The production and synthesis mechanism of submicron Ti(C,N)-based cermets by reactive hot-pressing technology from a Co–Ti–C–BN system

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The phase formation mechanism of Ti(C,N)–TiB2–Co composite cermets during the reactive hot-pressing process was investigated by delicate microstructure and phase analysis of Co–Ti–C–BN powder compacts sintered at different temperatures. The results showed that Ti–BN and Co–Ti solid diffusion reactions occurred. As the sintering temperature was increased 1020°C, Co–Ti liquid was formed by the eutectic reaction between Ti and the preformed CoTi2. Subsequently, TiB combined with B to yield TiB2 through the mass transfer of liquid, whereas Ti6.5N and Ti3N2 gradually transformed into TiN. With increasing sintering temperature, Ti(C,N) was fabricated by the diffusion of C into TiN unit cell, and B reacted with Ti affording TiB2. High-density submicron Ti(C,N)-based cermets could be synthesized at low temperatures due to the formation of Co–Ti liquid at 1020°C and an applied pressure of 34 MPa. The Ti(C,N)–TiB2–Co composite cermets prepared at 1150°C possessed the optimum relative density, average particle size, hardness, and fracture toughness of 99.8%, 0.571 μm, 1947 HV10, and 6.6 MPa·m1/2, respectively. Moreover, the dry friction and wear resistance of Ti(C,N)–TiB2–Co composite cermets is 2.5 times higher than that of YT15 cemented carbide.

Key-words: Powder metallurgy method, Microstructure, Reaction mechanism

1. Introduction

Ti(C,N)-based cermets have been widely used as cutting tools in the finishing and semi-finishing of carbon steels attributing to their high hardness, low friction coefficient to steels, and good high-temperature stability.1–3 To further improve the wear resistance, composite cermets combining Ti(C,N) and second-phase ceramic particles have been explored.3–6 As a good component of cutting tool materials, TiB2 has many advantages such as ultra-high hardness (32 GPa), low friction coefficient, excellent high-temperature oxidation resistance (>1000°C) as well as comparable thermal expansion coefficient with Ti(C,N).3,7–9 In indeed, Shankar et al.9 demonstrated that the hardness and toughness of Ti(C,N)-based cermets improved by adding TiB2 as the additive. Conventionally, Ti(C,N)-based cermets are produced by a two-step approach, i.e., the preparation of blended powder compacts, followed by sintering the compacts.3,10 However, TiB2 has a low diffusion coefficient. Furthermore, there is an oxygen-rich layer on the surface of commercial powder.8,11 Hence, a sintering temperature >1500°C and a pressure >32 MPa are required to obtain dense materials.9 As well known, high temperature would lead to de-nitriding and the excessive growth of Ti(C,N), deteriorating the mechanical properties of cermets.

As a displacement reaction under pressure, a novel reactive hot-pressing (RHP) technology possesses three sintering driving forces, including surface freedom energy of powders, chemical reaction energy of reactants, and mechanical pressure. Therefore, the sintering temperature and holding time reduced compared to the traditional powder metallurgy,12–15 favoring the production of materials with fine grains. In recent years, this technique has been widely used to produce super hard and ultra-high temper-
ature materials;\textsuperscript{16,17} however, there is a lack of knowledge on Ti(C,N)-based cermets. Since cermets are derived from the chemical reaction of reactants, knowledge about the reaction mechanism is required to optimize the sintering parameters and control the microstructure of sintered materials. Traditionally, the phase formation mechanism is explored by thermodynamic calculation, differential thermal analysis or differential scanning calorimeter analysis (DSC), and quenching of the combustion front method.\textsuperscript{18-21} These methods provide detail information; however, they may not be fully reliable due to the great disparity in experimental conditions (e.g., green density of powder compact and heating mode). Therefore, it is necessary to understand the phase transition and microstructure evolution behavior of powder compacts during the RHP process. Unfortunately, detailed studies regarding these aspects are rather limited because of the complex reaction process.

