Mechanical Properties of WC-Si$_3$N$_4$ Composites With Ultrafine Porous Boron Nitride Nanofiber Additive

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WC-10 wt.% Si$_3$N$_4$ composites toughened with ultrafine porous boron nitride nanofiber (0, 0.01, 0.05, 0.1, and 0.15 wt.%) were prepared for the first time by spark plasma sintering. Compared with the WC-Si$_3$N$_4$ composite sintered in the same condition, the obtained WC-10 wt.% Si$_3$N$_4$ composites with ultrafine porous boron nitride were found to possess better hardness and fracture toughness. In addition, the Si$_3$N$_4$ phase in the UPBNNF toughened composites did not exhibit traditional catastrophic fracture as indicated in most investigations. In this study, the phenomena are discussed, and a probable mechanism is elucidated. It is deduced that the approach could be extended to materials with a feature of internal liquid phase during the sintering process and could improve hardness and fracture toughness.

Keywords: porous nanofiber, WC, Si$_3$N$_4$, Young’s modulus, fracture mode

INTRODUCTION

Tungsten carbide (WC) has numerous advantages, including high Young’s modulus, high hardness, and excellent wear-resistance (Zhang et al., 2009; Kumar et al., 2011; Namini et al., 2019; Sakkaki et al., 2019; Fattahi et al., 2020a,b). However, the shortcoming of WC is brittleness. Therefore, most industrial WC-based materials are WC-Co composites, which are typically applied as cutting tools and molds (Chang et al., 2015; Norgren et al., 2015). Co is beneficial for improving fracture toughness because of its ductility and wettability to WC. In addition, binderless WC-based materials continue to be investigated due to their merits of corrosion-resistance and red hardness in comparison to binder-containing composites. In this manner, carbides are mostly used (e.g., VC, Cr$_2$C$_3$, TaC, and TiC (Kim et al., 2008; Poetschke et al., 2012; Nino et al., 2019). The toughening effects of oxides such as MgO, Al$_2$O$_3$, and ZrO$_2$ are also investigated on the WC matrix (El-Eskandarany, 2000, 2005; Basu et al., 2004; Zheng et al., 2012, 2013b).

Carbon (CNT) and boron nitride (BNNT) nanotubes have outstanding mechanical properties, which have attracted attention in materials reinforcement (Wang et al., 2011; Yadhukulakrishnan et al., 2012; Tatarko et al., 2014; Vasudevan et al., 2016; Jin et al., 2017; Li et al., 2018). CNT with exceptionally high Young’s modulus in the terapascal (TPa) range and tensile strength of as much as 60 GPa has been investigated as a toughening phase for a long time (Han et al., 2018). BNNT possesses high chemical stability in addition to previously mentioned advantages. However, difficulties remain in BNNT synthesis with large quantities and low costs (Golberg et al., 2007, 2010). As an alternative for environmental chemistry and hydrogen storage, Lin et al. (2016)
prepared an ultrafine porous boron nitride nanofiber (UPBNNF) with a high specific surface area of 515 m$^2$/g and a total pore volume of 0.566 cm$^3$/g using freeze-drying and pyrolysis processes. But studies on the toughening effect of the porous fiber are rare yet.

WC-Si$_3$N$_4$ composites have been considered in detail with respect to the sintering process, phase transformation, microstructure, and mechanical properties using spark plasma sintering (SPS) (Li et al., 2013; Zheng et al., 2013a, 2015). In this study, the WC-10 wt.% Si$_3$N$_4$ composites with addition of UPBNNF were prepared using SPS to investigate UPBNNF’s effects on the overall mechanical properties. The mechanical phenomena after testing were discussed on experimental data and fracture theory.

