches so that the BN disks would block the electric current from flowing through the sample (See Figure S2.1(c) in the supplementray materials(2)). All pyrolyzed and CTR reaction products were characterized by X-ray diffraction (Siemens D5000) for phase identification. The morphology and particle size of the synthesized powders were studied by scanning electron microscope (SEM JEOL JSM-6330F) and transmission electron microscope (TEM Phillips CM-200). Thermogravimetric analysis (TGA) was carried out for some samples in the air with the constant heating rate of 10 °C/min to determine the excess carbon content.

4.3 Results and Discussion

4.3.1 Characterization of Pyrolyzed Material

Figure 4(a) and (b) show the XRD patterns of the samples from recipe R6 (Ta to Hf molar ratio of 4 : 1, or abbreviated as Ta : Hf = 4 : 1 in this paper) and R7 (Ta : Hf = 1 : 1), respectively, after pyrolysis at 700 °C for 1 hour, indicating the formation of amorphous Ta and Hf oxides and carbon mixture after pyrolysis. This is favorable since crystallization of the Ta and Hf oxides might be accompanied by more segregation in oxides and negatively affects the homogeneity of the pyrolyzed material. The SEM image for the pyrolyzed powders gives an estimate for the particle size of ~50-100 μm with relatively dense structure (see Figure 4.2 (a) for the sample from recipe R6).

Figure 4.1:XRD patterns of synthesized powders for all recipes with different CTR conditions in a tube furnace.

Figure 4.2: SEM micrographs of (a) pyrolyzed powders at 700 °C for one hour from recipe R6 (Ta : Hf = of 4 : 1) showing formation of 50-100 μm -sized particles with low porosity (b) synthesized powders via CTR at 1600 °C for 1.5 hour from recipe R7 (Ta : Hf = 1 : 1) showing the formation of uniform nano-sized powders ($\sim < 100$ nm). It is noted that this sample is actually phase separated into TaC and HfC, as indicated by XRD (see Figure 4.1(c)).

4.3.2 Observation of Phase Separation

To illustrate the possibility of forming phase-separated TaC-HfC nanocomposite powder, Figure 4.1(c) shows the XRD pattern for a sample from recipe R7 (Ta : Hf = 1: 1) synthesized via CTR at 1600 °C for 1.5 hours. Instead of forming a uniform, single-phase $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution powder, distinct peaks corresponding to individual HfC (JCPDS #98-008-5664) and TaC (JCPDS #98-008-5806) phases were observed for this sample. In addition, no other crystalline phases were identified by XRD. Figure 4.2 (b) is the SEM image of this sample, showing the formation of relatively uniform nano-sized (~ 50-100 nm) powder even though the sample is a composite of two individual carbide phase(s), as suggested by XRD. Understanding and controlling of phase separation

Upon carefully reviewing the TaC-HfC system, it is realized that there are several factors with respect to processing conditions and/or starting recipe that might contribute to the formation of separate TaC and HfC phases at CTR temperature of ~1600 °C, which is well above the critical temperature of 887 °C for the system. In the following, the results of a systematic study aimed at understanding the effects of those factors on controlling the phase(s) formed will be presented, and the implications of the experimental observations will also be discussed.

4.3.2.1 Effect of CTR cooling rate

The first factor studied is cooling rate after the CTR heat treatment. This is because the CTR temperature of ~1600 °C is well above the TaC-HfC system critical temperature. Therefore, it is possible that uniform solid solution powder could first form during CTR reaction. Then, upon slow cooling (e.g., at ~10 °C/min) inside the tube furnace, the uniform solid solution may go through phase separation (e.g., via nucleation-

growth or spinodal decomposition) and give a powder that becomes a two-phase mixture of TaC and HfC. To test such a hypothesis, a sample from recipe R7 (Ta: Hf = 1: 1) was synthesized via CTR at 1600 °C for 1.5 hours, followed by rapid cooling. The fast cooling rate, estimated to be ~500 °C/min, was realized by pulling the graphite sample boat directly out from the hot zone of the tube furnace to the cold zone (~80 °C) after CTR at 1600 °C for the designated time, as described in the experimental section. The expectation was that if the sample obtained using ~50 times faster cooling rate contains more solid solution comparing with the sample conventionally cooled at 10 °C/min, it would support the hypothesis that $Ta_{1-x}Hf_xC$ solid solution forms first under the CTR condition and then goes through phase separation in the slow cooling stage.

Figure 4.1(d) shows the XRD pattern for this sample with rapid cooling after CTR: Individual TaC and HfC peaks are still clearly visible without any hint of solid solution formation. Comparing XRD for this sample with the sample cooled at the normal rate of 10 °C/min (see figure 4.1(c)), it is concluded that significantly faster cooling after CTR does not help prevent phase separation. The implication is that for the $Ta_{0.5}Hf_{0.5}C$ sample from recipe R7, only individual carbides are formed after CTR at 1600 °C for 1.5 hours, while the expected $Ta_{0.5}Hf_{0.5}C$ single-phase solid solution has not been formed yet under this condition, probably due to the slow diffusion process, and the obtained nano powder remains phase separated upon cooling to room temperature.

4.3.2.2 Effects of Solvent, Pre-pyrolysis, and CTR Heating Rate

The second factor studied is related to solution processing. As mentioned in the introduction, uniform single-phase nano-sized $Ta_{0.8}Hf_{0.2}C$ solid solution powders had been synthesized by other researchers via CTR using precursors obtained from organic

solvent-based sol-gel or solvothermal processes [16][18]. In comparison, for the current study, recipes such as R7 are water based. It was observed that upon addition of TaCl_5 to DI water, hydrolysis is very fast, leading to instantaneous precipitation of fine TaOCl_3 particles. On the other hand, HfCl_4 dissolves completely in water and forms a uniform and colorless solution. As a result, it is possible that the observation of separate TaC and HfC phases in the CTR product might have originated from the precipitation of TaOCl_3 upon fast TaCl_5 hydrolysis. This could lead to the loss of homogeneity of the liquid solution and cause large segregation of Ta-rich and Hf-rich regions persisting in subsequent steps of drying, pyrolysis, and finally CTR. Because of the large scale of separation caused by rapid TaCl_5 hydrolysis and precipitation, it would take a longer time for Ta and Hf to inter-diffuse to obtain a uniform solid solution powder.

Thus, in order to test the hypothesis that a uniform liquid solution based on organic solvents, as adopted in other studies, would help reduce or even eliminate separation of Ta and Hf oxides in the solution processing (and later separation of carbides after CTR), less polar, organic solvent of 1-pentanol was used to reduce the rate of TaCl_5 hydrolysis, as described before for recipe R10 with the same Ta : Hf molar ratio of 1 : 1 as R7. This time, unlike when using water as the solvent, both TaCl_5 and HfCl_4 dissolve completely in 1-pentanol and form a uniform, translucent, light yellow-colored solution without any precipitation. However, the XRD pattern for the sample after CTR at 1600 °C for 1.5 hours (Figure 4.1(e)) shows partially overlapping but still separated diffraction peaks corresponding to slightly Hf-doped TaC and Ta-doped HfC phases. Such an observation suggests the use of an organic solvent (and resulting slower hydrolysis) may

help but is unlikely to be the critical factor to prevent phase separation of TaC and HfC for the final carbide products.

Similarly, the influence of removing the pre-pyrolysis step (i.e., the 700 °C /1 h heat treatment to convert the dried material from solution processing to intimate oxides-carbon mixture) and adoption of very fast heating rate (up to ~500 °C /min) for CTR have also been explored for the same recipe R7. (Please refer to supplemental materials section (b) for detailed discussion of the rationale of studying these two factors), and their results are briefly summarized as in Figure 4.1(f) and (g), respectively. Essentially, neither factor prevents the phase separation under the condition explored.

The observations that none of the factors discussed so far prevents the formation of separate TaC and HfC phases under the CTR condition explored (e.g., 1600 °C/1.5 hrs) are attributed to the combined effect of several factors: First, there is very low affinity between the oxide precursors of Ta₂O₅ and HfO₂. To the best of the authors' knowledge, there is no binary phase diagram published for Ta₂O₅ and HfO₂. Nevertheless, the available phase diagram for the Ta₂O₅-ZrO₂ [93] system shows that ZrO₂ has almost zero solubility of Ta₂O₅ while Ta₂O₅ can only accommodate ZrO₂ up to ~2 mol.%. Due to the close chemical and physical similarity of Zr and Hf, it is reasonable to assume similar behavior for the Ta₂O₅-HfO₂ system, that is Ta₂O₅ and HfO₂ would have very low affinity for each other and do not form a solid solution with appreciable solubility[94]. The implication is that, despite the careful efforts in solution processing to mix Ta and Hf salts uniformly (e.g., via the use of an organic solvent), the oxides of tantalum and hafnium, which can exist in amorphous form, will always segregate into

separate Ta₂O₅ and HfO₂ regions. Second, the CTR reaction under the conditions explored is rather fast. One evidence for this claim is given in Figure 4.1(h), which shows the XRD pattern for a sample from recipe R6 (Ta: Hf = 4 : 1) synthesized via rapid heating CTR at 1600 °C for a short time of only 10 minutes: Both TaC and HfC formed individually after only 10 minutes of CTR without any trace of remaining oxides at that temperature. (Note Figures like Figure 4.1(h) have been shrunk vertically for plotting purpose, which makes minor peaks corresponding to HfC less visible.) The combined effect of those two factors mentioned above is that the segregated (amorphous) Ta₂O₅ and HfO₂ regions will always go through separate CTR reactions to form TaC and HfC phases. Then rely on inter-diffusion of Ta and Hf in the high-temperature carbide phases to form a uniform, single-phase solid solution ternary carbide. On the other hand, the inter-diffusion of Ta and Hf at these temperatures can be slow [95], which explains why separate TaC and HfC remain even though the CTR temperature is significantly above the miscibility gap.

