Sintering and mechanical properties of TiB₂-TiC-Ni using submicron borides and carbides

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Abstract

A series of TiB₂-TiC-Ni composites were prepared to develop materials with enhanced mechanical properties for structural application. Submicron TiB₂-TiC powders were synthesized using a patented carbon coated precursor method. The composites had about 99% relative density after sintering at a temperature of 1550°C in flowing argon. TiB₂-TiC-Ni composites showed superior sintering and mechanical properties comparing with monolithic TiB₂ and TiC counterparts because of the enhanced microstructures. Phases, grain morphologies, pores sizes, sintering behaviors, and mechanical properties were correlated with the ratio of TiB₂/TiC and Ni content. The plate like TiB₂ grains were observed in the composites. Toughening mechanism was determined as metallic binder plastics deformation, bridging, and debonding of the TiB₂/TiC interface. TiB₂-TiC-Ni composites have good combinations of hardness and fracture toughness as 24.23 GPa, 7.41 $\text{MPa} \cdot \text{m}^{1/2}$, and 21.85 GPa, 8.44 $\text{MPa} \cdot \text{m}^{1/2}$, with Ni content of 5 and 10 wt%, respectively.

1 Introduction

Titanium diboride (TiB₂) has drawn enormous interest owing to its outstanding properties including high melting point (3225°C), high hardness (~35GPa), excellent electrical and thermal properties, and superior wear resistance[1, 2]. By adding metallic binders such as Co, Fe, Ni, Mo, Cr, and their alloys, TiB₂ based material has improved fracture toughness due to the plastics deformation of metallic phase and crack bridging toughening[3, 4]. Consequently, TiB₂ cermet is one of the most promising candidates for cutting tool materials to substitute traditional

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WC-Co cermet, due to its superior finishing properties, hardness, and wear resistance[5-7]. Similarly, titanium carbide (TiC) based cermet, TiC-TiN-(Ni, Mo, Co), is also an ideal candidate for cutting tool materials owing to its excellent wear resistance and high hardness[8-12]. Except cutting tool materials, both TiB₂ and TiC also have various other crucial applications from structural to electronic fields such as impact resistant armor, wear resistance components, corrosion resistance coatings, and electrode materials [1, 2, 13, 14]. Comparing with monolithic TiB₂ or TiC cermets, several reports indicate that TiB₂-Ti(C,N)-(Ni,Mo) composite has outstanding properties including hardness, fracture toughness, and strength[5-7, 15]. However, in that respect is no research study the influence of TiB₂/TiC composition (from 0 to 100%) on the composite properties.

One of the most significant problems of TiB₂ containing compound (monolithic TiB₂ ceramic, TiB₂ cermet, and TiB₂-TiC cermet) is the sintering process[1, 4]. Due to the oxygen impurity and the relatively low diffusion coefficient in commercial powders, a super high sintering temperature is required to achieve a high relative density (above 95%). The high sintering temperature always leads to exaggerated grain grown. As a consequence, microcracks exist in sintered TiB₂ due to anisotropic coefficient of thermal expansion (CTE) along a- and c-axis (grain size >15μm). Mechanical properties are also influenced because of coarse grain size[16]. The introducing of metallic additive can promote the sintering process through liquid phase sintering, thus reduce the sintering temperature[17, 18]. By adding above 20 wt% metallic binders, densifications can be accomplished at a temperature of ~1500°C through pressureless sintering (PS)[19]. However, the high fractions of metallic phase deteriorate their wear properties, and also restrict their applications at elevated temperatures. With reduced fractions of metallic binders (5 to 10 wt%), a sintering temperature up to 1700°C with applying external pressure simultaneously (hot pressing, HP), is necessary[5-7, 15, 20-22]. HP at the high temperature substantially reduces the production efficiency, increases costs, and restricts the product's shape. Another key issue of TiB₂ based cermet for the application of structural materials is the brittleness of TiB₂ itself. Several literatures indicate that fine microstructures are beneficial to the high fracture toughness[6, 7, 22]. It is necessary to study the toughening mechanism at the micro scale and tailor the microstructures, thus improve the fracture toughness.

Numerous literatures demonstrate that laboratory prepared powders have better sintering properties than that of commercially available ones[13, 23-25]. Powders with fine particle size, loose agglomeration, high purity, and regular shape are required for starting materials to enhance the sinterability [8, 13]. By using a novel carbon

coated precursors method, synthesized TiB_2 , TiC , and $\text{TiB}_2\text{-TiC}$ powders can satisfy the requirements of sintering powders[8, 24]. Therefore, exceptional sintering properties are demonstrated for TiC-Ni sintering system. Although the sintering properties of $\text{TiB}_2\text{-TiC-Ni}$ composites were tested, more details are needed[24].

In the present paper, by utilizing laboratory prepared TiB_2 , $\text{TiB}_2\text{-TiC}$, and TiC powders, by adding low fractions of Ni (5 and 10 wt%), their sintering properties will be studied through PS method at a relatively low temperature. Effects of TiB_2/TiC composition and Ni content on sintered density, phases, microstructures, and mechanical properties are observed. Correlations between microstructures and mechanical properties are discussed. A comprehensive comparison of current properties with literature reported properties are presented. The toughening mechanism of composites will also be analyzed.