**EXPERIMENTAL PROCEDURE**

For starting materials, we used WC (200 nm, purity > 99.9%, Xuzhou Jiechuang New Material Technology Co., Ltd., China), Si$_3$N$_4$ (~1 μm, > 95% α-phase, Xuzhou Jiechuang New Material Technology Co., Ltd., China), Y$_2$O$_3$ (5–10 μm, purity > 99.9%, Sinopharm Chemical Reagent Co., Ltd., China) and Al$_2$O$_3$ (~1 μm, purity > 99.9%, Beijing Mountain Technological Development Center, China), UPBNNF (diameter: 20–60 nm, length: tens of micrometers; Boron Nitride Research Center, Development Center, China), WC-10 wt.% Si$_3$N$_4$ was calculated based on the α (200)/β (200) ratio of the diffraction peak heights (PH) based on the method reported by Pigeon and Varma (1992). The PH data were collected at a 0.02° step$^{-1}$ between 25 and 29° of 2theta (time constant 2 s) with the contribution subtracted due to background noise:

$$\frac{\alpha}{\beta} \text{ phase ratio} = 4.9381(\text{PH}) + 0.1144(\text{PH})^2 + 0.08106(\text{PH})^3,$$

where α is the wt. fraction of the α phase and β is the wt. fraction of the β phase.

The microstructure as well as the Vickers indentations was examined using high-resolution scanning electron microscopy (HRSEM, Nova Nano 430, FEI, United States). The microstructure of composites containing WC-Si$_3$N$_4$ with and without UPBNNF were prepared using SPS to investigate UPBNNF’s effects on the overall mechanical properties. The mechanical phenomena after testing were discussed on experimental data and fracture theory.

RESULTS AND DISCUSSION

The displacement of the lower punch, which reflects the densification process of the sample, and the temperature were automatically recorded during sintering. Figure 1 shows shrinkage rate curves of the specimens heated to 1750°C without soaking time. As the shrinkage rate became positive, the powders were densified until the shrinkage rate was again reduced to zero. For the fine grain WC-10 wt.% Si$_3$N$_4$ and those specimens with the addition of UPBNNF, the densification process started at approximately 900°C. Much faster densification rates were observed for all specimens when the sintering temperature rose to 1400°C. Finally, the densification process ended at approximately 1600°C.

Figure 2 shows the XRD patterns of WC-10 wt.% Si$_3$N$_4$ with and without UPBNNF specimens. The wt. fraction of the β phase calculated from the XRD data in Figure 3 are listed in Table 1. The specimens containing UPBNNF had a higher wt. fraction of the β phase than the specimens without the fiber. The microstructures of composites containing UPBNNF that can be seen in Figure 4 are different from the WC-10 wt.% Si$_3$N$_4$ reported in our previous works (Li et al., 2013; Zheng et al., 2013a, 2015). In the microscopy examination processes that we performed, UPBNNF was hardly visible due to its small size and high porosity.
TABLE 1 | Characteristics of WC-Si$_3$N$_4$-UPBNNF specimens.

| Specimen | Density (g/cm$^3$) | $\beta$-Si$_3$N$_4$ (100%) | Hardness (GPa) | Elasticity modulus (GPa, calculated) | Elasticity modulus (GPa, tested) | Fracture toughness (MPa·m$^{1/2}$) |
|----------|-------------------|---------------------------|--------------|-------------------------------------|---------------------------------|----------------------------------|
| 10S      | 11.45             | 16.96                     | 17.76 ± 0.25 | 572                                 | 521                             | 7.70 ± 0.56                      |
| 10S0.01B | 11.39             | 20.44                     | 18.32 ± 0.33 | 567                                 | 793                             | 10.99 ± 0.41                     |
| 10S0.05B | 11.40             | 18.79                     | 20.56 ± 0.87 | 556                                 | 779                             | 10.57 ± 0.38                     |
| 10S1B    | 11.41             | 27.51                     | 19.04 ± 0.39 | 544                                 | 775                             | 10.50 ± 0.68                     |
| 10S0.15B | 11.37             | 24.83                     | 19.12 ± 0.56 | 532                                 | 755                             | 10.09 ± 0.76                     |

FIGURE 1 | Densification curves of the composite specimens.

FIGURE 2 | XRD patterns of the composite specimens.

FIGURE 3 | XRD patterns for $\alpha$-Si$_3$N$_4$ (100) and $\beta$-Si$_3$N$_4$ (200) crystal planes of the composite specimens.