In this study, the in situ synthesis mechanism of TiB\textsubscript{2}/Ti(C,N) cermets was addressed through the comparative studies on the phase compositions and microstructure of powder compacts during the RHP process. Moreover, high-density submicron Ti(C,N)-based cermets were prepared, and their microstructure and mechanical properties were investigated. These results could provide insights into the RHP technology and would be beneficial for improving the production of sub-\textmu m Ti(C,N)-based cermets.

2. Experimental

Commercial Co (99\% purity, <1 \textmu m), Ti (98\% purity, <6.5 \textmu m), C (98\% purity, <1.3 \textmu m), and BN (99\% purity, <0.5 \textmu m) powders were used as the raw materials. The reagent powders were mixed at a proper mole ratio (Co:Ti:C:BN = 1:10:4:4) for 8 h and then compacted into a cylindrical shape (h = 20 mm) at an applied pressure of 20 MPa for 5 min. Subsequently, the powder compact was heated to a designed temperature in a vacuum hot pressing sintering furnace (Model ZT-40-20y, China). When the sintering temperature exceeded 900\degree C, a mechanical pressure of 20 MPa was applied. The sintered samples were cut, ground, and polished. Then, the phase compositions of the polished surfaces were examined by X-ray diffraction (XRD) (Model D8 Advance, Germany) using Cu K\textsubscript{α} radiation source. The microstructures of the polished surfaces were examined by field-emission scanning electron microscopy (Model S-4800, Japan) equipped with energy dispersive spectrometry (EDS) (Model Link-ISIS, England). The EDS measurements were performed at an applied voltage of 15.0 kV. The hardness of the compacts was measured using a Vickers indenter (Model HVST-10, China) at a load of 98 N for 15 s. The fracture toughness was tested by the indentation method and calculated by applying Niihara formula. The relative density was calculated according to theoretical density, and the apparent density measured by the Archimedes method. The wear resistance was tested by a reciprocating dry friction and wear machine (Model UMT-3, USA), as described in Ref.\textsuperscript{21}

3. Results and discussion

3.1 In situ synthesis mechanism

Figure 1 shows the microstructure of the powder compacts. After the pre-pressing procedure, powder particles stack together, probably increasing the contact area among particles and decreasing the diffusion distance of atoms. According to the elemental mapping images, Co, Ti, and C grains were well distinguished, whereas fine BN particulates (<0.5 \textmu m) mainly accumulate on the surface of Ti. With increasing sintering temperature, the phase compositions of powder compacts gradually changed, as shown in Fig. 2. The sample quenched from 700\degree C showed new Ti\textsubscript{2}N and TiB phases in the XRD pattern [Fig. 2(c)]. Furthermore, the diffraction peaks of Ti shifted to lower angels, as indicated by the green dotted lines. Yang et al.\textsuperscript{22} investigated the phase evolution path of Ti–BN system during the RHP process, considering that N atoms preferentially diffused into Ti to form a solid solution of TiN\textsubscript{0.3}. As a result, the cell size of Ti increased and Ti peaks shifted to lower angels. With further dissolution of N, TiN\textsubscript{0.3} gradually transformed into Ti\textsubscript{2}N. Similarly, B atoms

![](image.png) Fig. 1. Microstructure and elemental mapping images of powder compact.
combined with Ti to produce TiB. Figure 3 shows the corresponding microstructure. TiB and Ti$_2$N display a needle-like shape$^{18}$ and a granular morphology, respectively, providing evidence for the solid diffusion reaction of Ti + BN $\rightarrow$ TiN$_{0.3}$ + Ti$_2$N + TiB. Moreover, TiB and Ti$_2$N distribute in different zones. It is speculated that the preformed TiN$_{0.3}$ and Ti$_2$N restricted the diffusion of B atoms. As a consequence, B atoms diffused to other zones and reacted with the unreacted Ti to yield TiB. The diffusion for a relatively long distance led to the formation of a small amount of TiB in comparison with Ti$_2$N, as shown in Fig. 2(c).

