TaC–NbC formed by spark plasma sintering with the addition of sintering additives

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TaC–NbC with and without the addition of 5 vol.% B₄C and 5 vol.% Si nano-powders as sintering aids were consolidated by spark plasma sintering at 1850°C. The effect of sintering aid addition on the densification and mechanical properties is evaluated along with secondary phase formations. Relative density >99% is achieved with a hold time of just 3 min for the addition of Si and 10 min for the addition of B₄C as sintering additives. High load instrumented indentation was performed and projected area of residual damage is compared to estimate relative fracture toughness. The addition of 5 vol.% Si as a sintering additive resulted in a 46% reduction in projected residual damage area and 14.5% more energy dissipation during indentation than the sample with 5 vol.% B₄C as the sintering additive resulting in a higher overall toughness.

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1. Introduction

Ultra high temperature ceramics (UHTC) have generated a lot of interest as candidate materials for high temperature aerospace applications such as leading edges for hypersonic aircrafts. Flight at hypersonic speeds generates enormous drag forces, which generates high temperatures at the sharp leading edges that are crucial to maintaining aerodynamic efficiency. UHTC (Group IV and V carbides and borides) have high melting points (>3000°C), making them ideal candidates for sharp leading edges and zero erosion throat inserts. Among the group V carbides, TaC has the highest melting point temperature of about 3950°C and NbC has the second highest at about 3600°C.¹⁾

The properties of UHTCs are highly influenced by the final grain size and morphology. According to the Hall-Petch relationship, the strength increases as the inverse square of the grain size which is influenced by the starting powder size, sintering additives, and processing time and temperature.²⁾ Because of their strong covalent bonds and the low self-diffusion coefficients of UHTCs, reaching full densification is a major challenge.

UHTCs such as TaC, NbC, VC, and HfC, have been consolidated using conventional hot pressing,^{3,4)} pressureless sintering,^{5,6)} vacuum plasma spraying,⁷⁾ and high frequency induction heating.^{8)–10)} These methods only reach a densification of up to 97.5% for the case of TaC consolidation and is similar in consolidating other UHTCs. Consolidation by spark plasma sintering (SPS), however, has achieved full densification at lower temperatures (1800–1900°C for SPS compared to 2100–2300°C for pressureless sintering and hot pressing) and shorter dwell times compared to other consolidation methods (10 min hold time in SPS compared to 30 min to several hours for pressureless sintering and hot pressing).^{11)–14)}

Sintering aids such as carbon, TaB₂, TaSi₂, MoSi₂, SiC, B₄C, and Si have been utilized to improve the densification and

mechanical properties of the sintered ceramic.^{3,4,10,14)} The use of sintering aids can lead to the reduction in temperature when densification begins to take place. Not only will this lead to increased final densification, but it will also reduce the amount of grain growth occurrence. Liu et al.¹⁴⁾ consolidated a TaC–20 vol.% SiC composite using SPS and saw an increase in mechanical properties (Young's modulus, Vickers hardness, flexural strength, fracture toughness) that they attributed to a decrease in residual porosity.

In this study, a pre-alloyed powder of Tantalum-Niobium Carbide (TaC–NbC) made up of 80 wt. % TaC and 20 wt. % NbC was used. NbC has a density which is half that of TaC (7.78 g/cm³ vs 14.5 g/cm³, respectively) and the addition of the 20 wt. % NbC reduced the density of pre-alloyed composition to 12.36 g/cm³.¹⁾ There have been previous studies on the sintering of TaC with and without the use of sintering additives, however the addition of NbC has not yet been studied.^{15)–19)} Because the properties of ultra high temperature ceramics make them candidate materials for high temperature space applications and rocket nozzle throat inserts, the high cost associated with sending something into space or the increased payload capacity of a rocket as a result of a lower weight material being used can make these systems more viable and cost efficient.

The sintering additives investigated in this study (B₄C and Si) were chosen based on their high temperature properties when considering the possible secondary phases formed during the sintering process.^{2,20)} With the addition of Si, the formation of SiC is expected which has a melting point of 2830°C. With the addition of B₄C, TaB₂ and NbB₂ have the possibility to form which have melting points of 3037 and 3050°C, respectively. Hence, the novelty of this work is twofold; (1) the addition of NbC to TaC reduces the density of the system and (2) samples are sintered to >99% relative density in as little as 3 min with improved toughness.