4.3.2.3 Effects of CTR Temperature and Holding Time

As explained above, due to the low affinity between Ta₂O₅ and HfO₂ and the large difference in driving force for the formation of TaC and HfC (see supplementary materials(2)), the two carbides would always form individually in CTR; then the solid solution forms via inter-diffusion between them, which can take a significant time. As a result, the formation of Ta_xHf_{1-x}C single-phase solid solution is expected to improve when using higher CTR temperatures and/or longer CTR dwell times. Indeed, Figure 4.3 (a) shows the XRD patterns (showing a zoomed section) for a sample from the Ta- rich recipe R6 (Ta : Hf = 4 : 1) after CTR at 1500 °C for 3 hours and the same sample after

additional annealing at 1600 °C for 10 hours in argon. The as-synthesized sample after CTR at 1500 °C for 3 hours shows clear separation of TaC and HfC phases, while after the additional annealing at 1600 °C for 10 hours, the individual TaC and HfC diffraction peaks merged completely to ones that correspond to a uniform, single-phase solid solution of $\text{Ta}_{0.8}\text{Hf}_{0.2}\text{C}$. However, it is noted that there are limitations on the use of higher CTR temperature or very long CTR dwell time to help the formation of a single-phase solid solution powders. First, they would lead to excessive grain growth, which is undesirable for the purpose of synthesizing nano-sized solid powders. Figure 4.3 (b) shows the SEM images of the sample from recipe R6 obtained from CTR at 1500 °C for 3 hours, while Figure 4.3 (c) is for the same sample after additional annealing at 1600 °C for 10 hours to convert the two-phase composite powder into a single-phase solid solution powder. All particles experience significant coarsening with primary grain size increased from ~50 nm to up to ~500 nm. Second, higher temperature or longer time would add to energy consumption and process cost. Last but not least, for the certain compositions, it may not be effective: Take the example of a Hf-richer sample from recipe R7 (Ta : Hf = 1 : 1), even 15 hours of CTR at 1600 °C or higher CTR temperature of 1700 °C did not seem to prevent the phase separation of TaC and HfC, as shown in Figure 4.1(i) and (j), respectively.

Figure 4.3: (a) XRD pattern for the sample from recipe R6 (Ta : Hf = 4 : 1) synthesized via CTR at 1500 °C, annealed for 10 hours at 1600 °C (b) SEM image of this sample before annealing showing the formation of uniform nano-sized powders (c) after annealing at 1600 °C for 10 hours indicating a noticeable grain growth.

4.3.2.4 Effect of Excess (amorphous) Carbon Content

The seeming difficulty in obtaining single-phase $Ta_xHf_{1-x}C$ nano solid solution powders prompts additional analysis of the various samples obtained. Figure 4.4 (a) and (b) are the TEM images for the sample from recipe R7 ($Ta : Hf = 1 : 1$) synthesized via CTR at 1600 °C for 1.5 hours. The images confirm the synthesized TaC-HfC composite powders are nano-grained with a primary particle size of ~50 nm, which is consistent with SEM observation (see Figure 4.2 (b)). In addition, the images also suggest that each of the nano carbide particles seems to have a low-atomic-mass shell over it. (High-resolution TEM and EDS will be needed to characterize the solid solution nano powders further.) In addition, TGA analysis of this sample in air, as shown in Figure 4.5 (a), indicates that the sample has carbon excess of ~9.5 wt.%. Because XRD pattern for that sample (see Figure 4.1(c)) did not show the presence of any crystalline carbon, carbon must exist in amorphous form, and it is likely that the observed amorphous shell is amorphous carbon on the surface of individual TaC/HfC nanoparticles.

Considering that i) Ta_2O_5 - HfO_2 immiscibility and fast CTR kinetics lead to the formation of individual TaC and HfC phases and ii) excessive (amorphous) carbon might exist as shells over those individual carbide nanoparticles, the effect of excess carbon content (or starting composition) on phase separation of TaC and HfC in the synthesis was investigated. The hypothesis was that the excess carbon in the form of (amorphous) carbon shell over the individual carbide phases might dramatically inhibit the inter-diffusion of Ta and Hf cations between HfC and TaC grains and, as a result, slow the solid solution formation. To test this hypothesis, a sample from recipe R11 with lower carbon content than recipe R7 but the same Ta : Hf molar ratio of 1 : 1 was synthesized

via solution processing and subsequent CTR at 1600 °C for 1.5 hours. Figure 4.1(k) gives the XRD pattern for this sample: Individual peaks corresponding to phase-separated HfC and TaC along with $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution peaks in between, as expected from Vegard's law, were all detected. TGA for this sample indicates it indeed has a lower excess carbon content of ~4.6 wt.%, consistent with the lower carbon recipe R11 used (see Figure 4.5(b)). Therefore, it is evident that lower excess carbon content dramatically improves the inter-diffusion and the formation of a solid solution. Further annealing of this sample for an additional 3 hours enhances the solid solution formation noticeably with the individual carbide peaks almost disappearing, as shown in Figure 4.1(l). In comparison, as mentioned before for figure 4.1 (i), for a sample from recipe of R7 (Ta : Hf = 1 : 1) with higher starting sucrose content, CTR for 15 hours at 1600 °C did not give the same effect in promoting the formation of a uniform solid solution phase.

Figure 4.4: TEM images of TaC-HfC nanocomposite powders synthesized via CTR at 1600 °C for 1.5 hours from recipe R7 (Ta : Hf = 1 : 1) showing the formation of nano-sized particles ($\sim < 50$ nm) often covered by a low-atomic mass shell that is assumed to be amorphous carbon.

Figure 4.5: TGA analysis in air of synthesized powders at 1600 °C via CTR in the tube furnace from aqueous recipes of (a) R7 (Ta : Hf : C = 1 : 1 : 6.5 before CTR) and (b) R11 (Ta : Hf : C = 1 : 1 : 4.87 before CTR).

These results suggest that excess carbon content seems to play a dominating role in determining the phase separation in $Ta_xHf_{1-x}C$ synthesis via CTR reaction: Excess carbon would slow down the inter-diffusion dramatically and greatly inhibit the solid solution formation leading to the formation of individual TaC and HfC phases. The excess carbon effect may also help explain the variations between observations made in this study and those reported in the literature. For example, Jiang et al. [18] reported the formation of single-phase $Ta_{0.8}Hf_{0.2}C$ solid solution powder after 1600 °C /1 hour CTR, while in this study, when using recipe R6 with the same target Ta : Hf molar ratio, minor peaks corresponding to HfC were observed (see Figure 4.1(m)). To further confirm this explanation, experiments using an aqueous-based recipe R13 (Ta : Hf = 4 : 1) with reduced carbon content were carried out. For this sample, the peaks corresponding to HfC were disappeared and merged with TaC peaks (see Figure 4.1(n)). However, it should be noted that the observed peaks in Figure 4.1(n) do not have the symmetric shape. This non-symmetric distribution in the peak profile can be due to the chemical variation such as inhomogeneity of the solid solution. The lattice parameter (a) for this sample was calculated to be ~0.4486 nm using the peaks positions in Figure 4.1 (n), which is close to $Ta_{0.8}Hf_{0.2}C$ solid solution lattice parameter as expected from the Vegard's law and the reported JCPDS card (a=0.4487 nm, # 00-064-0146).

Hence, it is advised that in future synthesis great attention should be given to precisely control and optimize carbon precursor content in starting materials for the synthesis of $Ta_xHf_{1-x}C$ powders: A significant amount of excess carbon would make the uniform solid solution phase difficult to obtain, while too low carbon content might risk incomplete CTR and excessive oxide remaining in the product. It is also noted that the

observation concerning the dramatic influence of excess carbon on Ta and Hf cation inter-diffusion may also throw light into understanding the large variation in sintering kinetics observed for TaC-HfC materials.

4.3.2.5 Effect of DC Electric Field and Applied Pressure

Finally, as stated, the authors also performed CTR using pyrolyzed powders from recipe R7 (Ta : Hf = 1 : 1) in an SPS instrument at 1600 °C for 15 minutes with a low applied pressure of 5 MPa. The purpose was to find out the effect of the external electrical field on the phase formation/separation for $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ nano powder materials, and it was inspired by the reported advantages of applying electric field and pressure in SPS on accelerating mass transport and sintering kinetics for ceramic materials [89][90][66][96]. The SPS temperature, time, and pressure were all intentionally kept at the low end to avoid excessive sintering/grain growth since the goal was to synthesize $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ nanopowders and not to sinter the powders into a dense ceramic body. Figure 4.6 (a) shows the XRD pattern for this sample. The diffraction peaks corresponding to individual TaC and HfC phases disappeared completely, while the peaks corresponding to the single-phase $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution (matching JCPDS card #98-005-4915 and the expectation from Vegard's law) were observed. The SEM image of this sample shows the formation of fine uniform powder with a grain size of ~100 nm (see 4.7 (a)). EDS analysis confirmed the Ta : Hf atomic ratio of 1 to 1, while carbon to total metal (Ta plus Hf) atomic ratio is much higher than 1 to 1, which is consistent with the TGA result for other samples from recipe R7 (see Figure 4.5 (a)). In comparison, when SPS was carried out at the same temperature of 1600 °C but only for 1 minute, the XRD pattern

shows the formation of clearly phase separated TaC and HfC without the detectable amount of either carbide solid solution or oxides. The results from these two experiments suggest that the condition provided by SPS greatly accelerates the inter-diffusion between TaC and HfC and promotes the formation of single-phase $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution; only ~15 minutes of isothermal hold is required to achieve the transformation from individual carbides to the solid solution phase, and the solid solution phase would remain upon cooling to room temperature.

In order to confirm if the above observation of accelerated solid solution formation in SPS using sample from recipe R7 is due to the electric field alone and not the low pressure (5 MPa) applied in SPS, another experiment was performed in the SPS at the same temperature of 1600 °C for the same time of 15 minutes under an even higher pressure of 10 MPa. As described before in the experimental section, for this time, the pyrolyzed powders, instead of touching the graphite die punches directly, were sandwiched between two insulating BN disks (see Figure S2.1(c) in the supplementary materials section (2)) so that almost no DC electrical current would pass through the sample. The XRD pattern for this sample is given in 4.6(b). Diffraction peaks corresponding to individual TaC and HfC were clearly observed with no hint of any solid solution formation. Hence, it is concluded that the applied pressure (5-10 MPa) does not play a major role in forming of single-phase $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution powder, and it is the applied DC electrical field that helps the inter-diffusion between TaC and HfC and accelerates the solid solution formation process. Simple estimation shows that the $\text{Ta}^{+4}/\text{Hf}^{+4}$ migration length due to the DC electrical field at 1600 °C for 15 minutes (as used for the CTR via SPS experiment) would be only on the order of ~1 nm, which is

much shorter than the particle radius. (The readers could refer to supplemental materials (2) for details of the estimation.) Such an analysis suggests that the acceleration of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution formation from individual TaC and HfC carbide phases in as short as 15 minutes when using SPS could not be due to the drift effect. Therefore, it is hypothesized that high concentration of vacancies are created under the high current/high flux condition of SPS, which speeds up the diffusion of cations.

Figure 4.6: XRD patterns of synthesized powders from aqueous recipe R7 (Ta : Hf = 1 : 1) via CTR in the SPS instrument at 1600 °C for 15 minutes: (a) under pressure of 5 MPa with current passing through the sample, (b) under pressure of 10 MPa while the electric current passing through the sample was suppressed using BN disks as insulator.