Continuous heating favors the diffusion of atoms. Faran et al.$^{23}$ and Ma et al.$^{24}$ investigated the phase diagram of Ti–B–N system and the interfacial reaction of Ti/BN joint. They argued that the decrease in the Gibbs free energy actuated the formation of a new phase, and Ti$_2$N–BN interface reaction affording TiN possessed the maximum driving force. After the prior formation of Ti$_2$N and TiN$_{0.3}$, N atoms continuously penetrated the Ti–TiN$_{0.3}$–Ti$_2$N–BN layer, further triggering the fabrication of TiN$_{0.3}$ and Ti$_2$N. And TiN was synthesized at the Ti$_2$N–BN interface. Therefore, in the sample quenched from 800°C, a new TiN phase was determined by the XRD analysis, and the intensity of the diffraction peaks of Ti$_2$N and TiN$_{0.3}$ increased [Fig. 2(d)]. In addition, CoTi$_2$ appeared, and the contents of Co and Ti significantly decreased. The DSC analysis of the reaction process of Co–Ti powder mixtures revealed that CoTi$_2$ should be prepared by the solid diffusion reaction between Co and Ti.$^{17}$

With a further increase in the sintering temperature, Co completely transformed into CoTi$_2$. In contrast, with the continuous penetration of N into Ti–TiN$_{0.3}$–Ti$_2$N–BN layer, the intensity of the diffraction peaks of Ti$_2$N and TiN$_{0.3}$ increased, whereas those of BN, TiN$_{0.3}$, and Ti decreased [Fig. 2(e)]. Figure 4 illustrates the corresponding microstructure. The elemental mapping images show the Co and Ti elements together, offering evidence for the occurrence of Co–Ti reaction. Notably, the diffraction peaks of TiB scarcely increased, probably because of the prior formation of TiN$_{0.3}$, as discussed in the products quenched from 700°C. Furthermore, TiC was not detected by the XRD, though the solid diffusion reaction of Ti + C $\rightarrow$ TiC is feasible. According to Ref.$^{25}$ there is a competition between Ti–N and Ti–C reaction, and the former is easier to occur than the latter. In general, the mapping data should be obtained after polishing the surface. However, when the samples were sintered at low temperatures (e.g., 900°C), only Co–Ti and Ti–BN solid-state diffusion reactions occurred, affording relatively loose samples. As a result, the rough surfaces were observed (Figs. 1 and 4), although the sintered samples were ground and polished.