2. Experimental procedure

2.1 Powder preparation

Tantalum–Niobium Carbide powder (TaC20NbC; 80 wt. %

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Table 1. List of starting powders composition, purity and size

Powder	Vendor	Purity and Composition (wt. %) ^{a)}	Particle Size ^{b)}
TaC–20NbC	Inframat Advanced Materials, LLC	Purity > 99.6%; ~71.0% Ta, ~20.6% Nb, ~7.2% carbon, O ≤ 0.2%	0.80 ± 0.26 μm
B ₄ C nanopowder	US Research Nanomaterials, Inc.	Purity > 99%; 77.48% B, 21.52% C, O < 0.1%, N < 0.08%, Si < 0.1%, Fe < 0.1%, Ni < 0.01%	Bi-modal distribution with means of 50 nm and 5 μm
Si nanoparticles	SkySpring Nanomaterials, Inc.	Purity ≥ 99%; Si ≥ 99%, Cu < 0.45%	100 nm

^{a)} Manufacturer Specifications, ^{b)} By SEM imaging.

TaC, 20 wt. % NbC) (Ta_{0.67}Nb_{0.33})C was purchased pre-alloyed from the manufacturer (Inframat Advanced Materials, LLC, Manchester, CT). Boron carbide (B₄C) nanopowder (US Research Nanomaterials, Inc., Houston, TX) and Silicon (Si) nanoparticles (SkySpring Nanomaterials, Inc., Houston, TX) were chosen as additives to enhance sintering in order to achieve as close to full relative density as possible. The characteristics of the starting powders are listed in **Table 1**.

Preliminary experimentation was performed with varying volume percentages (between 5 and 10 vol %) of sintering aid addition. The desired densification was achieved with the addition of 5 vol % sintering aid addition and did not benefit noticeably by increasing up to 10 vol % addition. Therefore, the compositions chosen were TaC–NbC with 5 vol % sintering additive in order to better maintain the properties of the TaC–NbC ultra-high temperature ceramic.

Preparation of sintering additives (B₄C and Si) in TaC–NbC was carried out by tip-sonication of the mixture in acetone for B₄C addition and methanol for Si addition. The powders were split into three 600 mL beakers and filled to 450 mL with their respective liquids and tip-sonicated (Model CPX600, Cole-Parmer Instruments, Vernon Hills, IL) using a 3/4 inches high-gain probe at 100% frequency for 45 min each. The mixtures were then dried overnight at 80°C. The powders were crushed using an agate mortar and pestle and dried for an additional 4 h to ensure no liquid remained.

2.2 Consolidation by spark plasma sintering

Spark plasma sintering (SPS) (Model 10-4, GT Advanced Technologies, Santa Rosa, CA) was used to consolidate the prepared powders. The powders were loaded into a graphite die that was covered in 4 layers of graphite felt in order to provide thermal insulation. SPS was initially performed in a vacuum atmosphere (pressure < 2 × 10^{−2} Torr) at 1850°C and 60 MPa with a heating rate of 100°C/min and a hold time of 10 min. At the end of the 10 min hold, the power is shut off, allowing for the die and sample to cool. Initial parameters were chosen to match that of TaC in a previous study from our research group and then refined after performing a controlled study investigating densification as a function of changes in temperature and pressure.²¹⁾ The sintered samples were cylindrical in shape with a thickness of approximately 5 mm and a diameter of 20 mm for the samples prepared with a pressure of 60 MPa and diameter of 15 mm for the sample prepared at 100 MPa.