However, it should be noted that, while applied DC electrical field accelerates the mass transport and faster inter-diffusion and facilitate faster formation of uniform solid solution, it has limitation in that the applied DC electrical field also leads to more

coarsening of the particles. As shown from the SEM image for the sample synthesized via CTR in SPS at 1600 °C for 15 minutes under the pressure of 5 MPa (see Figure 4.7 (a)): the grain size for the powder is ~100 nm, which is significantly larger than both the sample obtained with BN disks suppressing the electric current during SPS (see Figure 4.7 (b)) showing grain size of only ~50 nm and the conventional 1600 °C /1.5 hours CTR sample showing grain size of 50 nm (see for example Figure 4.3 (b)). The obtained result is also consistent with earlier reports that SPS greatly accelerated the sintering for UHTC such as TaC and HfC compared with conventional sintering [89][90][66][96].

Figure 4.7: SEM micrographs of synthesized powders from recipe R7 (Ta : Hf = 1 : 1) via CTR in the SPS instrument at 1600 °C for 15 minutes: (a) under pressure of 5 MPa with electric current passing through the sample, (b) under pressure of 10 MPa while electric current passing through the sample was suppressed using BN disks as insulator. Note that both samples consist of uniform fine powders. However, coarsening due to the electric current passing through the sample is noticeable for (a).

4.4 Conclusions

In this work, the synthesis of the nanocrystalline $\text{Ta}_{1-x}\text{Hf}_x\text{C}$ solid solution and related nanocomposite powders was achieved using aqueous solution-based processing from low-cost TaCl_5 , HfCl_4 , and carbon sources of sucrose followed by pyrolysis and CTR. Phase separation of TaC and HfC was observed for Hf-rich samples of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ regardless of varying processing parameters such as CTR reaction temperature, holding time, and cooling/heating rates as well as solvent type. The strong tendency for forming phase-separated TaC-HfC nano powders composites instead of uniform solid solution powders is attributed to the difference in reactivity between oxides of Ta_2O_5 and HfO_2 and carbon, which is also related to the immiscibility of those two oxides. Such a difference always leads to the formation of individual TaC and HfC nanopowders even after a relatively short CTR time (e.g., 10 minutes at 1600 °C). On the other hand, it was discovered that reducing the excess carbon content or the application of a DC electrical field (as through the use of SPS) would significantly accelerate the diffusion and help the formation of single-phase $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ solid solution powders. (Readers may also refer to Table S2.1 in the supplementary materials for a summary of experimental observation and their implications.) This study illustrates the complexity of the composition-processing-structure relationship during synthesis of multicomponent UHTC nanomaterials. The knowledge generated about how to understand and control phase separation during the synthesis of nano-sized $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ single-phase solid solution versus two-phase composite powders would enhance understanding of other related phenomena as encountered in sintering of these materials as well as the synthesis of other related multicomponent UHTC materials.

4.5 Supplementary Materials (2)

4.5.1 Schematic(s) of the Set-up(s) used in this Study for Powder Synthesis via Rapid Heating/Cooling Rate CTR and SPS

Figure S2.1: Schematic of the set-up for the (a) and (b) rapid heating/cooling rate CTR experiment and (c) schematic of the modified SPS set-up for powder synthesis with suppression of electric current flow via placement of the pyrolyzed powders within the graphite die between two BN disks touching the graphite punches.

4.5.2 Effect of Pre-Pyrolysis and CTR Heating Rate on Phase Separation

The influence of the pre-pyrolysis step was also investigated in this study. As mentioned in the experimental section, after solution processing, a separate pre-pyrolysis step at 700 °C for 1 hour in an inert atmosphere was carried out to remove volatile species (e.g., H₂, HCl, and CO) from the dried products and obtain a fine mixture of amorphous Ta₂O₅-HfO₂ and carbon. To test if the observation of separate TaC and HfC phases is a result of this separate pre-pyrolysis step (that might augment the extent of separation between Ta and Hf oxide regions before CTR), direct CTR heat treatment at 1600 °C for 1.5 hours was carried out for a dried sample from recipe R7 (Ta : Hf = 1 : 1) without going through the separate pre-pyrolysis step. The result is shown in Figure

4.1(f) in the main text: Again the observation of well-separated individual TaC and HfC diffraction peaks indicates that the pre-pyrolysis does not matter in determining whether the end product is a uniform solid solution or a composite of individual carbides.

On the other hand, researchers had previously noticed the large difference in the chemical reactivities of Ta₂O₅ and HfO₂ with carbon to form TaC and HfC: Figure S2 shows the calculated standard Gibbs free energy change for the formation of both TaC and HfC via CTR reactions using thermochemical data of pure substances assuming p_{CO} of 1 atm. The plot shows that CTR for Ta₂O₅ to form TaC can occur at much lower temperatures than for HfO₂: For example at 1800 K (1527 °C), the standard Gibbs free energy change (ΔG°) for CTR of Ta₂O₅ to form TaC is ~ -173 KJ/mol, which is thermodynamically favored, while ΔG° for HfC is still positive (~ 48 KJ/mol). Because of this difference in oxides reactivity with carbon to form carbides, it was hypothesized that when using typical slow heating (e.g., ~ 10 °C/min) for CTR, Ta₂O₅ would start to react first with carbon to form TaC at lower temperature, while HfO₂ could not form until the temperature becomes much higher. Such a difference in reactivities might lead to separation of TaC from other phases. On the other hand, if the heating rate before CTR is high, it is hypothesized that both Ta₂O₅ and HfO₂ would reach above the CTR equilibrium temperature in a very short time, and CTR would occur at the same time preventing the phase separation of individual carbides. In fact, it was reported that fast heating rate of 100 °C/min for CTR seemed to enable the formation of uniform Ta_{0.8}Hf_{0.2}C solid solution powder at a temperature as low as 1500 °C.

In order to test this hypothesis of very high heating rate prevents TaC-HfC phase separation, a sample from recipe R7 (Ta : Hf = 1 : 1) was subjected to CTR at 1600 °C

for 1.5 hours with rapid heating (~ 500 °C /min) as explained in the experimental section. The XRD pattern for this sample is given in Figure 4.1(g) in the main text showing partially overlapping yet still separated XRD peaks, which suggests that fast heating seems to help somewhat, but it could not completely prevent the phase separation of TaC and HfC phases.

Figure S2.2: Gibbs free energy change as a function of temperature at $p_{\text{CO}} = 1$ atm. The temperature at which $\Delta G = 0$ is considered as the equilibrium temperature (T_{eq}).

4.5.3 Estimation of $\text{Ta}^{+4}/\text{Hf}^{+4}$ Migration Length due to the DC Electrical Field

To understand the electrical field effect on carbide solid solution formation, it is noted that, apart from the concentration gradient, electric field can also act as a driving force for the motion of atoms/ions. The application of a DC electric field E will cause a drift motion of ions (in this case Ta^{4+} and Hf^{4+}) with an average drift velocity of $\bar{v}$:

$$\bar{v} = \mu \cdot E \quad (S2.1)$$

where μ is the mobility for the species of interest. As a first approximation, the total cation flux (J_t) would be the diffusion flux due to the concentration gradient plus the flux caused by the electric field:

$$J_t = J_{\text{diffusion}} + J_{\text{drift}} = -D \frac{\partial C}{\partial x} + \bar{v}C \quad (S2.2)$$

where D is the diffusion coefficient and C is the concentration of diffusing atoms. Based on Einstein's relation, ion mobility and diffusion coefficient are related by:

$$\frac{\mu}{D} = \frac{q}{kT} \quad (S2.3)$$

where q is the electrical charge of the ion ($4 \times 1.6 \times 10^{-19} \text{ C}$ for Ta^{4+} and Hf^{4+}), k is the Boltzmann's constant and T is the absolute temperature. Here, the mobility of Ta cations at 1600 °C can be estimated: Consider the observation that a uniform solid solution with primary particle size of ~500 nm was formed from a 4TaC-1HfC phase separated sample after diffusion at 1600 °C for 10 hours (Please see SEM image and related XRD patterns for the sample from recipe R6 synthesized via CTR at 1500 °C for 3 h, which was then annealed for 10 hours at 1600 °C, as given in Figure 4.3 in the main text.), the inter-diffusion coefficient ($\tilde{D}$) can be estimated using:

$$x = \sqrt{\tilde{D}t} \quad (S2.4)$$

where t is the annealing time, which is 36000 sec (10 hours), and x is the diffusion length, which is assumed to be the average grain size of ~500 nm. The effective inter-

diffusion coefficient was estimated to be on the order of $7 \times 10^{-18} \text{ m}^2\text{s}^{-1}$. It is recognized that the estimated $\tilde{D}$ is for the specific composition of $\text{Ta}_{0.8}\text{Hf}_{0.2}\text{C}$ from recipe R6. Nevertheless, because the system of TaC-HfC forms a continuous solution at high temperature, and the diffusion coefficients for Ta and Hf are similar, the relative change in $\tilde{D}$ with respect to concentration would not be very large, and roughly the same number could be used to estimate the mobility for the composition of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$. Therefore, using equation (S2.3), the ion mobility could be estimated to be $1.7 \times 10^{-16} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. Consider the distance between the two graphite punches is $\sim 0.001 \text{ m}$ and the voltage U was kept constant of 5.7 V during the SPS heat treatment, the DC electric field would be:

$$E = \frac{U}{d} = \frac{5.7}{0.001} = 5700 \text{ V/m} \quad (\text{S2.5})$$

Therefore, using equation (S2.1), the drift velocity $\bar{v}$ can be estimated as $1.0 \times 10^{-12} \text{ ms}^{-1}$. Hence, the $\text{Ta}^{+4}/\text{Hf}^{+4}$ migration length due to the DC electrical field at 1600°C for 15 minutes (as used for the CTR via SPS experiment) would be only on the order of $\sim 1 \text{ nm}$, which is much shorter than the particle radius.