The sample quenched from 1000°C showed a significant change in the phase compositions. As shown in Fig. 2(f),
TiB disappeared, while Co₂B and TiB₂ appeared. In addition, the CoTi₂, Ti₂N, and TiN₀.₃ content decreased, and the diffraction peaks of TiN slightly shifted to lower angels. Zhan et al.²⁵) studied the phase evolution route of Ti–C–BN and Ni–Ti–C–BN systems. The results showed that the addition of Ni into Ti–C–BN powder mixtures promoted the synthesis of Ti(C,N) and TiB₂ by the preformed Ni–Ti liquid. It is inferred that analogous behavior existed in the Co–Ti–C–BN system. According to the Co–Ti phase diagram,²⁶) the eutectic reaction of L → CoTi₂ + Ti would occur at 1020°C. This reaction may occur at the measured temperature of 1000°C, because of the temperature hysteresis effect. The presence of a Co–Ti liquid could enhance the density of powder compact and the contact area among particles. Then, BN and C atoms surrounding diffused and dissolved into Co–Ti melt. In general, the atoms in the liquid state would move more rapidly. Therefore, N atoms passed through Ti–TiN₀.₃–Ti₂N–TiN–BN layer via the mass transfer of liquid, accelerating the transformation of TiN₀.₃ and Ti₂N to TiN. Similarly, the C atoms diffused and dissolved into TiN as well. Since the atomic radii of C (0.91 Å) (1 Å = 0.1 nm) is larger than that of N (0.75 Å), the dissolution of C into TiN would increase the cell size of TiN. As a result, TiN peaks began to shift to lower angles (blue dot lines in Fig. 2, corresponding to the initial formation of Ti(C,N). In contrast, B atoms combined with the preformed TiB to produce TiB₂ via the mass transfer of liquid. In general, atoms in the liquid could move freely and are more likely to collide with one another.²⁷) During the cooling process, Co₂B may form by the reaction of B and Co atoms in the melt and then crystallized out, and Co₂B was identified in the cooling sample. Figure 5 is the corresponding microstructure. A molten-like phase was clearly observed, demonstrating the formation of liquid. Based on the elemental mapping images, the molten-like phase comprises Co, Ti, and N in addition to a small amount of C and B. These could be viewed as a direct evidence of a large amount of TiN being fabricated, and Ti(C,N) was initially formed through the diffusion and dissolution of C into TiN. Moreover, B and C elements overlapped, mainly derived from the sluggish Ti–B solid diffusion reaction and the absence of Ti–C solid diffusion reaction.
With further increase in temperature, the spreading and wettability of liquid and the diffusion ratio of atoms enhanced. Hence, C atoms successively diffused and dissolved into TiN in the temperature range 1000–1100°C, promoting the continuing shift of TiN peaks and the synthesis of Ti(C,N). Moreover, B atoms diffused and dissolved into liquid, reacting with Ti in the melt to form TiB₂. Therefore, in the sample quenched from 1100°C, the TiB₂ and TiN peaks increased [Fig. 2(g)]. Figures 6(a) and 6(b) show the corresponding microstructure and EDS spectra of the powder compact quenched at 1100°C. Co, Ti, and C elements were observed in the molten-like phase, but B element was not observed. This can be explained by the fact that the formation reaction of TiB₂ almost completed. Clearly, this originates from the prior consumption of B atoms. For example, TiB was fabricated at approximately 700°C [Fig. 2(d)], and TiB₂ was synthesized at 1000°C [Fig. 2(f)]. In contrast, the amount of residual B is too less to be obviously identified. Detecting light elements is well known to be difficult because of the low fluorescence quantum yield and X-ray energy. Notably, a small number of weak peaks could not be identified (Fig. 1), although all the possible compounds in the Co–Ti–C–BN system were considered and carefully investigated. One reason may be the formation of solid solution, leading to the shift of peaks. Another reason may be the impurities in the raw materials, reacting with reactants to form metastable phases during the heating process. A small amount of unknown phases should not significantly affect the main reaction process.

With the progress of the reaction, the residual B, C, and N dissolved into the melt. With the consumption of Ti, C, N, and B in the liquid, free Co gradually released. When the temperature increased to 1200°C, the full conversion of Ti(C,N) and TiB₂ was achieved, and only Ti(C,N), TiB₂, and Co phases were detected by the XRD [Fig. 2(h)]. In addition, the intensity of the diffraction peaks of TiB₂ in Fig. 2(h) slightly increased compared to those in Fig. 2(g), clearly demonstrating a small amount of residual B atoms in the sample heated to 1100°C. Figure 7 shows the backscattering images and the corresponding EDS images of the sample quenched at 1200°C. As shown in Fig. 7(a), dark gray TiB₂ and white Co uniformly distribute in the grayish Ti(C,N) matrix. Figures 7(b) and 7(c) further provide evidence for the formation of free Co, released from the liquid.