2 Experimental

Monolithic TiB_2 powders, $\text{TiB}_2\text{-TiC}$ composite powders, and monolithic TiC powders were synthesized through a novel carbon coated precursors method[26, 27]. Powders with five different compositions, which were monolithic TiB_2 , 80 wt% $\text{TiB}_2\text{-20 wt% TiC}$, 60 wt% $\text{TiB}_2\text{-40 wt% TiC}$, 40 wt% $\text{TiB}_2\text{-60 wt% TiC}$, and monolithic TiC , were prepared. This could help study the effect of TiB_2/TiC composition on sintering and mechanical properties. Powders were identified as A, B, C, D, and E, respectively. Detailed of synthesis process were described in our previous publications[24, 26]. Synthesized TiB_2 powders has a particle size between 0.5 to 1 μm , and TiC is between 0.05 to 0.3 μm . Transmission electron microscopy (TEM, Hitachi, Model H-7650 TEM, ToKyo, Japan) micrographs of selected synthesized powders (only show A, C and E to represent monolithic TiB_2 powders, $\text{TiB}_2\text{-TiC}$ composite powders, and monolithic TiC powders) are shown in Fig. 1. Owing to the advantages of carbon coated precursors method, powders features regular shape, fine particle size, high purity, and loose agglomeration[24, 28]. Synthesized powders' surface areas were characterized by BET gas adsorption surface area analyzer (Micromeritics, Gemini 2360, Norcross, GA) and summarized in Table 1.

Two batches cermets with different Ni contents were prepared. By adding 5 wt% Ni powders (<1 μm , 99.5% pure, CERAC, Milwaukee, WI) (total weight percent of ceramic TiB_2 , $\text{TiB}_2\text{-TiC}$, or TiC powders were as 95 wt% for each sample), powders were mixed in a plastics vial together with two plastics balls for 1 hour using a SPEX 8000 Mixer/Mill (SPEX Corp., Metuchen, NJ). The application of plastics vial and balls was aimed to

minimize the introducing of contaminations during ball mill. Samples were recorded as A5, B5, C5, D5, and E5 respectively. Similarly, by adding 10 wt% Ni, another batch samples were also prepared and recorded as A10, B10, C10, D10, and E10. Samples with different compositions were also summarized in Table 1. Pellets were made in a single action, uniaxial press in a hardened steel die (ID=12.95 mm) under a pressure of 200MPa. The sintering process was conducted at 1550 °C for 1 hour in a tube furnace (CTF 17/75/300, Carbolite, Sheffield, UK) under flowing argon (0.1L/min). In order to study the effect of sintering temperature, C10 sample was also sintered at 1475°C for 1 hour in the tube furnace under flowing argon. Densities of sintered pellets were determined by Archimedes' method. A scanning electron microscope (SEM, FEI Quanta FEG450, Hillsboro, OR) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, United Kingdom) was used to investigate the polished surfaces using a backscattered electron detector (BSD). Sintered pellets were characterized by XRD (Rigaku D/Max-B, Tokyo, Japan) using Cu K α ($\lambda=1.54056 \text{ \AA}$) radiation at a voltage of 30KV and a current of 15 mA. Phases were identified through Jade software with the International Center of Diffraction Data (ICDD). Grain size of both TiB₂ and TiC for each sample were measured through linear intercept method performed on a Magnisci software (Divergent Rays Computing Inc, Toronto, ON, Canada). Pore sizes and volume fractions of each phase were determined through the Magnisci software as well. At least 300 grains or pores were counted from at least two images at a magnification of 1000 and one image at 2500 for each sample. Vickers hardness values were measured 10 times for each sample with a Shimadzu HSV-20 hardness tester at a load of 20 kg. The fracture toughness was determined using the Vickers hardness indentation method[29]:

$$K_{IC} = \delta \left(\frac{E}{H_V} \right)^{1/2} P C_0^{-3/2}$$

where: K_{IC} is the fracture toughness, δ is a constant value of 0.016 ± 0.004 , E is the Young's modulus (taken from literature data and the law of mixture was applied for composites)[1, 2], H_V is the Vickers hardness, P is the indentation load, and C_0 is the crack length measured from the center of the indent. It should be clarified that, the most widely used Shetty equation for cermet carbide's toughness determination, was not applied to current calculation due to the formation of median cracking[3, 30].

Fig. 1 TEM micrographs of synthesized powders. (a) monolithic TiB_2 powders, identified as A, (b) composite powders, 60 wt% TiB_2 -40 wt% TiC , identified as C, (c) monolithic TiC powders, identified as E. Notice the different magnifications to show detailed morphology of synthesized powders.

Table 1 A summary of synthesized powders and sintered samples

Composition of synthesized powders	Powders ID	Surface area, m ² /g	Powders impurities	Adding 5 % Ni	Adding 10 % Ni
TiB ₂	A	2.4		A5	A10
80% TiB ₂ -20% TiC*	B	4.7	Trace amount of	B5	B10
60% TiB ₂ -40% TiC	C	5.8	free carbon and	C5	C10
40% TiB ₂ -60% TiC	D	7.2	oxygen	D5	D10
TiC	E	11.3		E5	E10

*All percentages are weight percent

3 Results and discussion

3.1 Relative density

Fig. 2 illustrates the relative density after sintered at 1550°C for 1 hour with the function of TiB₂-TiC and Ni content. All samples reach above 94% relative density even with 5 wt% Ni additive. A5 sample has a relative density of 94%. By introducing TiC phase, the relative density increases to 94.5% for B5. With the increasing of TiC content, C5 and D5 have the highest relative density of 99.3% and 98.8%, respectively. For the sample of TiC-5Ni, the relative density is 96.2%. A similar relative density as a function of TiB₂-TiC composition can be observed by adding 10 wt% Ni. The relative density of C10 and D10 is ~99%. As a comparison, the relative density of TiB₂-10Ni and TiC-10Ni (A10 and E10) is 95.9% and 97.8%, respectively. It also should be mentioned that most samples contain 10 wt% Ni show slightly higher relative density for the ones with 5% Ni (A, B, D, and E). Overall, the composites with proper TiB₂/TiC ratio (C and D composite powders, C5, D5, C10, D10 composites) show the best sintering properties with relative density of ~99%.