4.5.4 Summary of Experimental Observation and Their Implications

Table S2.2: Summary of experimental observation and their implications

R ^a	Experiments						Result	Remark
	Tube Furnace							
	Solvent	Pyrolysis T(°C) ^b /t(h)) ^c	CTR T(°C)	CTR t(h)	CTR CR ^d (°C/min)	CTR HR ^e (°C/min)		
7	Water	700/1	1600	1.5	<u>10</u>	10	P.S [†]	Faster cooling does <i>not</i> prevent phase separation, suggesting individual carbides form first and it is the slow diffusion that prevents solid solution formation.
7	Water	700/1	1600	1.5	<u>500</u>	10	P.S	
7	<u>Pentanol</u>	700/1	1600	1.5	10	10	P.S	Organic solvent is <i>not</i> the critical factor to prevent phase separation.
7	Water	<u>NA</u>	1600	1.5	10	10	P.S	Pre-pyrolysis does <i>not</i> matter in controlling the phase-separation.
7	Water	700/1	1600	1.5	10	<u>500</u>	P.S	Heating rate is <i>not</i> the critical factor to prevent phase separation: Regardless of the CTR heating rate used, Ta ₂ O ₅ and HfO ₂ will always go through separate CTR reactions to form TaC and HfC phases. Then the solid solution formation starts via inter-diffusion of Ta and Hf into the HfC and TaC crystal lattices, respectively

7	Water	700/1	<u>1700</u>	1.5	10	10	P.S	For samples with significant excess carbon, CTR at higher temperature (e.g., 1700 °C) or longer dwell time is not effective in preventing phase separation for Hf richer samples.
7	Water	700/1	1600	<u>15</u>	10	10	P.S	
11	Water	700/1	1600	1.5	10	10	P.S & S.S ^g	
12	Water	700/1	1600	1.5	10	10	S.S	Excess amorphous carbon shell over the individual carbide phases dramatically inhibit the inter-diffusion of Ta and Hf cation and slow down the solid solution formation.
	SPS							
	CTR T(°C)	CTR t(h)	CTR HR (°C/min)	Pressure (MPa)	Electric current			
7	1600	0.25	100	5	<u>Yes</u>	S.S	High level of vacancies formed under the high current condition of SPS speeds up the diffusion of Ta and Hf cations.	
7	1600	0.25	100	<u>10</u>	<u>No</u>	P.S	Although applying continuous pressure during the CTR would help maintain the reactants contact, it does <i>not</i> prevent phase separation.	

a: Recipe b: Temperature c: Time d: Cooling Rate e: Heating Rate f: Phase-Separated
g: Solid Solution

Chapter V: Phase Control during Synthesis of Nanocrystalline Ultrahigh Temperature Tantalum-Hafnium Diboride Powders

This chapter details the study on controlling the phase separation of $\text{Ta}_x\text{Hf}_{1-x}\text{B}_2$ solid solution powders during the synthesis process via CTR and AMR methods.

5.1 Introduction

Borides, carbides and nitrides of group IV–V transition metals are considered as ultrahigh temperature ceramics (UHTCs). Recently, a great deal of attention has been paid to boride UHTCs due to their excellent thermal and chemical stability, high hardness, good thermal shock resistance and decent electrical conductivity. Among all boride UHTCs, hafnium diboride (HfB_2 , $T_m=3250\text{ }^\circ\text{C}$) and zirconium diboride (ZrB_2 , $T_m=3000\text{ }^\circ\text{C}$) are of particular interest because they maintain their strength at elevated temperatures (e.g., $1200\text{ }^\circ\text{C}$), have high resistivity to erosion/corrosion, and also form stable high melting point oxides (e.g., HfO_2 , $T_m=2758\text{ }^\circ\text{C}$). Hence, they are promising candidates for ultrahigh temperature aerospace applications such as rocket propulsion, hypersonic flight and atmospheric reentry.[26,60,86,87,97,98]

However, despite the outstanding properties mentioned above, non-ideal oxidation resistance is one of the major issues limiting the use of HfB_2 and ZrB_2 . For example, in a scenario such as hypersonic flight vehicles in the upper atmosphere, hafnium oxide (HfO_2) and zirconium oxide (ZrO_2) may become nonstoichiometric under low oxygen partial pressure conditions by forming oxygen lattice vacancies, which would enable significant oxygen ion transportation throughout the oxide layer and facilitate the

oxidation process. Another issue with these ceramics is their low fracture toughness, amounting to serious concerns with reliability under severe thermal shock and cyclic loading conditions. [26][25][24][99]

Previous studies have found that properties of binary UHTCs including borides could be further improved in terms of oxidation resistance and/or mechanical properties by tailoring the composition, such as using alloying elements to form solid solutions or composites. [20,65,87,100,101] In particular, researchers have observed that addition of TaB₂ could enhance the oxidation resistance of HfB₂ and ZrB₂ by forming tantalum pentoxide Ta₂O₅ (T_m= 1880 °C) during oxidation, which has a lower melting point than HfO₂ (T_m=2758 °C) and ZrO₂ (T_m=2715°C). Hence, during the oxidation process at high temperatures Ta₂O₅ melts before HfO₂/ZrO₂ and helps the formation of an oxide layer with higher density. On the other hand, introduction of Ta⁵⁺, which has a higher valence than Zr⁴⁺/Hf⁴⁺ would decrease the oxygen vacancy concentration in HfO₂/ZrO₂ and, as a result, reduce the oxygen ion transportation through the oxide layer and slow down the oxidation process. [97][26][25]

In addition to composition, particle size of the synthesized powders is also critical since reducing the size from micron to submicron or even nano (<100 nm) range could benefit post-synthesis processing by reducing the need for extensive milling/grinding and/or decreasing the sintering temperature/time. Achieving finer microstructure for sintered parts could also lead to improved mechanical properties due to the grain size reduction.[14,86,102][74] All these motivate the research on the synthesis of submicron/nano-sized Ta_{1-x}Hf_xB₂ and Ta_{1-x}Zr_xB₂ ternary solid solution and related composite powders.

Although synthesis of boride UHTC powders has been studied before [26][103][104][105], most of the reported methods suffer from some disadvantages, such as inferior product quality, high cost, or concerns with process safety. Moreover, those reported methods were mainly used to synthesize binary UHTC borides and very limited effort has been devoted to the synthesis of ternary UHTC boride solid solution or composite powders. To the best of authors' knowledge, only Xie et al. [26][27] has synthesized TaB₂-ZrB₂ powders using typical sol-gel method [106,107] followed by carbothermal reduction reaction (CTR) at temperatures up to 1800 °C under flowing argon. However, the high cost of the organometallic precursors, the use of non-aqueous solvents, and related issues with waste disposal make that method less favorable. In addition, it is noted that despite the phase diagram suggesting complete solid-solution formation at the CTR temperature (e.g., ~1400-1800°C) [108], only a TaB₂-ZrB₂ two-phase composite powder was obtained instead of a uniform single phase Ta_{0.25} Zr_{0.75}B₂ solid solution powder.

In this study, the authors chose the target system of Ta_{0.5}Hf_{0.5}B₂ since HfB₂ could form a higher melting point composite/solid solution with TaB₂ thanks to its higher melting point when compared with ZrB₂. Moreover, there is no report on the synthesis of nanocrystalline powders of Ta_{0.5}Hf_{0.5}B₂ single phase solid solution or related composites. Two methods were adopted for the synthesis. The first, named CTR-based method, starts from aqueous solution processing of low-cost tantalum pentachloride (TaCl₅), hafnium tetrachloride (HfCl₄), water soluble hydrocarbon of sucrose and boron trioxide (B₂O₃) as the metal, carbon and boron sources, respectively. It then resorts to subsequent heat treatment(s) of the solution processed products to convert the precursors into an intimate,

molecular-scale mixture of (amorphous) metal oxides, boron trioxide, and carbon that reacts further at high temperature (e.g., 1500 °C or higher) through the carbothermal reduction reaction (CTR) to yield the desired boride(s) with emission of carbon monoxide (CO) gas. A representative CTR reaction for the formation of a metal diboride MB₂ from the corresponding oxide M_xO_y, B₂O₃, and carbon can be written as below:

The second synthesis method is based on alkali metal reduction (AMR) reaction in which the same low-cost metal precursors of TaCl₅ and HfCl₄ are directly reduced by a strong alkali metal-based reducing agent such as sodium borohydride (NaBH₄) without the intermediate step of oxide formation. Previous studies have shown that binary transition diborides (e.g., ZrB₂ and TiB₂) could be synthesized using AMR of metal halides (e.g., ZrCl₄ and TiCl₄) [59][104]. As an example, the overall reaction for the formation of ZrB₂ via AMR is written as below:

It should be mentioned that AMR reactions as written above are only a simplification because at elevated temperatures (>500 °C), NaBH₄ may decompose and form sodium hydride (NaH) and boron hydride (BH₃) and the actual process would be more complex. Nevertheless, there has been no study on the synthesis of ternary transition diboride solid solution powders using the AMR method and this is explored in this study. For both synthesis methods, the synthesized powders were characterized using various techniques with the focus on understanding and controlling the formation of a single phase boride

UHTC solid solution powder versus a two boride composite powder in the synthesis process.

5.2 Experimental

In this study, totally, five recipes were adopted, as summarized in Table 5.1 . Recipe R8 and R9 are for the synthesis of $Ta_{0.5}Hf_{0.5}B_2$ using the first CTR-based method. The starting metal precursors used are tantalum pentachloride ($TaCl_5$, 99.8%, Alfa Aesar # 14164) and hafnium tetrachloride ($HfCl_4$, 98+%, Alfa Aesar # 11834), while sucrose (99.5%, Sigma # S9378) and boron trioxide (B_2O_3 , 98.5%, Alfa Aesar # 12290) were used as the carbon and boron sources, respectively. In terms of processing sequence, $TaCl_5$ and $HfCl_4$ were hydrolyzed separately in DI water giving a fine white tantalum oxychloride ($TaOCl_3$) precipitate suspension and a colorless hafnium oxychloride ($HfOCl_2$) solution, respectively, which were then mixed with sucrose and B_2O_3 . The obtained mixed suspensions were stirred continuously on a hot plate using a magnetic stir bar until they get dried (the solution temperature was measured to be $\sim 100^\circ C$).

Table 5.1: Molar ratio of the starting materials for all recipes

Recipe #	Solvent	Catalyst	$TaCl_5 : HfCl_4 : C_{12}H_{22}O_{11} : B_2O_3$ molar ratio
R8	DI water	NA	1 : 1 : 1.14 : 3.4
R9	DI water	Cu*	1 : 1 : 1.14 : 3.4
$TaCl_5 : HfCl_4 : NaBH_4$ molar ratio			
R14	NA	NA	1 : 1 : 6
R17	NA	NA	0 : 1 : 8
R18	NA	NA	1 : 0 : 8

* Cu added at weight ratio of 2% with respect to total weight of dried precursor powders obtained from aqueous solution processing followed by drying on a hot

The dried samples were then placed in a graphite boat and heat treated in a tube furnace at temperatures in the range of ~1500-1600 °C in flowing argon atmosphere (UHP grade, Airgas) at a flow rate of ~80 cc/min and heating/cooling rate of 10 °C/min. During the heat treatment, the dried materials first go through pyrolysis at ~400-600 °C during the heating stage to remove low molecular weight species such as water, carbon monoxide (CO), and other volatile organic species and yield a mixture of oxides and carbon. As the furnace temperature increases further to ~1500 °C or higher, the CTR reaction between oxides and carbon occurs (e.g., see Eq. 5.1) to produce the boride phase(s). For samples based on recipe R9, Cu metal powder (Fisher Chemical # 10965) as a potential catalyst or, more precisely, diffusion promoter, was also added to the dried sample followed by grinding and thorough mixing using a mortar and pestle prior to the CTR heat treatment.