2.3 Microstructure characterization

Sintered samples were ground using SiC paper to remove graphite that surrounded the surfaces as a result of SPS processing. Apparent bulk density measurements were carried out using the water immersion technique which employs Archimedes principle as well as using a Helium gas pycnometer (Accupyc 1340, Micromeritics Instrument Corporation, Norcross, GA). The relative density was calculated as a percentage of true

density, which was measured for each starting powder mixture using the Helium gas pycnometer. The ram displacement data and vacuum measurements that were logged during the SPS process were analyzed to provide insight on the densification process and sintering mechanisms that took place. Phase components of the sintered samples were analyzed using X-ray diffraction (XRD) (Bruker D5000) using Cu-Kα X-rays at a scan rate of 1°/min. and an SEM equipped with a field emission gun and energy dispersive X-ray spectroscopy (EDS) (JSM6330F, JEOL USA, Inc., Peabody, MA). Fracture surfaces were prepared by cutting off a 5 mm section of each sample using a low speed diamond saw and then fracturing the cut sections using a hammer strike. The cross-sections of the remaining samples were then ground using diamond paper to the 15 micron level followed by polishing using a diamond suspension to a 0.25 μm finish. The morphologies of the powders and fracture surfaces were carried out using a SEM after being gold-coated for greater electrical conductivity and image quality.

2.4 Mechanical property characterization

Vickers hardness was measured by indenting on the polished cross-sections of the sintered samples. Indentations were carried out using a microhardness tester (Model TU220, Instron Corp., Canton, MA) at a load of 1000 grams with a dwell time of 15 s. A total of 8 indents were performed on each sample and the average and standard deviation are reported. Instrumented indentation was performed using a linear, screw driven micro-load frame (SEMtester 1000, MTI Instruments Inc., Albany, NY). The micro-load frame has a load capacity of 4500 N with an accuracy of 0.2% and a linear movement resolution of 20 nm. The load frame is controlled using an interface and MTESTQuattro software (ADMET, Norwood, MA) which also outputs the load-displacement data. Indentation was performed with an approximately 1 μm, 120° conospherical diamond tip loaded across from the prepared sample. The indentations were carried out using load control with a loading function of 100 N/min. up to 500 N followed by a dwell of 5 min at 500 N load before being unloaded at 100 N/min. The load-displacement curves were compared as well as the resulting residual indentation fracture by way of SEM imaging.

3. Results and discussion

3.1 Density and microstructure

Previous studies on the densification of UHTCs by SPS have reported that increasing the pressure during sintering will increase the densification. Bakshi et al.¹¹⁾ were able to achieve full densification when spark plasma sintering TaC at 1850°C when using pressures of 255 MPa and up. To study the effect of pressure during sintering, a TaC–NbC sample was sintered at 100 MPa, which is the maximum pressure attainable with our current SPS setup. While the increased pressure did result in an increase in relative density, it was only a slight rise to 88.6% compared to the 86.9% for the sample sintered at 60 MPa as

Table 2. Properties of sintered compacts of TaC–NbC with and without sintering additives prepared by SPS at 1850°C and a heating rate of 100°C/min

Sample	SPS Parameters		Density (g/cm ³)		Average Grain Size (μm)
	Pressure (MPa)	Hold Time (min.)	Actual	Relative	
TaC–NbC Powder	N/A	N/A	12.36	100.0%	0.80 ± 0.26
TaC–NbC	60	10	10.75	86.9%	0.78 ± 0.18
TaC–NbC–100 MPa	100	10	10.95	88.6%	0.85 ± 0.22
TaC–NbC–5 vol.% B ₄ C	60	10	11.71	99.1%	0.83 ± 0.15
TaC–NbC–5 vol.% Si	60	3*	11.89	99.3%	2.26 ± 0.74

*Sintering time was changed to 3 min as most of the densification occurred in that period.

Fig. 1. Instantaneous relative densities during the spark plasma sintering process.

shown in **Table 2**. Since the increased pressure did not provide the desired densification, the emphasis of our study is on using sintering additives for improved densification.

Based on the composition of the powder (which sintering additive was being used), the SPS processing parameters were refined.