Literatures report the sintering temperature of TiC-Ni cermet is normally in the range of 1400 to 1550°C, which is similar to the current research[8-10, 12]. However, for TiB₂ containing cermet, hot pressing is necessary to produce dense sample (>94% relative density). Agaogullari et al report that TiB₂-Co and TiC-TiB₂-Ni-X pressureless sintered at ~1550°C only reach ~69 to 85% relative density[19, 31]. Zou et al claim dense TiC-TiB₂-Ni

can be prepared at 1650°C through hot pressing[5, 7, 15, 22]. Obviously, the synthesized powders show excellent sintering properties. The synthesized fine powders can greatly increase the capillary force and decrease the mass transport distance during liquid phase sintering[8]. It also should be noted that the high levels of free carbon and oxygen in commercially available powders leads to the alteration of surface free energy, and inhibit the diffusion and densification. The low contaminations of synthesized powders ensure the densification occurs at a relative low temperature. Details regarding the sintering behavior will be discussed later with the appearance of microstructures.

Fig. 2 Relative density of samples sintered at 1550°C for 1 hour in argon atmosphere

3.2 Phases composition

Fig. 3 shows the XRD patterns of selected sintered samples. Samples contain 10 wt% Ni, A10, C10, and E10, were selected in order to observe the Ni compounds. It should be clarified that the peak position of Ni (111) (44.507°) is close to TiB_2 (101) (44.437°), therefore Ni (111) peak cannot be observed for A10 and C10. From Fig. 3, except TiB_2 , TiC, and Ni, no other phases can be observed. This indicates that no serious chemical reaction occurs during sintering process. Previous literatures claim that Ni_xTi_y , Ni_xB_y (it is hypothesized as Ni_3B based on previous report[4, 17]), and Ti_2O_3 form after sintered because of the reactions between Ni, TiC, TiB_2 , and other impurities.

However, these three phases cannot be identified from XRD patterns. There are two reasons to address this problem:

- (1) low free Ti and oxygen contaminations in the starting powders benefitting from the synthesis process[8, 24, 28];
- (2) Ni_xB_y can be observed through EDS (as shown in Fig. 8a, will discuss later), however the content of Ni_xB_y is relatively low and has exceeded the detecting limitation of XRD.

Fig. 3 XRD patterns of selected sintered samples with content of 10 wt.% Ni: A10, C10, and E10.

3.3 Microstructures

BSD microstructures of sintered samples containing 5 and 10 wt% Ni are shown in Fig. 4 and Fig. 5, respectively. It is known that low atomic weight phases have darker imaging through BSD. Dark, charcoal grey, grey, and white phases are identified as pores, TiB_2 , TiC , and Ni respectively, which are also confirmed by element detection through EDS. As mentioned before, Ni_xB_y phase can be observed through EDS. However, due to the limitation of boron detection through EDS, it is not clear what exact nickel boride phase exist in the system. Volume

fractions obtained from the Magnsci software of pores, TiB_2 , TiC , and Ni are also in good agreement with the relative density and starting compositions (need convert weight percentages to volume fractions).

The grain size of TiB_2 and TiC is summarized in Table 2. A high solid fraction can accelerate the rate of grain growth because of decreased diffusion distance[32]. Therefore, sample with 10 wt% Ni have finer grain size correspondingly. TiB_2 - Ni samples have the largest grain size for A5 and A10. With the introducing of 20 wt% TiC as the secondary solid phase (B samples), grain growth of TiB_2 is inhibited, which also indicates that the grain shape accommodation is obstructed. So, instead of regular shape, polygon TiB_2 grains can be found. With the increasing content of TiC phase, the grain size of TiB_2 continues reducing while TiC increasing. The exaggerated TiC grain growth exists in C5, while C10 sample has a fine grain size owing to the high Ni content. For both C and D samples, TiB_2 mainly have polygon and plate like grains while polygon grains for TiC . When monolithic TiC as the ceramic matrix, apparent exaggerated grain growth can be found in both E samples, as shown in Fig. 4e and Fig. 5e.

Porosity levels as can be observed in Fig. 4 and Fig. 5 are consistent with the relative density shown in Fig. 2. A, B and E samples have relative high porosity level comparing with C and D. A few pores can be observed for C and D samples (Fig. 4c, d and Fig. 5c, d), which confirms the high relative density ($\sim 99\%$). The average pore size in μm measured from Magnsci is shown in Fig. 6. Large round pores can clearly be observed for A samples (Fig. 4a and Fig. 5a) locate in $\text{TiB}_2/\text{TiB}_2$ interfaces or close to the triple point. There are also a few fine pores located within some exaggerated grown TiB_2 grains. With the introducing of a small amount of TiC , large pores as can be observed in B samples are similar to A samples, but with some fine pores at TiB_2/TiC interfaces (Fig. 4b and Fig. 5b). With the TiC content increasing, only fine pores can be observed and are mainly located at TiB_2/TiC grain boundaries (Fig. 4c and Fig. 5c). There are no obvious pores within grains due to the inhibited grain growth. A BSD micrograph at higher magnification of C10 clearly shows the fine pores at grain boundaries between TiB_2 and TiC (Fig. 8). The pores of D5, E5, and E10 are primarily locating within exaggerated grown TiC grain, along with some fine pores near interfaces. D10 has a fine pore sizes comparing with D5, which is because that the high liquid content slows the TiC grain growth, and consequently mainly fine pores.