For the second synthesis method based on alkali metal reduction or AMR process, the metal precursors were kept the same, while sodium borohydride (NaBH_4 , 98+%, Acros Organics # 13432) was used as both the reducing agent and the boron source. Recipe R14 targets $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$, while R17 and R18 target pure HfB_2 and TaB_2 , respectively for comparison purpose. The metal salt of TaCl_5 and/or HfCl_4 together with NaBH_4 powders, were mixed using a mortar and pestle in a glove box (VAC Nexus I, Hawthorne, CA, USA) to avoid precursors reacting with/absorbs oxygen and/or moisture. Then, the mixed powders were poured into a graphite boat with a graphite cap. To achieve subsequent AMR reaction, the samples in the graphite boat were heat treated isothermally in a tube furnace at 700 °C for 24 hours in argon (UHP grade, Airgas) with a flow rate of ~ 80 cc/min. The obtained powders were then washed several times with hot

water (~70 °C) to remove impurities such as sodium chloride (NaCl). After having washed the samples, the products were separated by pouring off the water from the top of the container.

All products obtained from the two synthesis methods were characterized by X-ray diffraction (Siemens D5000) for phase identification. Scanning electron microscope (SEM JEOL JSM-6330F) and transmission electron microscope (TEM Phillips CM-200) were used to study the morphology and particle size of the synthesized powders. In addition, BET surface area of selected synthesized powders was measured with a Micromeritics TriStar II (TriStar II 3020 V1.03) gas adsorption analyzer. Thermogravimetric analysis (TGA) was carried out for selected powders in the air with the constant heating rate of 10 °C/min to determine the oxidation resistance.

5.3 Results and Discussion

5.3.1 Phase Separation in $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ Powders for CTR-based Method and its Mitigation

Figure 5.1 (a) illustrates the XRD pattern for a sample from recipe R8 after CTR at 1500 °C for 3 hours. Based on the Ta-Hf-B ternary phase diagram [108] a continuous solid solution of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ should form at this CTR temperature. However, herein, two sets of distinct diboride peaks are observed: One set of diffraction peaks corresponds very well with the JCPDS for HfB_2 (JCPDS# 98-008-5316), suggesting almost pure HfB_2 , while the other set suggests TaB_2 (JCPDS# 98-008-5398) but with peaks shifting consistently towards lower 2θ angles compared with pure TaB_2 . The implication of such an observation is that, contrary to the expectation of a single-phase solid solution, which should give a single set of merged peaks located in between corresponding HfB_2 and

TaB₂ diffraction peaks, a two-phase mixture of HfB₂ and Ta-rich Ta_{1-x}Hf_xB₂ (x estimated to be ~0.38 using Vegard's law) is obtained. This observation is similar to that from Xie et al.'s earlier attempt on synthesizing TaB₂-ZrB₂ powders, [26] for which instead of a single phase Ta_{0.25}Zr_{0.75}B₂ solid solution, two-phase composite powders of (almost) pure ZrB₂ along with solid solution (Ta_{1-x}Zr_x)B₂ (x estimated by the present authors to be ~0.65) were obtained despite the fact that Xie et al. started from careful sol-gel processing of organometallic Ta, Zr, and B precursors dissolved in organic solvents followed by heat treatments including CTR (e.g., at 1600-1800 °C for 2 hours). It is noted that two small peaks corresponding to TaC (JCPDS# 98-000-9884) could be observed at 2θ between 34-42° for the XRD pattern in Figure 4.1(a). This is attributed to slight boron deficiency due to B₂O₃ evaporation during the CTR process at high temperatures (1500 °C in this case).

Figure 5.1: XRD patterns of all samples synthesized via CTR method from different recipes at various temperature and time.

Figure 5.2 (a) is the SEM image of this sample showing the formation of uniform submicron-sized ($\sim 200\text{-}300\text{ nm}$) powder despite the sample is actually a composite of HfB_2 and Ta-rich $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ ($x \approx 0.38$) solid solution as suggested by XRD. Because increasing the CTR dwell time to 6 hours at $1500\text{ }^\circ\text{C}$ for a sample from the same recipe R8 did not seem to make much difference in reducing the extent of phase separation between the two diborides (see Figure 5.1 (b)), the CTR temperature was increased to accelerate the diffusion rate in the hope to achieve a single phase solid solution.

Figure 5.1(c) shows the XRD pattern for a sample from recipe R8 after CTR at $1650\text{ }^\circ\text{C}$ for 1.5 hours. The merging of diffraction peaks appear more obvious and the

relative intensity for HfB_2 peaks becomes weaker, but significant residual HfB_2 can still be observed. In addition, due to the higher CTR temperature used, the SEM images for that sample show noticeable grain growth with particle size increasing to $\sim 300\text{-}400\text{ nm}$ (see Figure 5.2 (b)). Therefore, concerns with excessive grain growth put an upper limit on the CTR temperature that could be applied in the pursuit of single-phase diboride solid solution powders with nano-sized grains.

Figure 5.2: SEM micrographs of synthesized powders from recipe R8 via the CTR-based method at (a) $1500\text{ }^{\circ}\text{C}$ for 3 hours and (b) $1650\text{ }^{\circ}\text{C}$ for 1.5 hours. Both samples shows relatively uniform submicron-sized particles with coarsening due to the higher CTR temperature more noticeable for the $1650\text{ }^{\circ}\text{C}/1.5\text{ hours}$ sample.

As to the origin for the persistent phase separation into two individual diborides during the synthesis of $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ (as well as $\text{Ta}_{1-x}\text{Zr}_x\text{B}_2$) powders, it is noted that our previous study on a similar $\text{Ta}_{1-x}\text{Hf}_x\text{C}$ system [9] had shown that although according to the TaC-HfC phase diagram, $\text{Ta}_{1-x}\text{Hf}_x\text{C}$ solid solutions should form at temperatures above 887 °C, this process is noticeably limited by the slow diffusion of the cations. Therefore, TaC-HfC two-phase composite powders instead of single phase solid solution powders are usually obtained from the CTR-based synthesis method. For the current boride system, as mentioned, the Ta-Hf-B phase diagram indicates complete solid solution at temperatures such as 1500 °C and above. [108] However, the results exhibited in Figure 5.1 (a-c) suggest that TaB_2 - HfB_2 system seems to have the same issue with slow cation diffusion. In fact, it was found in this study that for samples from the same recipe R8, CTR reaction to form the individual TaB_2 and HfB_2 phases finishes within ~15 minutes at 1600 °C (see Figure S3.1 in supplementary materials (3)). Therefore, it is the relatively slow interdiffusion of Ta and Hf cations between the two individual diborides (i.e., TaB_2 and HfB_2) relative to the fast CTR reactions (i.e., between Ta and Hf and B oxides and carbon to form TaB_2 and HfB_2 individually) that limits the formation of the uniform single-phase diboride solid solution such as $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$.

Also similar to the observed persistent phase separation for the TaC-HfC system, the underlying reason for the tendency of Ta_2O_5 and HfO_2 to react separately with carbon as well as B_2O_3 via CTR to form phase separated composite of HfB_2 and Ta-rich $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ can be attributed to several factors: First, the oxides of Ta_2O_5 and HfO_2 have very low solubility of each other, which means before CTR, the two oxides have great tendency to separate from each other, especially at higher temperature (e.g., $>\sim 1000$ °C)

when they evolve to be crystalline from the amorphous state after solution processing. [26][100][27][109] Although there is no published phase diagram for Ta₂O₅-HfO₂, literature suggests Ta₂Hf₆O₁₇ is reported to be the only composition in-between the two ends (i.e., Ta₂O₅ and HfO₂) for the Ta-Hf-O system and it forms only at very high temperatures (above 1800 °C) [110]. In this study, the authors also annealed a 50 : 50 mixture (by molar) from TaCl₅ and HfCl₄ solution processing at 1500 °C in air for 6 hours. The XRD result shows the formation of crystalline Ta₂O₅ and HfO₂ without any sign of significant solid solution formation (i.e., no shift in XRD peaks corresponding to Ta₂O₅ and HfO₂, see Figure S3.2 in supplementary materials (3)). These, together with the low mutual solubility in the system of Ta₂O₅ and ZrO₂, [109] which should have great similarity to HfO₂, lead to the conclusion that Ta₂O₅ and HfO₂ have very limited solubility of each other and the two oxides tend to separate from each other during heat treatment at elevated temperatures (e.g., >~1500 °C). Second, there is also a significant difference between Ta₂O₅ versus HfO₂ in terms of their *reactivity* with carbon as well as B₂O₃ to form TaB₂ and HfB₂, respectively. To illustrate this, Figure 5.3 shows the calculated standard Gibbs free energy change for the formation of both TaB₂ and HfB₂ via CTR reaction using thermochemical data of pure substances [111] assuming *p*CO to be 1 atm. The plot indicates that the CTR reaction for Ta₂O₅ to react with carbon and B₂O₃ to form TaB₂ could occur at much lower temperatures compared to HfO₂. For example, at 1500 K (1227 °C), the standard Gibbs free energy change (ΔG°) for CTR of Ta₂O₅-B₂O₃ is -179 KJ/mol, while this number for HfB₂ is still positive (239 KJ/mol) suggesting that at 1500 K under standard pressure, the CTR reaction for TaB₂ formation

is energetically favorable and could proceed, while it is thermodynamically forbidden for HfB_2 .

Figure 5.3: Calculated standard Gibbs free energy change as a function of temperature at $p_{\text{CO}} = 1$ atm for the formation of TaB_2 and HfB_2 from carbothermal reduction (CTR) reaction.

Because of these factors, i.e., the low solubility of Ta_2O_5 and HfO_2 in each other and the large difference between Ta_2O_5 versus HfO_2 in their reactivity with carbon and B_2O_3 to form the corresponding diborides, Ta_2O_5 and HfO_2 always go through separate CTR reactions to form TaB_2 and HfB_2 . Upon extended heat treatment at high temperature, these borides start to inter-diffuse to gradually form the ternary solid solution. It is worth mentioning that, as already explained in the experimental section, the hydrolysis of TaCl_5 in DI water is indeed very fast giving rise to the formation of a suspension of fine TaOCl_3 precipitates, while HfCl_4 dissolves completely in DI water forming a uniform colorless HfOCl_2 solution. These observations raise the concern that

the phase separation into individual diborides (TaB_2 and HfB_2) observed during the CTR might originate from the difference in hydrolysis behaviors of TaCl_5 and HfCl_4 , i.e., the precipitation of TaOCl_3 and resulting separation from the mixed solution. However, it is noted that even when using the delicate sol-gel processing starting from expensive organometallic precursors and less polar organic solvents, as carried out by Xie et al. that completely avoid separation in the solution processing stage, persistent phase separation between TaB_2 and ZrB_2 still occurred after CTR for the synthesis of TaB_2 - ZrB_2 powders [26][27], which should be very similar to the current TaB_2 - HfB_2 system given the great similarity between Hf and Zr. On the other hand, the current authors also had studied the effect of solution processing of TaCl_5 and HfCl_4 on the phase separation for a similar TaC-HfC system in a previous work [10]. The results showed that although using sol-gel method did prevent the separation of Ta and Hf species during the solution processing stage, it did not prevent phase separation during subsequent CTR to form carbides, especially for intermediate compositions such as $\text{Ta}_{50}\text{Hf}_{50}\text{C}$ with comparable Ta and Hf molar content. These lead to the conclusion that solution processing condition is not the key to preventing phase separation of individual binary diborides during CTR reaction for the current TaB_2 - HfB_2 system.

