Effect of TiB$_2$ content on the microstructure and mechanical properties of Ti(C,N)–TiB$_2$–FeCoCrNiAl high-entropy alloys composite cermet

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Composite cermet with different mass ratios of Ti (C,N)/TiB$_2$ and 10 wt% FeCoCrNiAl high-entropy alloys (HEAs) binder were fabricated by mechanical alloying and vacuum hot press sintering. The effect of the TiB$_2$ content on the microstructure and mechanical properties of the Ti(C,N)–TiB$_2$–HEAs cermet was systematically examined and is discussed in detail. The microstructure was analyzed by X-ray diffraction (XRD), scanning electron microscopy, and transmission electron microscopy (TEM). The results of this study show that a small amount of Fe$_2$B phase was detected in the XRD patterns besides the Ti(C,N) and TiB$_2$ phase. The TEM observation shows the presence of a HEAs binder phase, which was tightly bound to Ti(C,N) and TiB$_2$ phases. The grain size of the composite cermet gradually decreased with increasing TiB$_2$ content increased from 0 to 45 wt%. The relative density of the composite cermet first increased and then decreased with increasing TiB$_2$ content from 11.25 to 45 wt%. When the TiB$_2$ content reached 22.5 wt%, the composite cermet exhibited excellent comprehensive performance. The grain size, relative density, and hard phase of the composite cermet were the dominating factors that determined the mechanical properties with increasing TiB$_2$ content. The relative density, Vickers hardness, bending strength, and fracture toughness of the Ti(C,N)–22.5 wt% TiB$_2$–10 wt% HEAs composite cermet reached $98.86 \pm 0.20\%$, $154.4 \pm 20$ HV$_{10}$, 727 $\pm 20$ MPa, and $7.9 \pm 0.1$ MPa m$^{3/2}$, respectively.

Key-words : High entropy alloys, TiB$_2$ content, Ti(C,N)–TiB$_2$–HEAs composite cermet, Microstructure, Mechanical properties

1. Introduction

Titanium carbonitride has recently attracted significant attention owing to its excellent wear resistance, good red hardness, and low coefficient of friction, providing advantages during high speed machining.$^{1-3}$ Traditionally, Ti(C,N)-based cermet used nickel or cobalt as the binder phases to achieve high density, toughness, ductility, and strength.$^{4-6}$ TaC, Mo$_2$C, WC, and VC are often added to Ti(C,N)-based cermet to enhance the wetting, sintering behavior, material hardness, and strength.$^{7-9}$ However, the strength and toughness of Ti(C,N)-based cermet are usually inferior to those of the WC–Co cemented carbides. The wettablility of Ni binders and Ti(C,N) has been poor compared to that of WC–Co hard metals, and the Co material is expensive, restricting their wide application.$^{10-13}$

In recent years, significant efforts have been focused toward selecting a sintering binder and additive to improve the mechanical properties of Ti(C,N)-based ceramics. Various metallic sintering binders such as Fe and Cr$^{14,15}$ were used to fabricate Ti(C,N)-based composite cermet. However, the inherent defects of these metals limit the properties and applications of composite cermet materials. Therefore, the selection of the binder is critical. High-entropy alloys (HEAs), a new type of multicomponent alloy, possess many excellent properties, such as a high strength, hardness, wear resistance, and thermal stability.$^{16,17}$ Due to these excellent properties, the use of HEAs to replace traditional binders to improve the room-temperature and high-temperature performance of composite cermet has gradually gained significant attention, and some excellent research results were achieved.$^{18-22}$ Besides the binder, the addition of ceramic additives is a significant method to enhance the mechanical properties of Ti(C,N)-based ceramics. For example, the mechanical properties of Ti(C,N)–TiB$_2$ composite material are better than those of Ti(C,N) or TiB$_2$.$^{23,24}$ TiB$_2$ has a high melting point, hardness, and modulus of elasticity, good electrical conductivity and thermal conductivity, and excellent chemical stability.$^{25,26}$ In recent year, TiB$_2$-based ceram-
ics have received interest of researchers owing to their excellent performance. For example, Venkateswaran et al.\textsuperscript{27) }reported TiB$_2$–6 wt % Cu cermet with the hardness and fracture toughness of 17 GPa and 11 MPa m$^{1/2}$, respectively. Wu et al.\textsuperscript{28) }studied TiB$_2$–30 wt % (Fe–Ni) composite cermets, and the fracture toughness was 19.26 ± 0.72 MPa m$^{1/2}$. Zhang et al.\textsuperscript{29) }fabricated TiB$_2$–5 wt % CoCrFeNiAl HEAs composite cermets with a hardness and flexural strength of 2386 ± 18 HV$_5$ and 820 ± 9 MPa, respectively. The research results showed that the CoCrFeNiAl HEAs possess outstanding wettability to TiB$_2$ ceramics, which is the linchpin to reaching superior properties in a ceramic material.