Fig. 4 BSD micrographs of sintered samples containing 5 wt.%Ni. (a) A5, (b) B5, (c) C5, (d) D5, (e) E5.

Fig. 5 BSD micrographs of sintered samples containing 10 wt.%Ni. (a) A10, (b) B10, (c) C10, (d) D10, (e)

E10.

Fig. 6 Pore size in μm of samples sintered at 1550°C for 1 hour

Table 2 Grain size of TiB_2 and TiC for sintered samples

	Samples	TiB_2 grain size, μm	TiC grain size, μm
By adding 5 wt. %Ni	A5	12.5	N/A
	B5	3.5	1.2
	C5	2.2	1.5
	D5	1.4	2.8
	E5	N/A	7.2
By adding 10 wt. %Ni	A10	9.2	N/A
	B10	2.6	1.1
	C10	2	1.5
	D10	1.4	2.5
	E10	N/A	5.2

3.4 Sintering behavior

The principal driving force for liquid phase sintering is the capillarity and surface tension[33]. Fine particle size and low contact angle are beneficial to the densification because of the high capillarity and surface tension[8].

As can be observed in Fig. 1, the particle size of TiB_2 and TiC is submicron grade (0.5 to $1\mu\text{m}$) and nano grade (0.05

to 0.3 μm), respectively. The contact angle between TiC/Ni and TiB₂/Ni is $\sim 23^\circ$ and $\sim 40^\circ$ respectively from previous literatures[34]. It is noteworthy that the contact angle is varying with atmosphere, temperature, and impurity. However, it is clear that the wetting ability between TiC and Ni is better than that of TiB₂/Ni.

As the main coarsening mechanism, coalescence influences both grain size and pore size[33]. Coalescence, which is also named as Ostwald ripening, occurs due to the grain boundary curvature, and follows the solution-precipitation procedure as indicated in Fig. 7a: (1) dissolution of fine TiC/TiB₂ grains with high positive curvature; (2) diffusion toward coarse TiC/TiB₂ grains through liquid phase; (3) precipitation of dissolved fine on coarse TiC/TiB₂ grains. Coalescence of grains leads to the grain growth and shape accommodation, which is demonstrated by the regular TiB₂ grain shape (Fig. 3a, Fig. 4a). It should be acknowledged that the appearance of polygon TiC grains is dictated by the anisotropic surface energy of different crystallographic orientations[35, 36].

Differences in particle size and contact angel can explain that E samples (TiC-Ni, low contact angel, nano particle size) have higher relative density than A samples (TiB₂-Ni, high contact angel, submicron particle size). Pore filling is favorable for low contact angle systems during the intermediate stage of liquid phase sintering. However, for TiB₂-Ni samples, because of the high contact angle, large round pores may accumulate at the interfaces and triple points which are not able to be filled (Fig. 4a, 5a). Pore growth, similar to the grain growth through Ostwald ripening, is because of different solubility of large and small pores in the matrix. As a consequence, the large pores grow with the expense of small pores. The pores growth is not controllable because of the coalescence. Consequently, large pores form and lead to the low sintered density. The pores can either locate near grain boundaries or within exaggerated grown grains. Large round pores influence the relative density of TiB₂-Ni cermet (94% and 95.9% respectively for A5 and A10). These large pores are not able to be eliminated except applying external pressure (HP)[3, 4]. Wetting ability between TiC and Ni is better, thus the higher relative density comparing with TiB₂-Ni (96.2%, 97.8% respectively for E5 and E10). Trapped gas pores also form because of the solubility between the sintering atmosphere and TiC/TiB₂/Ni with the process of coalescence. It is known that the oxygen impurities in TiB₂ are mainly in the form of B₂O₃ and Ti_xO_y. Ni_xB_y forms via the reaction between Ni and TiB₂ as mentioned before. Both B₂O₃ and Ni_xB_y have relative high vapor pressures at the temperature range of $\sim 1550^\circ\text{C}$ [17, 25, 37]. Therefore, the atmosphere during the sintering process for TiB₂ containing samples includes argon and volatiles from B₂O₃ and Ni_xB_y. As a comparison, trapped gas pores in TiC-Ni cermet are mainly due to

the argon atmosphere. Trapped gas pores (argon and volatiles) in sintered TiB₂-Ni also contribute to the high porosity level than that of TiC-Ni cermet (mainly argon). TiB₂-Ni and TiC-Ni cermets have large pore size and it is not able to reach higher density in current sintering condition.