In order to better understand when densification is taking place, the instantaneous relative density throughout the SPS process is calculated and shown in **Fig. 1**. Instantaneous relative density is calculated based on the ram displacement data from the SPS process after subtracting out the displacement due to thermal expansion of the dies and Eq. (1).

$$\rho_{\text{instantaneous}} = \left(\frac{L_f}{L} \right) \rho_f \quad (1)$$

In order to calculate the thickness of the specimen (L) at time t throughout the SPS process, the initial thickness of the powder is first found by adding the total distance the rams travel throughout the process to the final thickness (L_f) of the SPS compact measured after sintering. From the initial thickness, the displacement of the ram is subtracted in order to get the instantaneous thickness at time t . The ratio of the final thickness to the instantaneous thickness is then multiplied by the final relative density (ρ_f) of the sample.

For the addition of 5 vol.% Si as a sintering additive, a 10 min hold achieved an almost full relative densification, however it was accompanied with large grain growth (average size of 3.1 μm). When grain coarsening occurs in UHTCs the mechanical properties are detrimentally effected compared with ceramics with refined microstructures.²⁰⁾ By analyzing the instantaneous relative density during the SPS process it was observed that the sample reached its greatest density after about a minute and a half into hold time at 1850°C as seen in Fig. 1. Based on this

Fig. 2. SEM micrographs of the fractured surfaces of TaC–NbC, TaC–NbC–5B₄C, TaC–NbC–5Si prepared by SPS.

information, a new sample was sintered with a 3 min hold at 1850°C which was chosen in order to ensure the desired densification be reached while limiting the undesired grain growth occurrence that is attributed to the additional holding time. By reducing the hold time from 10 to 3 min, grain growth occurrence was reduced from 3.11 to 2.26 μm while maintaining 99% or more relative density. The results presented throughout this manuscript are for the sample sintered with a 3 min hold. For the addition of 5 vol.% B₄C as the sintering additive, a holding time of 10 min was deemed necessary since densification continued occurring throughout the majority of the 10 min hold.

Figure 2 shows SEM fractographs of the sintered samples. For pure TaC–NbC, a relative density of roughly 87% was achieved with no grain growth. The fracture that occurred was mostly inter-granular in nature. For the samples with sintering additive,

Fig. 3. Representative cross-sectional image of sintered TaC–NbC–5 vol.% Si showing dense microstructure and grains after focused ion beam after milling.

Fig. 4. X-ray diffraction patterns for TaC–NbC composites with and without sintering additives after spark plasma sintering.

relative densities greater than 99% were achieved however some areas still showed localized porosity. These areas could be the areas with higher sintering additive concentration where faster consolidation occurred which resulted in the trapping of pores. The sample with 5 vol.% B₄C addition showed elongation of the grains after sintering which has been previously seen in the work of Bakshi et. al.¹¹⁾ Grain growth, however, was not evident.

Figure 3 shows the cross-section of the sintered sample with 5 vol.% Si addition achieved using a focused ion beam (FIB) to image the grains after rough milling followed by a precision milling cut. The sample sintered with 5 vol.% Si addition had an average grain size of 2.26 μm with a bi-modal size distribution where the majority of the grains had a size of about 1.5 μm but also isolated areas where the grains had a size of about 3.5 μm.

3.2 Phase compositions

Figure 4 shows the XRD plots for the starting powders as well as the sintered samples. The starting powder of TaC–NbC is not shown since the peak positions of the pre-sintered powder and sintered compact are the same. When 5 vol.% B₄C is added to TaC–NbC, the new peaks belong to TaB₂ and/or NbB₂ which would be formed by the following reactions:

It is not possible to distinguish between TaB₂ and NbB₂ using XRD since the peak positions are so similar (JCPDS: TaB₂ 38-1462, NbB₂ 35-0742).

Fig. 5. SPS processing and relative densification of TaC–NbC with 5 vol.% B₄C addition as a function of the sintering process. Stages of sintering (marked on figure as I–VI) are the following: (I) Initial increase in SPS ram pressure, (II) continued ramping of temperature, (III) rapid densification begins accompanied with an increase in chamber pressure, (IV) rapid densification, (V and VI) final densification.