There are a few published papers on the study of the effect of TiB$_2$ addition on the properties of sintered Ti(C,N)-based composite cermets. Hence, in this study, FeCoCrNiAl HEAs was used as the binder in Ti(C,N)-based composite cermets with five different mass contents of TiB$_2$. The effect of the TiB$_2$ addition on the microstructure and mechanical properties of the sintered Ti(C,N)-based composite cermets was investigated in detail.

### 2. Experimental

#### 2.1 Sample preparation

The parameters for the starting materials including particle size, purity, and manufacturer are listed in Table 1. Five samples labeled as B0–B4 representing various Ti(C,N)/TiB$_2$ mass ratios are listed in Table 2. First, the FeCoCrNiAl HEAs was prepared by mechanical alloying method. Then, the Fe, Co, Cr, Ni, and Al powders were put into a 1 L stainless steel vial with stainless steel grinding balls. The FeCoCrNiAl HEAs powder was synthesized at 250 rpm with a ball-to-powder weight ratio of 15:1 under high-purity argon using a full planetary ball mill (Mickey Technology Co., Ltd., Changsha, China), followed by adding Ti(C,N) and TiB$_2$ into the stainless steel vial, and the Ti(C,N), TiB$_2$, and HEAs mixture powders were obtained by wet ball-milling in a planetary ball mill vial containing a stainless steel ball and ethyl alcohol as media for 15 h at a rotation speed of 150 r/min. The mixed powder was dried at 70°C and passed through a 100-mesh sieve. Finally, the obtained powders were sintered in a graphite mold (an inner diameter of 30 mm). The sintering process was performed using a vacuum hot-pressing sintering (VHPS) furnace (model ZT-40-21Y, Shanghai, China) at 1500°C and with a 30 min dwell time under vacuum conditions at a pressure of 34 MPa.

### Table 1. Details of the starting materials parameters used for preparing Ti(C,N)–TiB$_2$–HEAs composite cermets

| Powders | Particle size (μm) | Purity (%) | Manufacturer |
|---------|--------------------|------------|--------------|
| Ti(C,N) | 1.00               | ≥99.8      | Qinhuangdao Nuogao New Material Development Co., Ltd., China |
| TiB$_2$ | 1.00               | ≥99.8      | Qinhuangdao Nuogao New Material Development Co., Ltd., China |
| Fe      | 5.00               | ≥99.9      | Shanghai Shuitian Science & Technology Co., Ltd., China |
| Co      | 5.00               | ≥99.9      | Shanghai Shuitian Science & Technology Co., Ltd., China |
| Ni      | 5.00               | ≥99.9      | Shanghai Shuitian Science & Technology Co., Ltd., China |
| Al      | 5.00               | ≥99.9      | Shanghai Shuitian Science & Technology Co., Ltd., China |

### Table 2. Chemical composition of the experimental Ti(C,N)–TiB$_2$–HEAs composite cermets (wt %)

| Compositions (wt %) | Mass ratio |
|--------------------|------------|
| Ti(C,N) | TiB$_2$ | HEAs | Ti(C,N) | TiB$_2$ |
| B0     | 90     | 0    | 10    | 9      | 0      |
| B1     | 78.75  | 11.25| 10    | 7      | 1      |
| B2     | 75     | 15   | 10    | 5      | 1      |
| B3     | 67.5   | 22.5 | 10    | 3      | 1      |
| B4     | 45     | 45   | 10    | 1      | 1      |

#### 2.2 Characterization

The phase analysis of the powders and the as-sintered composite cermets was investigated by X-ray diffraction (XRD) (D8 Advance, Germany). The mixed powders, sintered composite cermets, and morphology of the fracture surface were observed by scanning electron microscopy (SEM) in the backscattered electron (BSE) mode (FEI Nova Nano SEM450, USA). Energy dispersive spectroscopy (EDS) was performed using an energy dispersive spectrometer accessory (Model Link-ISIS, Oxford, England). The microstructures of the as-prepared cermets were observed by transmission electron microscopy (TEM) (JEOL JEM-2100, Tokyo, Japan). Image J software was utilized to estimate the grain size.