Coalescence is inhibited for TiB₂-TiC-Ni composites, as illustrated in Fig. 7 b. Set the coalescence of TiB₂ grains as an example, with the appearance of secondary TiC phase, fine TiB₂ grains can only dissolved into liquid phase without further diffusion toward coarse grains. The coalescence of TiB₂ is prevented during the second step of solution-precipitation. For TiC, however, considering the nano particle size, coalescence of TiC may occur in certain conditions, as illustrated in Fig. 7b of grey grains. When the TiC grain reaches a certain size, additional coalescence is restrained. The coalescence not only contributes coarse but also densification. Theoretically, the lack of coalescence will lead to a low relative density. Some pores are not able to be filled by the liquid penetration as shown in Fig. 7b, especially when liquid fraction is relatively low (5 and 10 wt%). As shown in Fig. 8b, with a sintering temperature of 1475°C, a significant amount of remaining pores can be observed, especially at the grain boundaries of TiC and TiB₂. It is necessary to increase the sintering temperature (1550°C for current paper) and eliminate the remaining pores through solid state sintering. TiB₂ grain shape accommodation is also inhibited. Instead of regular grains, polygon and plate like TiB₂ grains can be observed in TiB₂-TiC-Ni composites as mentioned before. Polygon grains are relative large comparing with those plate like grains as shown in Fig. 8a. As reported in previous literatures[1, 16, 38], TiB₂ has a hexagonal close packed structure (C32, $a = 3.033$ and $c = 3.23$), with the stacking of Ti planes and B network along the c-direction. The fastest growing planes of TiB₂ are the $\{1\ 1\ \bar{2}\ 0\}$ families with a low-activation energy diffusion path along $\langle 1\ \bar{1}\ 0\ 0 \rangle$ direction, which forms a two-dimensional network. Hence TiB₂ tends to grow into a plate like morphology initially (Fig. 8a red circles), with the c-axis perpendicular to the plate plane. With the continue growing of TiB₂ grains, plate like grains accommodate to polygon grains. This explains the appearance of fine TiB₂ plate like grains and relatively large polygon grains. Another advantage of the introducing of TiC phase is that fine TiC particles/grains can fill some large pores at the interface of TiB₂/TiB₂, due to the good solubility of TiC in liquid Ni. Fine pores form as discussed before. Part of these fine pores can be eliminated through solid state sintering as mentioned. In short, the introducing of TiC phase is beneficial to high relative density. However, it is interesting that all B samples have similar relative density with A samples correspondingly. Although a sufficient high sintering temperature is supplied, the volatiles from impurities in TiB₂ and poor wetting ability of TiB₂/Ni still lead to the formation of large pores. With the decreasing

of TiB_2 content, volatiles have been minimized, consequently have the highest relative density (C and D samples). With the occurrence of exaggerated grown of TiC grains (D5, E5, E10, especially E samples), large entrapped gas pores form and result in the reduction of relative density.

Fig. 7 Coalescence process of monolithic and composite. (a) coalescence of monolithic; (b) coalescence of composite, dark grey ones represent TiB_2 grains and grey ones represent TiC grains

Fig. 8 High magnification BSD micrographs of C10 sample at different sintering temperatures for one hour. (a) C10 sample sintered at 1550°C along with EDS spectrums of the binder phase (selected blue point), (b) C10 sample sintered at 1475°C

3.5 Hardness

Fig. 9 shows the Vickers hardness of sintered samples over TiB_2/TiC compositions and Ni contents. The Vickers hardness for A5 and A10 is 19.94 and 17.62 GPa, respectively. With the introducing of TiC, the hardness

slightly decreases to 19.36 and 17.35 GPa for B5 and B10 samples. C samples have the highest hardness, which is 24.23 and 21.85 GPa with 5 and 10 wt% Ni. Hardness decreases with more TiC for D and E samples.

Hardness is greatly dependent on relative density. It is obvious that samples with high relative density (C and D samples) have high hardness. Except relative density, hardness is also influenced by Ni content, the hardness of ceramic matrix (can be influenced by TiB₂/TiC composition because TiB₂ and TiC have different hardness, TiB₂: 25-35GPa, TiC: 24-32GPa[1, 2]), and microstructures[39]:

$$H = aH_s \times C_{ss} + bH_s \times V_s + H_L \times V_L(1 - G^{-\frac{1}{2}})$$

Where H is the hardness, a and b are constants, H_s is the hardness of the ceramic matrix, V_s is the volume fraction of ceramic, H_L is the hardness of Ni, V_L is the volume fraction of Ni, C_{ss} is the contiguity, and G is the grain size. C_{ss} can be measured using the number of intercepts per unit length of test line N[32]:

$$C_{ss} = \frac{2N_{ss}}{2N_{ss} + N_{SL}}$$

Where N_{ss} and N_{SL} is the ceramic-ceramic and ceramic-Ni intercepts per unit length N. From above equation, obviously, samples contain 5 wt% Ni have higher hardness than with 10 wt% Ni for each TiB₂/TiC composition. Another factor need consider is that the hardness of TiB₂ (25-35GPa) is somewhat higher than TiC (24-32GPa). B samples have similar relative density comparing with A samples but a slightly lower hardness. Although the fine grain size of B samples contributes to a high hardness, the presence of TiC decreases the hardness. Except high relative density, fine grain size in C and D samples (~1.4-2.8μm) also results in the high hardness. It is worth mentioning that the difference between the hardness of C and D samples is much more notable comparing with A and B samples. The most obvious reason is that C samples have higher TiB₂ content than that of D samples, as discussed before. Another reason should be attributed to the different volume fractions of ceramic phase. The density of TiB₂ (4.52g/cm³) is slightly lower than TiC (4.93g/cm³), as a consequence, the volume fraction of ceramic phase in C is higher than D (for instance, 97.31 vol% for C5 and 97.26 vol% for D5). The high volume fraction of ceramic phase causes the high hardness, as indicated in above equation. The relative high ceramic phase volume fraction in C sample also results in a high contiguity. The high contiguity aids the hardness because of greater rigidity from the ceramic-ceramic contracts. The measured contiguity of C5 and D5 is 0.78 and 0.71, respectively. The high volume fraction of ceramic phase and contiguity in C samples give another reason of the notable higher hardness of C sample comparing with D sample. The hardness of present paper is remarkably higher than previously

reported TiC-TiB₂-Ni composite with similar binder content. The hardness from literatures is in the range of 20.22 to 22.54 GPa with binder content of 5 to 10 wt%[5, 6, 15, 40]. This is also ascribed to the high relative density and fine grain size as discussed.