Therefore, in order to obtain single-phase $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ solid solution powders using the CTR-based synthesis method for such a system, it seems necessary to accelerate the inter-diffusion between the two individual diborides. To achieve this, the authors hypothesized that the presence of a liquid phase “catalyst” or diffusion promoter during the CTR process might help accelerate the diffusion leading to the formation of single-phase solid solution at lower CTR temperatures and/or for shorter holding times.

Figure 5.1 (d) shows the XRD pattern for a sample after CTR at 1500 °C for 3 hours from recipe R9, which is identical to recipe R8 with the exception that 2 wt.% Cu metal powders was added to the dried precursor powders (obtained from aqueous solution processing followed by drying on an hot plate) as the “catalyst” or diffusion promoter. Compared to the sample without Cu at the same CTR temperature and time (see Figure 5.1(a)), the sample with Cu addition shows much greater extent of solid solution formation with diffraction peaks of HfB_2 decreased significantly, while the peaks for Ta-rich solid solution shift more towards lower 2θ angle and broaden and merge more with the HfB_2 peaks, suggesting more Hf incorporation into the lattice (see Figure 5.1 (a) vs. Figure 5.1(d)). When the CTR temperature was increased further to 1650 °C, as shown in Figure 5.1 (e), the individual HfB_2 and Ta-rich TaB_2 peaks have almost completely merged together, implying that $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution powder with very little residual HfB_2 phase has been successfully prepared. Compared to the sample from recipe R8 synthesized via CTR under the same condition (see Figure 5.1 (c)), the samples show better results in terms of solid solution formation. It is noted that for both samples, no Cu were detected. This suggests most of the Cu added had evaporated, which is reasonable due to its low melting point (~ 1085 °C) and relatively high vapor pressure. On the other hand, although Cu addition seems to facilitate inter-diffusion of cations and formation of solid solution, characterization of the samples microstructure indicates that it also leads to coarsening of the obtained powders. As shown from the SEM images for the sample from recipe R9 synthesized via CTR at 1650 °C for 1.5 hours, the particle size for the powder increased to $\sim 600\text{-}700$ nm (see Figure 5.4 (a)), which is significantly larger than the sample obtained from recipe R8 (without Cu) synthesized at the same CTR

temperature and time showing particle size of ~300-400 nm (see Figure 5.4 (b)). This, similar to the adoption of higher CTR temperature, shows the limitation with the CTR-based method in trying to obtain single-phase solid solution nanocrystalline powders.

Finally, it is noted that other than copper metal, some other additives or “catalysts” as potential liquid diffusion promoters during CTR had also been considered. However, due to drawbacks such as high vapor pressure (e.g., molten salt of sodium chloride or NaCl) or reactivity with carbon (e.g., silicon) and/or boron (e.g., iron), those other additives did not yield as significant results as copper.

Figure 5.4: SEM micrographs of synthesized powders after CTR at 1650 °C for 1.5 hours from (a) recipe R9, which contains copper metal (Cu) as a “catalyst” or, more precisely, a diffusion promoter and (b) recipe R8, which does not contain Cu, respectively. Particle coarsening due to the presence of the liquid Cu as a diffusion promoter during the CTR process is noticeable for the sample from recipe R9 with Cu (a).

5.3.2 Preparation of Nanocrystalline $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ Solid Solution Powders via AMR Method

From the previous section, it is seen that for the CTR-based method, the TaCl_5 and HfCl_4 precursors go through solution-based processing and turn into (amorphous) oxides of Ta_2O_5 and HfO_2 that react further with carbon as well as B_2O_3 in subsequent high temperature carbothermal reduction reaction or CTR to form the diborides. However, as mentioned, Ta_2O_5 and HfO_2 have very low affinity for each other and do not readily form a solid solution, while they also have very different reactivity with carbon and B_2O_3 . The result is that Ta_2O_5 and HfO_2 would always react separately with carbon as well as B_2O_3 to form TaB_2 and HfB_2 , which then need to inter-diffuse to each other at high temperatures to form the $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ solid solution phase, and the overall reaction for the formation of $(\text{Ta-Hf})\text{B}_2$ solid solution powder via CTR is a multi-step process. Although higher CTR temperature or the addition of a diffusion promoter (e.g., copper metal powder) seems to help accelerate the diffusion and solid solution formation, they result in undesirable grain coarsening, which is contrary to the objective of trying to obtain nanocrystalline diboride solid solution powders.

On the other hand, as mentioned in the introduction, the synthesis of metal diboride has also been achieved using the alkali metal reduction or AMR method. It is noted that during AMR the metal chlorides directly get reduced by a strong reducing agent such as NaBH_4 and it does *not* involve the formation of metal oxides. Hence, the authors hypothesized that this AMR-based method might be applicable for the synthesis of nanocrystalline powders of single-phase ternary UHTC diboride solid solutions by

completely avoiding the metal oxides formation stage and associated tendency for phase separation in the resulting ternary diborides.

Figure 5.5 (a) shows the XRD pattern for a pure HfB₂ sample synthesized from R17 after AMR at 700 °C for 24 hours in a covered graphite boat in the flowing argon atmosphere. All diffraction peaks match JCPDS card #98-008-5316 for HfB₂, suggesting high product purity. The pattern shows dramatic peak broadening indicating the formation of very small grains on the order of ~6 nm as estimated by Scherrer equation. Figure 5.5 (c) shows the XRD pattern for a pure TaB₂ sample synthesized from recipe R18 via AMR also at 700 °C for 24 hours. The diffraction peaks match perfectly with JCPDS card # 98-008-5398 for TaB₂. However, compared with HfB₂, peaks corresponding to TaB₂ are broader suggesting the formation of even smaller grains (size estimated to be ~ 3.5 nm). In comparison, Figure 5.5 (b) shows the XRD pattern for a sample from recipe R14 synthesized via the AMR method also at 700 °C for 24 hours with the target composition of Ta_{0.5}Hf_{0.5}B₂. Unlike the samples synthesized from the CTR-based method, the diffraction peaks corresponding to individual TaB₂ and HfB₂ merged completely into a single set of broad peaks that correspond to Ta_{0.5}Hf_{0.5}B₂ solid solution (JCPDS # 98-004-9539). The SEM image for this Ta_{0.5}Hf_{0.5}B₂ solid solution sample shows highly agglomerated powders with particle size of ~50-100 nm (see Figure 5.6). The BET surface area for the sample is measured to be 4.9 m²/g, and the estimated average particle size using this number is ~100 nm (See supplementary materials (3)) for the calculation steps), which is consistent with the SEM observations (see Figure 5.6 (a)). Figure 5.6(b) shows the TEM image for this sample. It confirms the formation of nanopowders with individual grain size on the order of ~3-5 nm.

Figure 5.5: XRD patterns of three samples synthesized via the alkaline metal reduction (AMR) method from different recipes after the AMR reaction at 700 °C for 24 in close graphite boat in a tube furnace with flow argon atmosphere: (a) from recipe R17 targeting pure HfB_2 , (b) from recipe R14 targeting $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$, and (c) from recipe R18 targeting pure TaB_2 .

The measured d-spacing from the lattice fringes is ~ 0.34 nm, as shown in Figure 5.6 (c), which is very close to that for the (0001) plane of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ (JCPDS# 98-004-9539). Overall, SEM and TEM analysis suggest uniform morphology for the obtained nanoparticles. Therefore, it appears that in order to obtain nanocrystalline single phase $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ solid solution powders, the AMR-based method offers certain advantages over the CTR-based method as the former avoids the formation of oxides and the complication involving phase separation due to low solubility of Ta_2O_5 and HfO_2 and the large difference in the oxides' reactivity against carbon and B_2O_3 .

Figure 5.6: SEM (a) and TEM (b and c) micrographs of the synthesized powder via AMR reaction at 700 °C for 24 hours from recipe R14 showing the formation of uniform nanocrystalline $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution powders with grain size much smaller than ~50 nm. The measured d-spacing of ~0.34 nm from TEM is very close to the expected value for the (0001) plane of the $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution.

The oxidation resistance of TaB₂, HfB₂, and Ta_{0.5}Hf_{0.5}B₂ solid solution nanopowders synthesized via the AMR method was evaluated using TGA in air and the results are shown in Figure S3.4 (see supplementary materials(3)). It shows that the Ta_{0.5}Hf_{0.5}B₂ solid solution powder does not offer dramatically improved oxidation resistance versus pure HfB₂ (see Figure S3.4). In fact, the onset oxidation temperature for AMR synthesized HfB₂ nanopowder is ~700 °C, while it is only ~600 °C for Ta_{0.5}Hf_{0.5}B₂ (and ~600 °C for TaB₂). The lower oxidation onset temperature for TaB₂ and Ta_{0.5}Hf_{0.5}B₂ nanopowder comparing with HfB₂ is hypothesized to be related to the smaller grain size of the synthesized TaB₂ and Ta_{0.5}Hf_{0.5}B₂ solid solution powders, which make the Ta_{0.5}Hf_{0.5}B₂ solid solution powder kinetically more susceptible to oxidation. This is supported by the XRD patterns for the samples showing higher crystallinity and narrower peaks for the HfB₂ nanopowder versus both TaB₂ and Ta_{0.5}Hf_{0.5}B₂ (see Figure 5.5). The air TGA results for the powders from AMR-based synthesis route also show that the weight gain was 46%, 36.28% and 41.73% for TaB₂, HfB₂ and Ta_{0.5}Hf_{0.5}B₂, respectively, which are reasonably close to the theoretical weight gain of 43.44% for pure TaB₂, 39.98% for pure HfB₂ and 41.71% for Ta_{0.5}Hf_{0.5}B₂ solid solution.

Finally, as mentioned in the experimental section, when using the AMR method, the obtained powder had to be washed in hot water to remove the NaCl reaction product, which might cause partial oxidation of the sample. This might be one of the reasons that EDS analysis of the AMR powder contains relatively high oxygen content of 2 wt%, which is equivalent to ~8 at.%. It might also explain the relatively thick amorphous layer around the synthesized boride powders, as seen in the TEM in Figure 5.6(b).