Since there are no Si peaks in the sintered sample, a secondary phase must be formed as a result of sintering TaC–NbC with 5 vol.% Si addition. It is believed that β-SiC (shown in Fig. 2) is formed which overlaps with the main peaks of the TaC–NbC and is formed by the following reaction:

There is a slight shift (about 0.08 degrees) to increasing 2θ values of the four main peaks of TaC–NbC that provides evidence to this occurrence. Shifts in the other overlapping peaks were not noticeable which is to be expected due to the small amount of Si added to the system. While other researchers have seen the formation of TaSi₂ as a result of the addition of Si in the TaC system, this was only seen when adding concentrations greater than 37 vol.%.^{14),22)}

3.3 Densification process and sintering mechanisms

Figure 5 shows the SPS process outputs of temperature, chamber pressure, and ram pressure as well as the calculated relative instantaneous density of the TaC–NbC sample with the addition of 5 vol.% B₄C as the sintering additive. The densification process can be split up into 6 stages (marked on figure) based on the slope of the densification curve with the most significant densification occurring in stages 3–5. In stage 1, an increase in densification is observed from about 47 to 54% which is attributed to the increase in mechanical ram pressure from 5 to 60 MPa. The sharp increase in chamber pressure is a likely result of the release of trapped air around the powder which is forced out due to the increase in SPS ram pressure. Stage 2, which is up to about 1330°C, does not have any significant densification. Significant densification begins to occur at the beginning of stage 3, encompassing a temperature range of 1330 to 1630°C. The increase in chamber pressure that is seen leads to the assumption that a reaction is occurring that releases a volatile substance. When hot pressing TaC with B₄C, Zhang et al.³⁾ saw the reduction of surface oxides which led to gas generation in the form of B₂O₃ and/or CO. However, the densification in stage 3 as well as the densification that takes place in stage 4 could also be attributed to particle rearrangement and mass diffusion as well as a possible evaporation-condensation process.¹³⁾ In stage 5, starting from the hold temperature of 1850°C up until 5 min into the holding time, densification increased from 80 to 96%. This can be attributed to the closing of pores. Stage 6 only saw a small

Fig. 6. SPS processing and relative densification of TaC–NbC with 5 vol.% Si addition as a function of the sintering process. Stages of sintering (marked on figure as I–VI) are the following: (I) Initial increase in SPS ram pressure, (II) continued ramping of temperature, (III) rapid densification begins, (IV) rapid densification, (V and VI) final densification.

increase in densification which can be attributed to continued elimination of porosity.

Figure 6 shows the SPS process outputs of temperature, chamber pressure, and ram pressure as well as the calculated relative instantaneous density of the TaC–NbC sample with the addition of 5 vol.% Si as the sintering additive. This densification process can be split up into 6 stages (marked on figure) with the most significant densification occurring in stages 3 and 4. Again, stage 1 densification is a result of the increase of mechanical ram pressure which results in greater powder packing and the release of trapped air. Stage 2 did not contain significant densification; however the increase in the chamber pressure could be an indication of a reaction between surface oxides and the silicon which would result in the release of SiO or CO gas.²²⁾ Stages 3 and 4, taking place between 1287 and 1725°C, brings the beginning of significant densification. The densification mechanism attributed to these stages is particle rearrangement by creep flow up to 1413°C (melting point of Si) and then wetting of the TaC–NbC particles and the formation of TaSi₂ and SiC. From the beginning of stage 3 to the end of stage 4, relative densification increased from about 53 to 92%. It is assumed that the final densification, occurring in stages 5 and 6, is a result of the closing of pores as well as a possible evaporation-condensation mechanism that resulted in increased mass transportation and grain growth.

3.4 Mechanical properties by high load instrumented indentation

An increase in Vickers hardness is observed with the addition of sintering additives as shown in **Table 3**. Compared with the Vickers hardness of TaC–NbC without any sintering additive, an increase in hardness of 188 and 194% was seen with the addition of B₄C and Si as sintering additives, respectively. This is mainly contributed to the increase in densification of the sintered samples. Compared with results from other studies using TaC with sintering additives, the achieved hardness values were very similar. Zhang et al.²³⁾ achieved a hardness value of 15.1 GPa when adding a similar amount (1 wt. %) of B₄C to TaC and hot pressing at 2100°C. Zhong et al.²²⁾ showed a hardness of 13.2 GPa when adding 0.78 wt. % Si to TaC and sintering by SPS at 1700°C.