Values for the hardness and fracture toughness of WC-10 wt.% Si$_3$N$_4$ with different ratios of UPBNNF composites are listed in Table 1. All specimens containing UPBNNF were better in terms of both hardness and fracture toughness as compared to the WC-10 wt.% Si$_3$N$_4$. Table 1 also shows the tested Young's modulus values of specimens as well as the theoretical upper boundary calculated from Voigt's formula, and the UPBNNF-containing specimens had abnormally high values (the highest reached 793 GPa) that were superior to the value of pure WC (700 GPa), with nearly changeless density. If the calculated values are obtained based on tested value of 10S, the calculated values along with growth of UPBNNF additive amount are 520, 519, 518, and 517 GPa, respectively. The crack path details of all composites are presented in Figure 5, where tearing and scratch patterns on Si$_3$N$_4$ in the composites containing UPBNNF are visible. The crack pattern of Si$_3$N$_4$ grains in composites is different from the transgranular crack pattern of Si$_3$N$_4$ with clean edges. When the crack passes the Si$_3$N$_4$ grains in the composites, it appears healed, which is also unlike the traditional crack pattern of ceramic matrices. Under a 10-kg load, UPBNNF is rarely observed. Therefore, a 30-kg load is employed to produce a bigger crack. In the crack images of Figure 6, UPBN6 can be observed in the UPBNNF-containing specimens. In particular, single fibers can be seen between the broken parts of Si$_3$N$_4$.

In the aforementioned results, the fracture mode identified in the results can be noticeable. In general, Si$_3$N$_4$ ceramics are known for catastrophic fracture, and thorough fracture of Si$_3$N$_4$ grains with clean edge is observed (a fine image of fracture
of Si$_3$N$_4$ grains is provided in Riley (2000), Li et al. (2004), Klemm (2010), Zhou et al. (2014), and Hu et al. (2019). However, different cases of tears and scratches emerge on the Si$_3$N$_4$ grains in the composites with UPBNNF, as shown in Figure 5, which means fractures of Si$_3$N$_4$ occur partly under a given load. The phenomena has been barely observed in other Si$_3$N$_4$-containing composites. It can be deduced that the whole fracture process involves two steps at least during a given time interval under a limited load. Therefore, these crack patterns are not the traditional catastrophic fracture mode of Si$_3$N$_4$.

Theories on fracture and toughening can be simply divided two theoretical categories: the microstructural and the atomic. Fracture and toughening phenomena are usually elucidated by microstructure theory with respect to interface energy that is sufficient in most cases (Marshall and Evans, 1985; Becher et al., 1988; Becher, 1991). Furthermore, analysis on fracture is based on thermodynamics. According to second law of thermodynamics, there must be extra work to block the crack propagation in the traditional way. As reported, deformation work of UPBNNF cannot lead the different fracture mode of WC (Li et al., 2020). Combining mentioned analysis on UPBNNF, the probable reason is extra elastic work in the process of crack propagation of Si$_3$N$_4$ grains containing UPBNNF. The source of the elastic work cannot be found in the microstructure scale. Therefore, atomic theory is necessary when the fracture mode of materials is concerned in this case. A simple theory is the cohesive strength model. In this model, fracture is determined based on the cohesive strength of atoms, which is proportional to Young’s modulus (Lawn, 1993). The Si$_3$N$_4$ in a nanopore could possess higher cohesive strength as a result of being restrained by the nanopore based on the previously mentioned elevated Young’s modulus of parts of Si$_3$N$_4$. Thus, the fracture mode of Si$_3$N$_4$ in the composites with UPBNNF is consistent with an increase in Young’s modulus. Young’s modulus and fracture at the atomic scale are both the variations in force and distance between atoms (Lawn, 1993; Hsieh and Tuan, 2005).