Fig. 9 Vickers hardness of samples sintered at 1550°C for one hour over TiB₂/TiC composition and Ni content

3.6 Fracture toughness

Fracture toughness obtained from Vickers indentation technique is shown in Fig. 10. Fracture toughness is dependent on hardness. Theoretically, high hardness sample is expected to have low fracture toughness. The calculated fracture toughness for A5 and A10 is 9.61 and 8.45 $MPa \cdot m^{1/2}$, respectively. With the introducing of TiC, fracture toughness decreases to 8.62 and 8.1 $MPa \cdot m^{1/2}$ for B5 and B10. C and D samples have high Vickers hardness, consequently low fracture toughness. The fracture toughness of C5 and C10 is 7.41 and 8.44 $MPa \cdot m^{1/2}$, respectively. Fracture toughness increases with the continual increasing of TiC content and approaches to 8.2 and 8.67 $MPa \cdot m^{1/2}$ for E5 and E10. There is an exception for D10 sample with a relatively low fracture toughness of 8.11 $MPa \cdot m^{1/2}$ comparing with 8.44 $MPa \cdot m^{1/2}$ for C10 sample.

Hardness and fracture toughness are the two most important properties of cermet for the structural application. It is necessary to obtain a sample with the combination of high hardness and fracture toughness. Fig. 11

illustrates a comparison of present properties (red ones) with previous results (black ones). Previous results are taken from following references[4-6, 12, 15, 40]. Three groups samples, A, C, and E, which represent TiB₂-Ni, TiC-TiB₂-Ni, and TiC-Ni, are included. Red circles, red cubes, and red cross stands for TiB₂-Ni, TiB₂-TiC-Ni, and TiC-Ni, respectively. One thing need concern is that previous reports have different loads for Vickers hardness examination and fracture toughness determination techniques. This may influence the comparison, but the graph looks reasonable after add sufficient data points. Previous results indicate that: (1) TiB₂-Fe-Ni-Cr (results of reference 4) has a better combination of hardness and toughness than conventional carbide cermet (both TiC and WC based, results of references 4 and 12) at low toughness range (lower than $\sim 14 \text{ MPa} \cdot \text{m}^{1/2}$); (2) since the metallic binder content of TiB₂-Ti(C,N)-(Ni,Mo) composite (results of references 5, 6, 15, 40) from previous research is relative low (3 to 10 wt%), with the hardness higher than 20 GPa, composite appears to have slightly better properties. Present TiB₂-Ni and TiC-Ni cermets have similar properties comparing with literature results. TiB₂-TiC-Ni composites show significantly better properties than that of previous TiB₂-Ti(C,N)-(Ni,Mo) based materials; a higher toughness at similar Vickers hardness. The appearance of the high hardness is discussed before, and it is necessary to understand the toughening mechanism.

Crack propagation paths of selected sintered TiB₂-TiC-Ni composites are presented in Fig. 12. Intergranular fracture dominates the fracture mold at TiB₂/TiC grain boundaries. Crack deflection can be observed at where intergranular fracture happens. Transgranular cracks present mainly at some exaggerated grown TiC grains (blue arrows). Crack bridging can also be observed at some fine and coarse grains interfaces (red arrows). It is well known that the metallic phase in cermet supplies plastics deformation and the crack bridging-induced toughening. Therefore, sample with a high Ni content has a high fracture toughness correspondingly, as illustrated in Fig. 10. Also, considering the different thermal expansion coefficient (CTE) of TiC and TiB₂ and the appearance of TiB₂/TiC interfaces, stress field toughening mechanism is proposed. Wen et al studied the toughening mechanism of TiB₂-TiC composite obtained from reaction processing method[38]. TiB₂ has anisotropic CTE with $\alpha_a = 7.19 \times 10^{-6} \text{K}^{-1}$ and $\alpha_c = 9.77 \times 10^{-6} \text{K}^{-1}$, while TiC is isotropic with $\alpha_a = 7.2 \times 10^{-6} \text{K}^{-1}$ [1, 16]. TiB₂ has higher CTE along c-axis, and similar CTE along a-axis comparing with TiC. This leads to a weak interfacial bonding at a-axis interface, and a large shear stress at c-axis interface, as indicated in Fig. 8. Interfacial stress prompts cracks propagate along the interfaces (debonding of the interfaces, as shown in Fig. 12). The formation of a debonded interface spreads the strain displacement imposed on the bridging TiB₂ grains, which generates a larger crack

opening displacement per unit of stress[41]. The increased crack opening displacement with distance behind the crack tip significantly enhances the fracture toughness. D samples do not show remarkable better properties, as blue cubes illustrated in Fig. 11. This is likely because of the polycrystalline growth of TiC grains as discussed in 3.4. Zou et al report that exaggerated grain growth of TiC deteriorates the fracture toughness, which can explain the relative “low” fracture toughness of D samples[15]. This is also demonstrated by the transgranular fracture of TiC grains.