The bulk density of the as-sintered samples was measured by the Archimedes principle. The hardness was tested using a Vickers hardness tester (Model HVST-10, China) with a load and loading duration of 98 N and 15 s, respectively. The fracture toughness was measured via the indentation method and calculated using a Palmqvist-type crack around indentation according to the Niihara formula:\textsuperscript{30) }

$$K_{IC} = 0.035(H/\epsilon)^{1/2}(E\Phi/H)^{0.4}(l/\alpha)^{-1/2}/\Phi$$

where $H$, $E$, $a$, $l$, and $\Phi$ are the Vickers hardness, elastic modulus (480 GPa), indentation half-length, crack length and shape factor (=3), respectively. The transverse rupture test was carried out using an electronic universal testing instrument (Model WD-10, China) by applying a three-point bending method.

### 3. Results and discussion

#### 3.1 Morphology and phase constituents of the powders

Figure 1 shows the SEM-EDS analysis of FeCoCrNiAl HEAs powder after 30 h of milling, indicating that the
powder size after 5 h of milling became obviously larger
than that of the original powders, attributed to cold weld-
ing effects, and portions of the alloy powder were agglom-
erated. With increasing milling time, the collisions, deforma-
tion, cold welding, and crushing continued to affect the
alloy powder shape. These effects first decreased the par-
ticle size and then finally reach equilibrium (10–20 μm)
with the formation of agglomerates with an irregular
orientation [Fig. 1(e)]. Moreover, the EDS results show
that the as-milled HEAs powder has the same composition
as the designed cermets [Fig. 1(f)].

Figure 2 illustrates the SEM image and the EDS maps
of the Ti(C,N)–22.5 wt% TiB2–10 wt% HEAs composite
cermet powders, indicating that the mixed powder was
quite uniform after 15 h of wet mixing, providing sufficient
wetting of the binder and ceramics phases during sintering.
In general, a uniform distribution of the mixed powder has
a positive effect on the microstructure and properties of the
composite cermets.1,14,28)

3.2 Phase constituents and microstructure of
the composite cermets

Figure 3 shows the XRD patterns of the Ti(C,N)–
x wt% TiB2–10 wt% HEAs composite cermets. Clearly,
with increasing TiB2 content, the intensity of TiB2 diffraction
peaks also increased significantly. Apart from Ti(C,N)
and TiB$_2$ phases, a minor peak corresponding to Fe$_2$B was discovered in the XRD patterns; however, its amount is very small, because of only 2.2 wt% Fe in the cermets. Figure 4 shows the TEM images of the Ti (C,N)–22.5 wt% TiB$_2$–10 wt% HEAs composite cermets. The dark granular phases were distributed between the bright phases in Fig. 4(a). The electron diffraction analysis [Fig. 4(b)] demonstrates that the dark granular phase was a single-phase BCC structure. The additional EDS maps [Fig. 4(c)] of the dark granular phase show the presence of only five elements: Fe, Co, Cr, Ni, and Al, indicating the presence of the HEAs and that a phase transformation did not occur after sintering. However, in Fig. 3, the HEAs peaks are not present, attributed to the low content of the HEAs.

The SEM–BSE images of Ti (C,N)–x wt% TiB$_2$–10 wt% HEAs composite cermets are shown in Fig. 5. Clearly, the cermets are shown as four different colors. With increasing TiB$_2$ content, the dark gray phase increased

![Figure 3: XRD analysis of the sintered Ti(C,N)–x TiB$_2$–10 wt% HEAs composite cermets with different TiB$_2$ mass content: (a) 0 wt%, (b) 11.25 wt%, (c) 15 wt%, (d) 22.5 wt%, (e) 45 wt%.

![Figure 4: TEM characterization of Ti(C,N)–22.5 wt% TiB$_2$–10 wt% HEAs composite cermets. (a) Bright field TEM micrograph; for the marked open circle in yellow, (b) and (c) represents the corresponding SAED pattern and EDS point analysis, respectively.

![Figure 5: SEM-BSE images of the sintered Ti(C,N)–x TiB$_2$–10 wt% HEAs composite cermets with different TiB$_2$ mass content: (a) 0 wt%, (b) 11.25 wt%, (c) 15 wt%, (d) 22.5 wt%, (e) 45 wt%.}
The EDS analysis [regions 1, 2 and 3 in Figs. 5(a) and 5(d) and Table 3] shows that the dark gray phase was TiB2, the gray phase corresponds to Ti (C,N), and the relatively uniform white phase between TiB2 and Ti (C,N) was the HEAs phase. However, as the TiB2 content increased from 0 to 22.5 wt %, a small amount of black phase resembling a pore is observed as shown in Figs. 5(d) and 5(e). To confirm these black phases, Fig. 5(f) shows the secondary electron image of the same observed area in Fig. 5(e). Comparing these two images indicates that these black particles are not pores. The EDS analysis [regions 4 and 5 in Figs. 5(e) and 5(f), and Table 3] shows that these particles may be alumina particles. Figure 6 shows the TEM analysis results of the composite cermets containing 22.5 wt % TiB2. Combining the EDS and electron diffraction pattern analyses confirmed that the particles were alumina. The TEM and SEM analysis results confirmed the presence of Al2O3 in the composite cermets, mainly due to the fact that the Al element in the HEAs reacts with TiO2 and B2O3 in TiB2, and the inevitable oxidation of the Al element occurs during the sintering process due to its lively nature.