Based on the above results and analysis, the phase evolution path of Co–Ti–C–BN system could be described as follows: (1) Co + Ti + C + BN → (2) Co + Ti + C + BN + Ti₃N + Ti₂N → (3) Ti + C + BN + Ti₃N + Ti₂N + TiB + TiN + CoTi₂ → (5) Ti + C + BN + Ti₃N + Ti₂N + TiB + TiN + Co–Ti (liquid) → (6) Ti + C + BN + Ti₃N + Ti₂N + TiB + TiN + Co–Ti–B–C–N (liquid) → (7) Co + C + BN + Ti₃N + Ti₂N + TiN + Ti(C,N) + TiB₂ + Co–Ti–B–C–N (liquid) → (8) Co + C + BN + Ti₃N + Ti₂N + TiN + Ti(C,N) + TiB₂ + Co–Ti–B–C–N (liquid) → (9) Co + TiB₂ + Ti(C,N).
residual C and B into liquid. Consequently, Ti(C,N) was fabricated by the diffusion of C into TiN. Simultaneously, B reacted with Ti forming TiB₂. With the consumption of Ti, C, B, and N atoms in the melt, free Co gradually liberated, indicating the presence of Ti(C,N), TiB₂, and Co in the sample.

3.2 Microstructure and mechanical properties

The investigation of the reaction process revealed that complete conversion of Ti(C,N)–TiB₂–Co cermet can be achieved in the temperature range 1100–1200°C. In general, with increasing sintering temperature, the particle size increases and the mechanical properties of cerments deteriorate. In order to ascertain the minimum temperature and prepare cerments with fine grains, powder compacts were again sintered at 1150, 1200, and 1250°C. Furthermore, a large number of pores were observed in the sample heated to 1200°C (Fig. 7), deteriorating the mechanical properties. Therefore, the mechanical pressure was increased to 34 MPa at the sintering temperature for 30 min.

Figure 9 shows the XRD patterns of the cerments sintered at different temperatures. All the samples comprised Ti(C,N), TiB₂, and Co phases. The minimum temperature for producing high-purity Ti(C,N)-based cerments is accepted to be ~1150°C. According to the analysis of the reaction process, the full conversion is ascribed to the preformed Co–Ti liquid (1020°C). Notably, the peak of Co at ~44°C overlaps with that of TiB₂, and other peaks of Co phase were not observed. Similar phenomenon was also observed in the Co–TiC–TiB₂ cerments. In a previous study, the diffraction peaks of B₄C in the Cu–Zr–B₄C system (Cu:Zr:B₄C = 2.2:3:1 in mole ratio) could not be identified as well. The relative diffraction intensity of the phase in the mixtures can be described by the following equation:

$$I_p = n|F|^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot e^{-2M}$$

where $n$, $F$, $(1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$, $\theta$, and $e^{-2M}$ refer to the multiple factor, structure factor, angle factor, Bragg angle, and temperature factor, respectively. $F$ is related to the scattering power of unit cell, such as the atomic characteristics and location in the unit cell. Therefore, the absence of other peaks of Co should derive from its atomic characteristics and crystalline lattice.

Figure 10 illustrates the fractured microstructure and relative density of the cerments sintered at different temperatures. No obvious macropores exist in the cerments. Moreover, the relative densities exceed 99.0%, indicating that the minimum temperature for producing high-density cerments is ~1150°C. As well known, the solution-precipitation mechanism plays an important role in the densification behavior of cerments prepared by traditional powder metallurgy (e.g., pressureless sintering). During the sintering process, metal binder Ni or and Co would initially melt into liquid. Subsequently, the higher energy
regions (e.g., small grains) preferentially dissolve into the melt and then precipitate on the concave regions (e.g., large particles) through the transfer of liquid, assisting densification.29) The melting points of Co and Ni are 1495 and 1455°C, respectively. Hence, a sintering temperature greater than 1400°C is required to obtain dense Ti(C,N)-based cermets. In a previous study,30) the densification behavior of Co–Ti–C–BN powder mixtures was investigated, indicating that the dissolution of B, C, and N into Co–Ti liquid and the subsequent production of Ti(C,N) and TiB2 could be viewed as the solution–precipitation mechanism to some extent, resulting in rearrangement densification. In contrast, applied pressure could accelerate densification. Knaislová et al.31) produced TiAl–Ti5Si3 ceramics from the Ti–Al–Si system in the temperature range 1100–1324°C and found that high pressure decreased the porosity. Xu et al.32) compared of Ti(C,N)-based cermets prepared by pressureless sintering and hot-pressing sintering and argued that the applied pressure could rearrange particles during the sintering process. Quach et al.33) reported that the applied pressure was sufficient to break soft agglomerates and rearranged particles, contributing to densification. Hence, the low formation temperature of Co–Ti liquid (1020°C) and the applied pressure of 34 MPa should be responsible for the production of high-density Ti(C,N)–TiB2–Co cermets at ~1150°C.