In order to check if the crystallinity of the nano diboride solid solution powders synthesized via the AMR method could be improved and also gain more understanding about the amorphous impurities (suspected to be Na and/or boron containing compounds such as B_2O_3) surrounding the nanopowders, $Ta_{0.5}Hf_{0.5}B_2$ solid solution (from R14) as well as HfB_2 (from R17) powders from AMR (at 700 °C for 24 h) were further annealed at 1500 °C for 3 hours in flowing argon. The XRD patterns for both samples show high intensity diffraction peaks suggesting a significant improvement in the crystallinity of the products after the annealing (see Figure 5.7 vs. Figure 5.5 for before the annealing). Furthermore, the XRD peaks for these samples after annealing are much narrower as compared to before annealing. This could be attributed to the grain growth during the annealing process, which was confirmed by comparing the SEM images of the samples before and after annealing, as shown in Figure 8: For both samples, the particles experience significant coarsening after the 1500 °C /3 hours annealing with individual grains grow from nanometer range to submicron range.

Figure 5.7: XRD patterns of two samples synthesized via the alkaline metal reduction (AMR) method at 700 °C for 24 hours and then annealed at 1500 °C for 3 hours in flow argon: (a) from recipe R17 targeting pure HfB_2 , (b) from recipe R14 targeting $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution

In addition to the high annealing temperature used, grain growth of the diboride (including solid solution) powders can also be accelerated by the amorphous impurities (suspected to be Na and/or boron containing compounds such as B_2O_3) surrounding the crystalline diboride (solid solution) powders, as observed in TEM (see Figure 5.6). Such amorphous impurities are expected to turn into liquid form during heating and significantly promote mass transport. The significant weight loss of the samples observed after annealing (~35% and 48% for $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution and HfB_2 , respectively) could be associated with the evaporation of such amorphous impurities. It is worth noticing that the weight loss and also the grain growth of the $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution are less than that of HfB_2 (see Figure 5.8(c) and 5.8(d)). This could be due to the lower

amount of NaBH_4 used in recipe R14 than R17 resulting in formation of less amorphous impurities. The formation of the amorphous impurities and associated weight loss during high temperature annealing constitutes a limitation for the current AMR method and additional studies are required to further optimize the process and mitigate the impurity content.

Figure 5.8: SEM micrographs of the HfB_2 (a, b) and $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution (c, d) powders synthesized via the AMR method (at 700 °C for 24 hours) before (a, c) and after (b, d) the separate annealing at 1500 °C for 3 hours. The grains grow significantly after the 1500 °C/3 h annealing for both HfB_2 (from R17, compare (b) versus (a)) and $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution (from R14, compare (d) versus (c)) samples.

Finally, it is recognized that the current study is confined to powder, while UHTC materials are mostly utilized as consolidated ceramic bodies. Therefore, additional study aimed at optimizing the processing to reduce the oxygen content need to be carried out. In addition, studies aimed at understanding the sintering behavior of the synthesized (Ta-

Hf)B₂ solid solution nanopowders and the mechanical and chemical properties for the densified ceramic bodies will also be carried out in future to fully understand their properties including both advantages and disadvantages.

5.4 Conclusions

In this study, submicron-sized TaB₂-HfB₂ powders were synthesized via aqueous solution processing of low-cost TaCl₅, HfCl₄, sucrose and B₂O₃ as carbon and boron sources, respectively followed by CTR (e.g., at 1500 °C for 3 hours). Despite the phase diagram suggesting single phase solid solution formation, the products tend to contain two separate phases of Ta-rich Ta_{1-x}Hf_xB₂ and almost pure HfB₂. The tendency for the formation of phase separated TaB₂-HfB₂ composite powder is attributed to the low mutual solubility of Ta₂O₅ and HfO₂, the large difference in reactivity of those oxides with carbon and B₂O₃ to form the corresponding diborides, and the slow cation (Ta and Hf) inter-diffusion relative to the CTR reactions to form the individual borides. Although higher CTR temperature or addition of diffusion promoter such as copper metal powder during the CTR process help improve solid solution formation by accelerating the diffusion, they also lead to particle coarsening and deviate away from the goal of obtaining nanocrystalline Ta_{1-x}Hf_xB₂ solid solution powders. In comparison, it was observed that direct reduction of TaCl₅ and HfCl₄ via the alkali metal reduction or AMR method by a strong reducing agent such as NaBH₄ leads to the formation of a single phase Ta_{0.5}Hf_{0.5}B₂ solid solution nanopowders. The relative success for the AMR-based method is attributed to the avoidance of tantalum and hafnium oxides formation and the associated complication involving boride phase separation in the CTR reaction,

while the relatively low reaction temperature (e.g., 700 °C) ensures the formation of nano-sized grains. Further studies aimed at optimizing the synthesis process to improve purity and understanding the properties for the synthesized nanocrystalline single phase $\text{Ta}_{1-x}\text{Hf}_x\text{B}_2$ solid solution powders especially their sinterability and the mechanical and chemical properties of the sintered ceramic bodies will be carried out in future.

5.5 Supplementary Materials (3)

5.5.1 XRD Pattern for the Synthesized Sample from Recipe R8 at 1600 °C for 15 Minutes

Figure S3.1: XRD pattern of the synthesized powders from recipe R8 (Ta: Hf molar ratio of 1:1) at 1600 °C for 15 minutes.

5.5.2 Annealing of Ta₂O₅-HfO₂ Mixture for 6 hours at 1500 °C

Figure S3.2: XRD pattern of the annealed Ta₂O₅-HfO₂ mixture (Ta: Hf molar ratio of 1:1) at 1500 °C for 6 hours

5.5.3 BET Analysis of Ta_{0.5}Hf_{0.5}B₂ Solid Solution Powders Synthesized via AMR Method

Figure S3.3 shows the nitrogen gas adsorption-desorption isotherm for Ta_{0.5}Hf_{0.5}B₂ solid solution powders synthesized via AMR method. This plot displays the volume of nitrogen adsorbed versus relative pressure (P/P_0).

Figure S3.3: Nitrogen adsorption-desorption isotherm for $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution powders synthesized via AMR method.

The correlation coefficient of the linear regression (r) was greater than 0.99. The surface area and pore volume calculated from Figure S3 are $4.95 \text{ m}^2/\text{gr}$ and $0.027 \text{ cm}^3/\text{gr}$, respectively. These results suggest that the synthesized powders have low porosity, which is consistent with the SEM images for this sample.

The average particle size could be estimated using the equation below:

$$\text{Average particle size} = \frac{6000}{\text{BET surface area} \left(\frac{\text{m}^2}{\text{gr}} \right) \times \text{density} \left(\frac{\text{gr}}{\text{cm}^3} \right)} \quad (\text{S3.1})$$

The density of the $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution was calculated using equation S2:

The densities of pure HfB₂ and TaB₂ are 11.2 g/cm³ [24] and 12.6 g/cm³ [98], respectively. Therefore for a composition of Ta_{0.5}Hf_{0.5}B₂ the density would be approximated as:

$$\rho_{50:50} = (0.5 \times 11.2) + (0.5 \times 12.6) = 11.9 \frac{\text{gr}}{\text{cm}^3} \quad (\text{S3.2})$$

Hence, using equation S1 the calculated average particle size for Ta_{0.5}Hf_{0.5}B₂ solid solution powders is estimated to be ~ 100 nm.

5.5.4 TGA Analysis of Boride Powders Synthesized via AMR Method

The TGA test was carried out in air for binary HfB₂ and Ta_{0.5}Hf_{0.5}B₂ solid solution powders synthesized via AMR method with heating rate of 10 °C/min. The TGA analysis for these samples as shown in Figure S3.4 indicates that Ta_{0.5}Hf_{0.5}B₂ solid solution nanopowders did not show significantly enhanced oxidation resistance than nano HfB₂ powder. This might be due to the different grain size of the synthesized HfB₂ versus the TaB₂ and Ta₅₀Hf₅₀B₂ powders. From XRD pattern (see Figure 5.5), it seemed that the HfB₂ are better developed in crystallinity with larger grains than TaB₂ and the Ta₅₀Hf₅₀B₂ solid solution powders. This may make the TaB₂ and Ta₅₀Hf₅₀B₂ solid solution powders more susceptible to oxidation at elevated temperatures. The underlying reason for the difference in crystallinity and grain size is still under investigation.

In addition, as can be seen in Figure S3.4, there is a weight loss from room temperature up to ~150 °C for all samples, which could be attributed to moisture removal. Based on the TGA results, the weight gain due to oxidation of binary TaB₂, HfB₂ and Ta₅₀Hf₅₀B₂ solid solution powders are ~ 46%, 36.28% and 41.73%, respectively (the baseline for the weight gain calculation was set a lower value after the initial weight loss caused by

moisture removal). The obtained results are very close to the theoretical weight gain (43.44% for pure TaB₂, 39.98% for pure HfB₂ and 41.71% for Ta₅₀Hf₅₀B₂ solid solution).

Figure S3.4: TGA analysis of synthesized TaB₂, HfB₂ and Ta_{0.5}Hf_{0.5}B₂ solid solution powders via AMR method in air.

Chapter VI: Summary

6.1 Synthesis of B₄C Powders

The present study investigated the synthesis of uniform submicron-sized B₄C powders using CTR of finely mixed B₂O₃ and carbon obtained from low-cost water-soluble precursors. The effects of CTR thermal profile, CTR atmosphere and precursors on product phase purity and morphology were systematically studied. Major conclusions are again listed below:

- Morphology of B₄C product from CTR is determined primarily by reaction kinetics: At low temperature (e.g., 1250 °C), CTR reaction proceeds via heterogeneous nucleation and growth at favorable sites leading to significant non-uniformity including nanobelts and micron sized particles. At high temperatures (e.g., 1750°C) the CTR reaction proceeds via homogenous nucleation with almost no growth leading to uniform particle and the exact size depend on reaction temperature/time. Very high temperatures (>1800 °C) and very short dwell time (on the order of several seconds) could give rise to formation of uniform B₄C nanoparticles. On the other hand at intermediate temperatures (e.g., 1450 °C), mixed mechanism of both nucleation and growth leads to a great variety of morphologies.
- Other factors could also influence B₄C product morphology to an extent: Higher argon flow rate/using vacuum would lower pCO resulting in faster reaction kinetics and, as a result, smaller and more uniform B₄C particles. Moreover, more uniform B₄C powders would be obtained using lower B₂O₃:C molar ratio.

However, the amount of residual carbon in the final product powders would increase due to the insufficient B_2O_3 .