### Table 3. Results of BSE/EDS analysis for Ti(C,N)–TiB2–HEAs composite cermets in Fig. 5

| Type of study | Location | Element at % |
|---------------|----------|--------------|
|                | Ti       | C      | N       | B      | O      | Fe     | Co     | Cr     | Ni     | Al     |
| BSE/EDS       | Figure 5(a) 1 | 32.0 | 30.7 | 36.3 | —     | —     | —     | —     | 1.0    | —     | —     |
|                | 2        | 4.1   | 3.3   | —     | 1.2   | 19.9  | 16.8  | 18.1  | 20.7   | 15.9  |
|                | 3        | 60.1  | —     | —     | 38.1  | —     | —     | —     | 1.8    | —     | —     |
|                | Figure 5(e) 4 | 2.4  | 8.1   | 8.9   | —     | 29.6  | 1.0   | —     | 2.3    | —     | 47.7  |
|                | Figure 5(f) 5 | 5.7   | 7.0   | 8.0   | —     | 36.1  | 1.1   | —     | 2.9    | —     | 39.2  |

Figure 6. TEM characterization of Ti(C,N)–22.5 wt % TiB2–10 wt % HEAs composite cermets. (a) Bright field TEM micrograph; for the marked open circle in yellow, (b) and (c) represents the corresponding SAED pattern and EDS analysis, respectively.

3.3 Density and mechanical properties

Figure 7 shows the density of the Ti(C,N)–x TiB2–10 wt % HEAs composite cermets with different TiB2 contents. With increasing TiB2 content from 0 to 11.25 wt %, the relative density decreased, because Ti(C,N) is more sinterable than TiB2. With increasing TiB2 content increased to 22.5 wt %, the relative density increased to the highest (98.86%). This is attributed to the fact that TiB2 content affected the densification process of composite cermets. Figure 8 shows that as the TiB2 content increased from 11.25 to 22.5 wt %, the grain size of the ceramic phase [Ti(C,N) and TiB2] gradually decreased. In general, when the grain is fine, its interfacial energy and sintering activity increase, both of which promote the dissolution–precipitation, grain rearrangement particle rearrangement, and provides a sufficient amount of the composite cermets liquid phase. These factors can promote the densification of the composite cermets. Therefore, the composite cermets with relatively fine grains had a higher density than those with coarse grains during the liquid phase sintering; nevertheless, the starting ceramic phase had the same grain size. However, with increasing TiB2 content to 45 wt %, the relative density decreased to 95.64%. The low density is mainly attributed to the high melting point, the low diffusion coefficient, and the relatively high impurity content (oxides of titanium and boron) of the TiB2.
Because of these disadvantages, the sintering of pristine TiB2 requires a very high temperature (approximately 2000°C).34) The relative density of TiB2 bulk ceramics was only 88%, although the sintering temperature was as high as 2100°C.37) Therefore, with increasing TiB2 content to 45 wt%, the insufficient sintering of the TiB2 had a dominant effect on the low relative density of the composite cermets.

Figure 9 shows the microhardness of the Ti(C,N)–x wt% TiB2–10 wt% HEAs composite cermets. With increasing TiB2 content, the microhardness increased gradually. When the TiB2 content increased to 45 wt%, the microhardness reached a maximum of 2006.18 ± 20 HV10. The hardness, relative density, and grain size of the ceramic have a synergistic effect on the hardness of the composite cermets. In this study, when the content was 0 wt%, i.e., in the absence of TiB2, the grain size had a significant effect on the hardness. The lower hardness is attributed to the larger grain size and the lower hardness of the Ti(C,N) compared to TiB2. Figure 8 shows that the average grain size reached 3.613 μm, and some coarse grains even reached 5–7 μm, which could reduce the hardness according to the Hall–Petch formula. The process of grain growth was accomplished by the mutual annexion of grains, carried out through the gradual movement of grain boundaries. When the movement of a grain boundary meets second phase particles, its movement is hindered, thus reducing the grain growth rate. In the absence of TiB2, the material only had the Ti(C,N) hard phase. The movement of the grain boundaries was not substantially hindered during the sintering process, resulting in the rapid growth of the grains. However, with increasing TiB2 content, the aggregation of the Ti(C,N) particles decreased; therefore, the growth of the crystal grains decreased.33) With increasing TiB2 content from 11.25 to 22.5 wt%, the ceramic hardness and relative density had a synergistic effect on the hardness. The high relative density (Fig. 7) increased the bearing capacity of the matrix material.14) When the TiB2 content further increased to 45 wt%, the material obtained the highest hardness in this study, mainly attributed to the dominant role of high hardness TiB2 even though it had a low density.