As shown in results, one unusual observation is that the Young’s modulus of the composites was even higher than the highest value, which is rarely present in other composites regardless of whether the second phase exists as a particle or fiber. Examples of these types of composites include Si$_3$N$_4$-SiC, Si$_3$N$_4$-TiN, Si$_3$N$_4$-ZrO$_2$, TaC-TaB$_2$, and ZrB$_2$-TiC (Akimune, 1990; Pezzotti, 1993; Blugan et al., 2005; Zhang et al., 2008; Guicciardi et al., 2010; Bódis et al., 2017). It is known that Young’s modulus of materials as an intrinsic property is determined by the bonding between the individual atoms, which means Young’s modulus is a characterization of force and distance between atoms (Meyors and Chawla, 1999). For materials containing pores, Young’s modulus descends with higher porosity (Pabst and Gregorová, 2004). On evaluating Young’s modulus of composites, the mixture rule is usually applied, and the value is located between the high and low values regardless of the calculation methods (Meyors and Chawla, 1999; Hsieh and Tuan, 2005). In addition, different methods are also applied to obtain this value. However, results derived from the examination methods or calculated by the mixture rule show only minimal differences. Therefore, all
methods are adopted in materials investigations (Koopman et al., 2002; Cha et al., 2003; Basu et al., 2004; Wang et al., 2012; Xia et al., 2020). In brief, the addition of a phase with a low Young's modulus leads to decreasing value of composites. UPBNNF possesses two features that result in negligible Young's modulus in WC-Si$_3$N$_4$ composites: high porosity and a turbostratic...
structure that is related to a low Young's modulus of high tensile strength (HT) carbon fiber (Frank et al., 2012; Lin et al., 2016). In fact, the value of a BN fiber with a normal structure is only tens of GPa (Economy and Anderson, 1967). Therefore, the Young's modulus of UPBNNF itself has no effect on the composites. The only probable explanation is based on the most fundamental mechanism whereby the bonding of atoms is affected.

Meanwhile, there is no increase of Young's modulus found in WC-UPBNNF composites (Li et al., 2020). Young's modulus of some WC composites reported in published papers are listed in Table 2, which were all tested by the pulse-echo overlap ultrasonic technique. There are no abnormal phenomena, too. Thus, we consider that in addition to the liquid phase in the $\text{Si}_3\text{N}_4$ sintering process, the major point of influence is the nanosized pores of UPBNNF. For nanocrystalline materials (grain size $< 50$ nm), the properties could be modified at an atomic scale, but most of the modification is employed on functional ceramics (Gleiter, 1989; Jin and Bao, 1996; Maglia et al., 2013). It is rarely observed that Young's modulus of ceramics can be modified to increase thereafter, as no effective means are available to intervene at the atomic scale. Restricting the sizes of grains to less than 50 nm during the sintering process is difficult. However, it is possible that the bonding of atoms of $\text{Si}_3\text{N}_4$ can be affected after sintering by the presence of UPBNNF. As reported in the papers about WC-$\text{Si}_3\text{N}_4$ materials (Li et al., 2013; Zheng et al., 2013a, 2015), a liquid phase is generated during sintering, and then pores of UPBNNF can be filled with the liquid phase. In fact, reordering happened on groups of atoms in liquid phase sintering, and some groups were trapped in nanopores of UPBNNF. The bonding of atoms of $\text{Si}_3\text{N}_4$ in a pore is restrained after sintering, which means that the force and distance between atoms are also restricted. As a result, the Young's modulus of parts of $\text{Si}_3\text{N}_4$ increases, and in turn the values of whole $\text{Si}_3\text{N}_4$ and composites increase. Because of agglomeration, excess fraction of the fiber results in another decrease in Young's modulus. By contrast, directly observing the phenomenon is difficult. Regarding interaction between nanopores and filler materials, numerical modeling is mostly used. Even though accurate observation is employed on nanopores, there are too many requirements on the specimen itself (Lee et al., 2018; Gu et al., 2019; Hou et al., 2019; Nehra et al., 2019). WC-$\text{Si}_3\text{N}_4$ bulks after ball milling and sintering are too crude to meet the requirements. In addition, although some BN phases like BN nanoplates observed were reported (Ahmadi et al., 2017; Germi et al., 2018; Mahaseni et al., 2018), the turbostratic structure and pore leading to bad contrast hindered the intention of observation for UPBNNF in this case.