- Moisture adsorption for both pyrolyzed powders, which contains carbon and B_2O_3 and final CTR product not only causes weight gain but also results in significant changes in micromorphology via the formation of boric acid crystals through the reaction of B_2O_3 including residual B_2O_3 in CTR products with moisture.

6.2 Synthesis of $Ta_xHf_{1-x}C$ Nanopowders

Synthesis of single-phase $Ta_xHf_{1-x}C$ solid solution nanopowders via CTR of finely mixed amorphous tantalum-hafnium oxide(s) and carbon obtained from a low-cost aqueous solution processing of $TaCl_5$, $HfCl_4$, and sucrose was studied. The influences of starting compositions and processing conditions on phase separation during the formation of carbide phase(s) were investigated and the major conclusions are again listed below:

- Despite the success with the synthesis of nano $Ta_{0.8}Hf_{0.2}C$ solid solution powders, phase separation of TaC and HfC was observed in most cases for $Ta_{0.5}Hf_{0.5}C$, in spite of varying parameters such as solvent used/hydrolysis rate, cooling rate, heating rate, and holding time.
- The strong tendency to form phase-separated TaC-HfC nano powder composites instead of nano $Ta_xHf_{1-x}C$ solid solution powders is believed to originate from the low affinity of Ta_2O_5 and HfO_2 for each other, which leads to formation of individual TaC and HfC nano grains. These formed TaC and HfC nanopowders do not readily form uniform solid solution powders despite long holding above the critical temperature (887 °C) due to slow diffusion.

- It was found that excess carbon has a dramatic effect on slowing down the inter-diffusion of Ta and Hf and therefore delays the solid solution formation.
- When using SPS for conducting the CTR at low pressure (5 MPa) and low temperature (1600 °C), uniform solid solution of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{C}$ with nano grains was obtained, suggesting that electrical field might significantly accelerate the cation diffusion through creation of high concentration of vacancies, which are created under the high current/high flux condition of SPS.

6.3 Synthesis of $\text{Ta}_x\text{Hf}_{1-x}\text{B}_2$ Nanopowders

Synthesis of nanocrystalline $\text{Ta}_x\text{Hf}_{1-x}\text{B}_2$ solid solution and composite powders using two low-cost methods of CTR and Alkali metal reduction reaction (AMR) were studied. The major conclusions are listed below:

- Submicron-sized $\text{TaB}_2\text{-HfB}_2$ composite powders were synthesized via aqueous solution processing of low-cost TaCl_5 , HfCl_4 , sucrose and B_2O_3 followed by CTR at 1500-1650 °C for different holding times from 10 minutes to 3 hours. However, phase separation of TaB_2 and HfB_2 was observed regardless of using various CTR temperatures and holding times.
- The tendency for formation of phase-separated $\text{TaB}_2\text{-HfB}_2$ submicron-sized composite powders could be due to the low affinity of Ta_2O_5 and HfO_2 for each other and the difference in reactivity of the corresponding oxides with carbon, which give rise to phase separation of individual binary diborides even after long CTR time (e.g., 1500 °C for 6 hours).

- Adding Cu during the CTR process noticeably improved solid solution formation thanks to faster diffusion with the presence of a liquid phase (metal).
- Direct reaction of TaCl_5 and HfCl_4 with NaBH_4 leads to formation of single-phase $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution nanopowders at a significantly lower temperature of 700 °C thanks to the avoidance of the tantalum and hafnium oxides formation and the associated CTR reaction.

6.4 Recommendation for Future Work

The present work developed low-cost methods for synthesis of highly applicable nanocrystalline ternary UHTC solid solution/composite powders with no composition constraints. Based on the current work, the author suggests the following future work to be undertaken:

6.4.1 Synthesis of Nanocrystalline High Entropy UHTC Powders

Preparation of high entropy alloys (HEAs) has attracted noticeable research interests. HEAs would form when five or more elements are mixed with equal concentrations (by molar) and produce single-phase solid solutions without any trace of intermetallic formation. These alloys have shown outstanding mechanical and physical properties [112][113]. The observation of such superior properties for HEAs motivates the research on study of high entropy UHTCs. The researchers believe that these ceramics may possess improved hardness and oxidation resistance. To the best of author's knowledge, high energy ball milling of UHTC powders mixture (a mixture of more than five binary UHTCs) for several hours followed by sintering via SPS at very high temperatures (e.g.,

~2000 °C) is the only method known for the synthesis of these ceramics. However, the author believes that the low-cost methods developed in this thesis for the synthesis of ternary UHTC solid solutions (e.g., AMR method for synthesis of borides) could also be used for the synthesis of high entropy UHTCs.

6.4.2 Flash Sintering of the Synthesized Nanocrystalline $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ Solid Solution Powders

There are several studies on the sintering of UHTCs using various methods such as hot pressing, pressureless sintering and SPS. However, there are very few studies on the sintering of borides/carbides using flash sintering (FS) [115][116]. In this method sintering often occurs in a conventional furnace in combination with an electrical field, which is applied using a pair of electrodes. The applied electrical field and resulting current and furnace temperature can be easily controlled. This would allow better understanding of electrical field effect on the sintering process. Moreover, compared to SPS, FS requires shorter sintering time and lower furnace temperature (and sometimes no/less pressure), which makes this method more beneficial due to its lower cost and better energy efficiency. Therefore, the author believes that consolidation of the synthesized nanocrystalline $Ta_xHf_{1-x}C$ and $Ta_xHf_{1-x}B_2$ solid solution powders using FS would help achieving sintered parts with fine microstructures and as a result better mechanical properties.

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APPENDIX

Appendix 1: Preliminary Study on Modified Flash Sintering of $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution nanopowders

Ultrahigh temperature ceramics (UHTCs) require high sintering temperature and long dwell time due to their extremely high melting point, strong covalent bonding and low self-diffusivity. UHTCs are typically densified by hot pressing at temperatures higher than 1600 °C and pressures of 20-30 MPa [1]. However, hot pressing cannot process samples with complex shapes and geometries. Recently, one type of field assisted sintering techniques named flash sintering (FS) has been used to densify high temperature ceramics such as yttria-stabilized zirconia (YSZ). FS is characterized by application of electrical field directly through the sample under no pressure.[2] In this technique sintering occurs very fast, sometimes within a few seconds, which helps prevent grain growth.

In 2010, Yang et al [3] showed that applying an electric field of 20 V/cm could lower the sintering temperature of 3YSZ (3 mol% yttria-stabilized zirconia) from 1400 °C to 1300 °C. Cologna et al. [2] made a breakthrough based on Yang's study. They used the flash sintering method to consolidate 3YSZ in a few seconds at noticeably low temperature of 850 °C in presence of an electrical field equal to 100 V/cm. According to Cologna et al. the generated heat at the grain boundaries decreases the local resistance leading to a stronger joule heating which, in turn intensifies the localized heating at grain boundaries. Based on the Ohm's law, in constant voltage the generated power could be calculated as follows:

$$P = \frac{V^2}{R} \quad (1)$$

where P is the power dissipation, V is the applied voltage and R is the specimen resistance. As a first-order approximation, the total power dissipation could be rewritten as below:

$$P = \frac{V^2}{R_C + R_{GB}} \quad (2)$$

where R_C is the sum of the crystal matrix resistance and R_{GB} is the grain boundary resistance. Assuming that $R_{GB} \gg R_C$, then the power dissipation (P) would be dominated by the grain boundaries. Hence, a local rise in temperature at grain boundaries will reduce R_{GB} and increase power (see equation (2)), leading to increased temperature. Higher temperatures at grain boundaries would enhance the grain boundaries diffusion and as a result assist the sintering process.

For ceramics such as YSZ, which possess relatively high electrical resistivity high voltage is required in order to generate the necessary energy for triggering the “flash” or runaway process. While for $Ta_{0.5}Hf_{0.5}B_2$ solid solution, the “flash” process can be triggered at much lower voltages (less than 10 V) due to its high electrical conductivity. Lower voltage is expected to result in more homogenous microstructure after sintering.

Here, the author reports the sintering of $Ta_{0.5}Hf_{0.5}B_2$ solid solution nanopowders (without any sintering aid) using a modified flash sintering technique, in which densification occurs in the presence of a DC electrical current in a short time of 5 minutes as a result of the joule heating effect. Low pressure of ~10 MPa was applied during the sintering process to ensure effective electrical contacts between the electrodes and the

sample and also the particles. Figure A1 shows the set-up used in this study for the sintering process.

Figure A1: Modified flash sintering set-up used in this study

The $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution powder synthesized via AMR method from recipe R14 was first poured into a BN tube (inner diameter of 1/8"). Then the both ends of the BN tube were closed by two graphite punches (diameter of 1/8"). The BN tube was then put into a 1/4-inch alumina tube covered with two 1/4-inch graphite punches, which also work as electrodes. Please note that the reason for putting the sample into a smaller tube of BN was to increase the current density by decreasing the sample area. The alumina tube was wrapped with insulator material to avoid the heat loss during the sintering process. The set-up was placed under a pneumatic press to apply a constant pressure of ~10 MPa. This would help keeping the powders in contact during the sintering process. The voltage was then increased slowly (manually) until the maximum current of 90 A

could pass through the sample for 5 minutes. Figure A2 shows the change of electric current with voltage. At $V=4.8$ V the electric current passing through the sample increased suddenly from 8.1 A to 90 A (see Figure A2). The rapid change in electric current can be observed when so-called “flash” occurs. It should be noted that contrary to oxides (e.g., YSZ), no preheating was required here as borides possess high electrical conductivity allowing electric current to flow through them starting from room temperature.

Figure A3: Change of current with voltage for $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution

Figure A3 shows the SEM image of the sample surface after flash sintering. The micron-sized pores observed in the SEM image suggest that limited sintering or densification had occurred. Helium gas pycnometer (Accupyc 1340, Micromeritics

Instrument Corporation, Norcross, GA) with help of Dr. Zhang was employed to measure the density of the sample. The average density calculated for this sample was 8.24 g/cm^3 , giving a relative density of $\sim 72\%$. However, since the sample was very small ($1/8$ " pellet) and might have open pores the result obtained from Helium gas pycnometer is not very reliable.

Figure A3: SEM image of the surface of the sample after sintering

Vickers hardness for the sample was measured by a LECO LM810AT microindentation hardness tester (LECO Corporation, St. Joseph, MI) at a load of 200 gf and a dwell time of 10 s. The average hardness for 5 indents was calculated to be ~ 4.4 GPa.

These results show that sintering of the $\text{Ta}_{0.5}\text{Hf}_{0.5}\text{B}_2$ solid solution powders occurred, but only to a limited extent. Further studies aimed at understanding the effects

of current density, time, presintering of the sample and sintering aid on the relative density, microstructure, and mechanical properties of the samples need to be carried out.

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