Fig. 10 Fracture toughness of samples sintered at 1550°C for one hour over TiB_2/TiC composition and Ni content

Fig. 11 A comparison of present results with literature results. Black ones are literature reported results. Red circles, red cubes, and red cross are A, C, and E samples respectively. Blue cubes are D samples.

Fig. 12 Crack propagation paths of selected sintered $\text{TiB}_2\text{-TiC-Ni}$ composites, red and blue arrows illustrate grain bridging and transgranular crack propagation, respectively. (a) C5, (b) D5, (c) C10, (d) D10

4 Conclusion

In this present work, $\text{TiB}_2\text{-TiC-Ni}$ composites were fabricated with improved mechanical properties for structural applications. Sintering behavior, phases compositions, microstructures, and mechanical properties were studied. By utilizing high quality powders of TiB_2/TiC , a sintering temperature of 1550°C without applied external pressure can have relative density of 99% theoretical density. The introducing of a secondary TiC phase greatly inhibits the grain growth and therefore, the resulting composites have fine microstructures with grain size of ~ 1.5 to $2.8\ \mu\text{m}$. Plate like TiB_2 grains also form owing to the anisotropic growth rate along a and c-axis planes of TiB_2 . Due to the fine microstructures, the composites have outstanding mechanical properties with a combination of hardness and fracture toughness as $24.23\ \text{GPa}$, $7.41\ \text{MPa} \cdot \text{m}^{1/2}$, and $21.85\ \text{GPa}$, $8.44\ \text{MPa} \cdot \text{m}^{1/2}$. The toughening mechanisms include Ni binder phase plastics deformation and crack bridging, and debonding of $\text{TiB}_2\text{-TiC}$ interface caused by stress filed. It was also reported that the high content of TiC deteriorated the fracture toughness because of exaggerated grain growth of TiC .

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Reference:

- [1] B. Basu, G.B. Raju, A.K. Suri, Processing and properties of monolithic TiB₂ based materials, *International Materials Reviews* 51(6) (2006) 352-374.
- [2] D. Vallauri, I.C. Atías Adrián, A. Chrysanthou, TiC–TiB₂ composites: A review of phase relationships, processing and properties, *Journal of the European Ceramic Society* 28(8) (2008) 1697-1713.
- [3] R. González, M.G. Barandika, D. Oña, J.M. Sánchez, A. Vilellas, A. Valea, F. Castro, New binder phases for the consolidation of TiB₂ hardmetals, *Materials Science and Engineering: A* 216(1–2) (1996) 185-192.
- [4] R. Telle, L.S. Sigl, K. Takagi, Boride-Based Hard Materials, *Handbook of Ceramic Hard Materials*, Wiley-VCH Verlag GmbH 2000, pp. 802-945.
- [5] M. Gu, C. Huang, B. Zou, B. Liu, Effect of (Ni, Mo) and TiN on the microstructure and mechanical properties of TiB₂ ceramic tool materials, *Materials Science and Engineering: A* 433(1-2) (2006) 39-44.
- [6] L. Wang, H. Liu, C. Huang, B. Zou, X. Liu, Effects of sintering processes on mechanical properties and microstructure of Ti(C,N)–TiB₂–Ni composite ceramic cutting tool material, *Ceramics International* 40(10) (2014) 16513-16519.
- [7] B. Zou, C. Huang, J. Song, Z. Liu, L. Liu, Y. Zhao, Mechanical properties and microstructure of TiB₂–TiC composite ceramic cutting tool material, *International Journal of Refractory Metals and Hard Materials* 35 (2012) 1-9.
- [8] R. Koc, C. Meng, G.A. Swift, Sintering properties of submicron TiC powders from carbon coated titania precursor, *Journal of Materials Science* 35(12) (2000) 3131-3141.
- [9] S. Cardinal, A. Malchère, V. Garnier, G. Fantozzi, Microstructure and mechanical properties of TiC–TiN based cermets for tools application, *International Journal of Refractory Metals and Hard Materials* 27(3) (2009) 521-527.
- [10] S. Park, S. Kang, Toughened ultra-fine (Ti,W)(CN)–Ni cermets, *Scripta Materialia* 52(2) (2005) 129-133.
- [11] S.-Y. Ahn, S. Kang, Formation of Core/Rim Structures in Ti(C,N)-WC-Ni Cermets via a Dissolution and Precipitation Process, *Journal of the American Ceramic Society* 83(6) (2000) 1489-1494.