Eventually, synergic toughening is evident on the WC matrix, which is based on toughened $\text{Si}_3\text{N}_4$ and UPBNNF, as shown in Figure 6. By contrast, the synergic mechanism is not consistent with traditional ceramic-ceramic toughening theory. According to the traditional toughening model, weak interfacial bonding between non-binder second phases and the matrix is beneficial due to the fragile second phases without toughening effects in complex stress environments (Mahaseni et al., 2018). Energy is consumed by debonding, interfacial friction, and so on. In brief, energy must be consumed by generating new interfaces, but must not be alongside main cracks. Why the synergic toughening is possible in this study? It was observed that $\text{Si}_3\text{N}_4$ is strongly bonded to the matrix by UPBNNF, so do UPBNNF itself. As a result, debonding between WC matrix and $\text{Si}_3\text{N}_4$ was more difficult, and the energy had to be consumed in other approaches like $\text{Si}_3\text{N}_4$ fracture. Usually, fracture in the ceramic second phase does not have considerable attribution to the toughening matrix due to the transitory nature of the fracture (Germi et al., 2018). However, as observed and elucidated, the ultimate fracture of $\text{Si}_3\text{N}_4$ grain in the composites can occur during a certain time interval. The aforementioned effects may consume more energy than traditional methods that lead to toughening.

The following is a brief summary of the previous discussion. First, it is possible that Young's modulus of ceramics is elevated using nanopores. High specific stiffness, which is a ratio of

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**TABLE 2** | Young's modulus of some WC composites reported in published papers.

| Specimen   |   0°  | 6Co° | 1CNT° | 6ZrO2° | 8ZrO2° | 1Si3N4° | 3Si3N4° | 6Si3N4° | 8Si3N4° |
|------------|-------|------|-------|--------|--------|---------|---------|---------|---------|
| Young's modulus | 704   | 649  | 658   | 575    | 559    | 650     | 596     | 542     | 522     |

| Specimen   | 10Si3N4° | 12Si3N4° | 15Si3N4° | 0.05UPBNNF° | 0.075UPBNNF° | 0.1UPBNNF° | 0.125UPBNNF° |
|------------|----------|----------|-----------|-------------|-------------|------------|-------------|
| Young's modulus | 517     | 486      | 470       | 684         | 666         | 642        | 630         |

The specimens' names are in terms of second phases with weight fraction in WC matrix.

Data sources: a, Li et al., 2020; b, Basu et al., 2004; c, Cao et al., 2018; d, Cao et al., 2021; e, Zheng et al., 2015.
Young's modulus to density, is often desired in mechanical design. However, the rule of mixture is a theoretical limitation, and no elevation exists beyond the intrinsic properties of materials that are simply affected at the atomic scale. Materials with high Young's modulus usually have a high density and result in increasing density after the addition into the matrix of a low Young's modulus. Second, ceramics with an internal liquid phase during sintering such as Si$_3$N$_4$ can employ a different fracture mode at the micrometer scale. Although no ductility can occur on the ceramics, serial and multiple fractures during a certain time interval may be closed to ductility in analogy with series approximation to a smooth function in calculus. Finally, a fiber with a deformation ability and modified ceramic phase such as those of the aforementioned Si$_3$N$_4$ enables the toughening of other ceramics jointly.

CONCLUSION

In this study, WC-10 wt.% Si$_3$N$_4$ -x (x = 0, 0.01, 0.05, 0.1, and 0.15) wt.% UPBNNF composites were prepared by SPS. The following conclusions were drawn and thus present a means of improving the mechanical properties of ceramics.

(1) The addition of UPBNNF to WC-10 wt.% Si$_3$N$_4$ could be effective at enhancing hardness and maintaining fracture toughness.

(2) Tears and scratches patterns appear on Si$_3$N$_4$ grains in indentation crack paths of WC-Si$_3$N$_4$ composites with the addition of UPBNNF, an observation that is different from that of the traditional fracture mode of Si$_3$N$_4$ in which a catastrophic fracture occurs with clean edges.

(3) A collaborative toughening effect of UPBNNF and Si$_3$N$_4$ in WC-Si$_3$N$_4$ composites works under strong interfacial bonding.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

TC: idea conceiving and writing. XL: supervising and project leader. SQ: supervising on mechanical tests. JL: assistant on preparing composites. LL: providing hardness tester. YH: supervising on porous fiber preparing. TS: preparing porous fiber. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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