Figure 10 shows that Ti(C,N) particles display a typical polyhedral morphology.34–36) In general, ceramic particles prepared by the RHP technology exhibit a spherical shape, probably attributed to the formation of a large amount of liquid. When ceramic particles are precipitated from the saturated liquid, they tend to keep the spherical shape to decrease the interface area and the interfacial energy. In contrast, the Co content in Co–Ti–C–N system is ~5.27 wt %, and a small amount of liquid is present during the RHP process. In this case, liquid mainly accelerates the diffusion of atoms, and thus promotes the synthesis of Ti(C,N). The straight grain boundary is well known to decrease the interfacial tension and an increase in the stability of interface, obtained through atomic diffusion. Therefore, polyhedral Ti(C,N) particles were prepared. Figure 11 shows a statistical plot of the average size of cermets sintered at different temperatures. With increasing temperature from 1150 to 1250°C, the average particle size increases from 0.571 to 0.842 μm. Clearly, elevated temperatures promote the diffusion of atoms and the growth of grain.

Figure 12 shows the hardness and fracture toughness of the cermets sintered at different temperatures. The sample sintered at 1150°C possesses a hardness and fracture toughness of 1947 HV10 and 6.6 MPa.m1/2, respectively. With increasing temperature, the hardness and fracture toughness gradually decrease, displaying a similar variation trend with the average particle size. This implies that the fine-grain strengthening plays an important role in improving the mechanical properties. Owing to the optimum mechanical properties, the wear resistance of cermets prepared at 1150°C was measured. For comparison, the wear resistance of YT15 cemented carbide (hardness: 1600 HV10) was tested as well. Figure 13 shows the microstructure and corresponding groove depths of Ti(C,N)-based cermets and cemented carbide. According to the measured groove depths of Ti(C,N)-based cermets and cemented carbide [Fig. 13(c)], the wear resistance of Ti(C,N)–TiB2–Co composite cermets is 2.5 times higher than that of YT15 cemented carbide. The high wear resistance of
Ti(C,N)-based cermets is attributed to the high hardness and low friction coefficient.21)

4. Conclusion

The reaction mechanism of Co–Ti–C–BN system during the RHP process is as follows: First, Ti–BN solid state reaction to form Ti₃Nₓ and TiB, and Co–Ti solid state reaction to form CoTi₂ occurred. Second, Co–Ti liquid is formed by the eutectic reaction between CoTi₂ and Ti. Via the mass transfer of liquid, TiB reacted with B to yield TiB₂, while Ti₀.₃N and Ti₂N rapidly converted to TiN. With increasing temperature, Ti(C,N) was fabricated by the diffusion of C into TiN unit cell, and B reacted with Ti affording TiB₂.

High-density submicron Ti(C,N)-based cermets were in situ synthesized at 1150°C and an applied pressure of 34 MPa by the RHP method, affording Co–Ti liquid at 1020°C. Ti(C,N)–TiB₂–Co composite cermets possessed the optimum average particle size, hardness, and fracture toughness of 0.571 μm, 1947 HV₁₀, and 6.6 MPa.m¹/₂, respectively, as well as a higher wear resistance in comparison with YT15 cemented carbide.

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