Figure 9 shows the bending strength of the Ti(C,N)–x wt% TiB2–10 wt% HEAs composite cermets. With increasing TiB2 content, the bending strength first increased to 727 ± 20 MPa and then decreased. In general, porosity and grain size have a primary effect on the bending strength of a material.14,19,38 Equations (2) and (3)28,29 describes the relationship between the bending strength and porosity and grain size of a material:
\[ \sigma = \sigma_0 \exp(-k\alpha) \]  
\[ \sigma = \sigma_0 + kd^{-m} \]

where \( \sigma \) is the strength of the material, \( \sigma_0 \) is the strength of the material, \( \alpha \) is the residual porosity, \( d \) is the grain size; \( k \) and \( m \) are the experimental coefficients. The formulas indicate that the bending strength of a material has a positive correlation with porosity and negative correlation with grain size. This function is in accordance with the experimental results of the bending strength. When the TiB\(_2\) content was 0 wt\%, the relative density was the highest, and when the content was 45 wt\%, the grain size was the smallest. However, both bending strengths were relatively low, which could be attributed to the dominant effect of former relatively large grain size and later relatively low density. Truly, the bending strength is relatively low for this study. The main reasons are that the oxygen (0.45\%) of FeCoCrNiAl HEAs binder results in the formation of Al\(_2\)O\(_3\) in the grain boundary. In addition, compared to SPS, VHPS has a longer holding time at high temperature, promoting the formation of a small amount of brittle phase (Fe\(_2\)B), which will have a negative effect on the wetting of HEAs and Ti(C,N) or TiB\(_2\) and lead to the existence of pores. Therefore, the bending strength is relatively poor. These analyses of the reasons for the relatively low bending strength have been supplemented in the manuscript. The material enhancement studies will be investigated in the future research.

**Figure 10** shows the fracture surface images obtained from the SEM of the Ti(C,N)–x wt\% TiB\(_2–\)10 wt\% HEAs composite cerments after the bending strength test. In Fig. 10, obviously, the mainly fracture modes of the composite cerments is transgranular fracture (area A, Fig. 10) and intergranular fracture (area B, Fig. 10). The pull-out grains (area C, Fig. 10) were also observed. Intergranular fracture might result in poor mechanical properties, because of the weak bonding of the ceramic particles.\(^{25}\) However, when transgranular fracture emerged, the material might process excellent mechanical properties. This is mainly because high energy barrier needs to be overcome, when cracks propagate across the ceramic particles.\(^{14}\)

**Figure 9** shows the function of fracture toughness as a function of TiB\(_2\) content. The fracture toughness and fracture strength had similar tendencies. As the TiB\(_2\) content increased from 0 to 45 wt\%, the fracture toughness of composite cerments increased first to the maximum value of 7.9 MPa m\(^{1/2}\) and then decreased. The fracture toughness is well known to indicate the ability of a material to resist the crack propagation.\(^{40}\) In general, toughening effects during crack propagation include crack deflection, branching, and surface peeling.\(^{3,40}\) The porosity, grain size, and hard particles in the material have important effects on the crack propagation,\(^{41-43}\) and they also affect the fracture toughness of the composite cerments. **Figure 11** shows the crack propagation pattern of the Ti(C,N)–x wt\% TiB\(_2–\)10 wt\% HEAs composite cerments. When the TiB\(_2\) content was 22.5 wt\%, transgranular fracture (TiB\(_2\) particles) and crack deflection were found during the crack propagation process. Crack deflection increases the mean free path of the crack, consumes more fracture energy, and ultimately improves the fracture toughness of the composite cerments.\(^{40}\)

4. **Conclusions**

The effect of the TiB\(_2\) content on the microstructure and mechanical properties of Ti(C,N) TiB\(_2–\)FeCoCrNiAl HEAs composite cerments was investigated. Based on the above results and discussion, the following conclusions were drawn:
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