- [12] C. Park, S. Nam, S. Kang, Enhanced toughness of titanium carbonitride-based cermets by addition of (Ti,W)C carbides, *Materials Science and Engineering: A* 649 (2016) 400-406.
- [13] Z. Fu, K. Mondal, R. Koc, Sintering, mechanical, electrical and oxidation properties of ceramic intermetallic TiC–Ti₃Al composites obtained from nano-TiC particles, *Ceramics International* 42(8) (2016) 9995-10005.
- [14] C.C. Onuoha, G.J. Kipouros, Z.N. Farhat, K.P. Plucknett, The reciprocating wear behaviour of TiC–304L stainless steel composites prepared by melt infiltration, *Wear* 303(1–2) (2013) 321-333.
- [15] B. Zou, C. Huang, J. Song, Z. Liu, L. Liu, Y. Zhao, Effects of sintering processes on mechanical properties and microstructure of TiB₂–TiC+8wt% nano-Ni composite ceramic cutting tool material, *Materials Science and Engineering: A* 540 (2012) 235-244.
- [16] M.K. Ferber, P.F. Becher, C.B. Finch, Effect of Microstructure on the Properties of TiB₂ Ceramics, *Journal of the American Ceramic Society* 66(1) (1983) C-2-C-3.
- [17] M.A. Einarsrud, E. Hagen, G. Pettersen, T. Grande, Pressureless sintering of titanium diboride with nickel, nickel boride, and iron additives, *Journal of the American Ceramic Society* 80(12) (1997) 3013-3020.
- [18] S.H. Kang, D.J. Kim, E.S. Kang, S.S. Baek, Pressureless Sintering and Properties of Titanium Diboride Ceramics Containing Chromium and Iron, *Journal of the American Ceramic Society* 84(4) (2001) 893-895.
- [19] A.A. Ogwu, T.J. Davies, The densification and mechanical properties of a TiC and TiB₂ hardmetal sintered with a reactive alloy binder, *physica status solidi (a)* 153(1) (1996) 101-116.
- [20] J. Song, C. Huang, M. Lv, B. Zou, S. Wang, J. Wang, J. An, Effects of TiC content and melt phase on microstructure and mechanical properties of ternary TiB₂-based ceramic cutting tool materials, *Materials Science and Engineering: A* 605 (2014) 137-143.
- [21] J. Song, C. Huang, B. Zou, H. Liu, L. Liu, J. Wang, Effects of sintering additives on microstructure and mechanical properties of TiB₂–WC ceramic–metal composite tool materials, *International Journal of Refractory Metals and Hard Materials* 30(1) (2012) 91-95.
- [22] J. Song, C. Huang, B. Zou, H. Liu, J. Wang, Microstructure and mechanical properties of TiB₂–TiC–WC composite ceramic tool materials, *Materials & Design* 36 (2012) 69-74.
- [23] R. Koc, G. Glatzmaier, J. Sibold, β -SiC production by reacting silica gel with hydrocarbon gas, *Journal of Materials Science* 36(4) (2001) 995-999.

- [24] Z. Fu, R. Koc, Synthesis of TiC-TiB₂ composite powders from carbon coated TiO₂ precursors, *Ceramics International* 42(10) (2016) 12231–12238.
- [25] W.-M. Guo, G.-J. Zhang, Y. You, S.-H. Wu, H.-T. Lin, M.A. Einarsrud, TiB₂ Powders Synthesis by Borothermal Reduction in TiO₂ Under Vacuum, *Journal of the American Ceramic Society* 97(5) (2014) 1359-1362.
- [26] R. Koc, G.C. Glatzmaier, Process for synthesizing titanium carbide, titanium nitride and titanium carbonitride, U.S. Patent No. 5,417,952, 1995.
- [27] R. Koc, J.R. Mawdsley, J.D. Carter, Synthesis of metal borides, U.S. Patent No. 9,073,758, 2015.
- [28] R. Koc, J.S. Folmer, Carbothermal synthesis of titanium carbide using ultrafine titania powders, *Journal of Materials Science* 32(12) (1997) 3101-3111.
- [29] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements, *Journal of the American Ceramic Society* 64(9) (1981) 533-538.
- [30] D.K. Shetty, I.G. Wright, P.N. Mincer, A.H. Clauer, Indentation fracture of WC-Co cermets, *Journal of Materials Science* 20(5) (1985) 1873-1882.
- [31] D. Ağaoğulları, H. Gökçe, İ. Duman, M.L. Öveçoğlu, Influences of metallic Co and mechanical alloying on the microstructural and mechanical properties of TiB₂ ceramics prepared via pressureless sintering, *Journal of the European Ceramic Society* 32(9) (2012) 1949-1956.
- [32] R.M. German, *Liquid phase sintering*, Plenum Press, New York and London, 1985.
- [33] R.M. German, P. Suri, S.J. Park, Review: liquid phase sintering, *Journal of Materials Science* 44(1) (2009) 1-39.
- [34] R. Asthana, S. Mileiko, N. Sobczak, Wettability and interface considerations in advanced heat-resistant Ni-base composites, *Bulletin of the Polish Academy of Sciences Technical Sciences* 54(2) (2006).
- [35] S. Zaima, Y. Shibata, H. Adachi, C. Oshima, S. Otani, M. Aono, Y. Ishizawa, Atomic chemical composition and reactivity of the TiC(111) surface, *Surface Science* 157(2) (1985) 380-392.
- [36] W. Liu, X. Liu, W.T. Zheng, Q. Jiang, Surface energies of several ceramics with NaCl structure, *Surface Science* 600(2) (2006) 257-264.
- [37] S. Baik, P.F. Becher, Effect of Oxygen Contamination on Densification of TiB₂, *Journal of the American Ceramic Society* 70(8) (1987) 527-530.

- [38] G. Wen, S.B. Li, B.S. Zhang, Z.X. Guo, Reaction synthesis of TiB_2 – TiC composites with enhanced toughness, *Acta Materialia* 49(8) (2001) 1463-1470.
- [39] G. Grathwohl, R. Warren, The effect of cobalt content on the microstructure of liquid-phase sintered TaC-Co alloys, *Materials Science and Engineering* 14(1) (1974) 55-65.
- [40] H. Liu, Q. Shi, C. Huang, B. Zou, L. Xu, J. Wang, In-situ fabricated TiB_2 particle-whisker synergistically toughened Ti(C, N)-based ceramic cutting tool material, *Chinese Journal of Mechanical Engineering* 28(2) (2015) 338-342.
- [41] P.F. Becher, Microstructural Design of Toughened Ceramics, *Journal of the American Ceramic Society* 74(2) (1991) 255-269.