The resulting load-displacement curves from high load instrumented indentation are shown in **Fig. 7**. Load-displacement curves are being shown only for the samples with sintering additives due to their similar density. In comparing the two

Fig. 7. High load instrumented indentation load-displacement curves for TaC–NbC with and without sintering additives.

Table 3. Indentation properties of spark plasma sintered TaC–NbC compacts with and without sintering additives

Sample	Hardness (GPa)	Projected Damaged Area (mm ²)	Relative Density
TaC–NbC	7.63 ± 0.47	1.020	86.90%
TaC–NbC–5B ₄ C	14.32 ± 0.59	1.025	99.07%
TaC–NbC–5Si	14.83 ± 0.95	0.555	99.32%

curves with sintering aid addition, it is observed that a greater displacement is achieved to reach the same load when Si is the additive. When calculating the areas under the curves, the total work of indentation is 88.12 mJ for the sample with the addition of 5 vol.% B₄C and 103.05 mJ for the sample with the addition of 5 vol.% Si. Therefore the sample with the addition of 5 vol.% Si addition dissipated 14.5% more energy during the indentation.

Figure 8 shows the residual damage as a result of instrumented indentation at a high load of 500 N. In **Fig. 8(a)**, the indenter tip impression can be clearly seen, however there are long cracks emanating out from the site of the indent that are not discernable at a low magnification. Therefore **Fig. 8(b)**, which is a zoomed in image of the location marked in **Fig. 8(a)**, is provided as a representative image showing the stemming cracks. Since the SEM images of the indentations cannot accurately capture the entire crack length of all cracks that have formed, a map of the residual damaged area (**Fig. 9**) was made by tracing the crack lengths originating from point of indentation and connecting the ends of the cracks to calculate the projected area of residual damage as depicted in the schematic of **Fig. 8(c)**.

The total projected area of residual damage (stated in **Table 2**) was very similar for the TaC–NbC sample and the TaC–NbC–5B₄C sample while the TaC–NbC–5Si sample showed ~46% less projected residual damaged area. This is in agreement with the finding from the load-displacement curves that show the sample with 5 vol.% Si dissipates a greater energy during indentation and therefore has a higher relative fracture toughness than the sample with the addition of 5 vol.% B₄C addition. The increase in relative toughness with the addition of Si was expected since metals have a greater ability to plastically deform compared to ceramics and has been previously seen when Si or TaSi₂ have been added to a TaC matrix. Zhong et al.²²⁾ observed pullout of the TaC grains after fracturing indicating a weakened bonding between the TaC grains which instead favored toughening mechanisms such as interface debonding and crack deflection. Silvestroni et al.²⁴⁾ also observed an increase in fracture toughness of 28% when 15 vol.% TaSi₂ was added to the TaC matrix, which was a result of the composite matrix being under a

Fig. 8. (a) SEM image of indentation impression on TaC–NbC, (b) zoomed in SEM image of area marked on (a) showing cracks protruding from indentation, and (c) a schematic of the cracks as a result of indentation with shaded projected residual damaged area.

Fig. 9. Map of projected residual damage resulting from high load instrumented indentation for spark plasma sintered TaC–NbC with and without sintering additives.

compressive stress. Hence, our finding are consistent with the same although with a novel high load (500 N) instrumented indentation technique on TaC–NbC based ceramics.

4. Conclusions

With the addition of just 5 vol.% B₄C or 5 vol.% Si as sintering additive, nearly full relative densification of the sintered TaC–NbC is achieved with hold time as short as 3 min. The secondary

phases formed by the addition of B₄C as sintering aid are TaB₂ and NbB₂ which have melting points of 3040 and 3050°C, respectively. With the addition of Si as the sintering additive, the secondary phase formed is SiC with a melting point of 2830°C. Each of the secondary phases formed have melting points that are high enough to allow the system to remain viable for use in high temperature applications. While the increase in hardness achieved using sintering additives is attributed to the increase in density, the use of 5 vol.% Si resulted in a 46% less projected residual damage area and 14.5% more energy dissipation during high load indentation than with the addition of 5 vol.% B₄C and therefore has a higher overall relative toughness.

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