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Fabrication and properties of Ti(C,N) based cermets reinforced by nano-CBN particles

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Abstract

Titanium carbontride (Ti(C,N)) based cermets with and without nano-cubic boron nitride (CBN) particles were prepared by microwave sintering in argon and nitrogen environment, respectively. Two kinds of core–rim microstructure, black core–grey rim and white core–grey rim, are shown in the cermets by scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis (EDX). It is found that, for the cermet with 1.5% nano-CBN particles sintered at 1500 °C for 30 min in argon, its transverse rupture strength (TRS) and hardness are improved to about 25.9% and 1.4%, respectively. The SEM analysis shows that the inhibition effect of nano-CBN particles on the dissolution of Ti(C,N) is weakened with the increase of content of nano-CBN particles. Moreover, for the cermet sintered in argon reinforced by 1.5% nano-CBN particles, more fine black core–grey rims are found in the microstructure compared to the others. For the material sintered in nitrogen, its microstructure accompanied with many white core–grey rims in number and big black core and thin outer rim in size, results in high hardness and low TRS.
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Keywords: B. Microstructure; C. Mechanical property; Titanium carbontride based cermets; Nano-CBN

1. Introduction

Titanium carbontride (Ti(C,N)) based cermets are normally made of Ti(C,N) solid solution as main hard component and Co/Ni as binder. Compared to WC–Co based hardmetals, it has excellent wear resistance and chemical stability at high temperature. As a result, Ti(C,N) matrix cermets are successfully utilized as cutting tool in semi-finishing and finishing work on steel and cast iron at higher cutting speed [1–3]. However, the low toughness and thermal shock resistance of Ti(C,N) based cermets limits their applications for heavy turning and interrupt milling. Thus, a variety of carbides are added to improve the sinterability, toughness, hot hardness and thermal shock resistance [4–7], such as Mo_2C, WC, and TaC/NbC. Recent investigations [8–10] pay an intense attention to preparing an ultra-fine microstructure or adding nano-particles, such as TiN [11–14], in order to improve property of Ti(C,N) matrix cermets. Cubic boron nitride (CBN) is known to have good cutting tribological characteristics, which could be effective in preventing the adhesion for cutting operations of steel and cast iron [15]. Therefore, the effect of adding nano-CBN particles on the property and microstructure of Ti(C,N) based cermets is the main objective in this paper.

2. Experimental

Ultra-fine $TiC_{0.7}N_{0.3}$ powders (<1.0 μm), Co powders (<1.0 μm), Ni powders (<1.0 μm), WC powders (<1.0 μm), Mo_2C powders (<1.0 μm) according to the chemical composition (in weight) of $TiC_{0.7}N_{0.3}$–15% WC–18% (Co + Ni)–10% Mo_2C–x% nano-CBN particles were firstly mixed in the planetary ball mill for 48 h using WC–Co balls, where x is 0.5, 1.0, 1.5, 2.0 or 2.5. The mixed powders dampened with hexane (about 1.5 ml/g of powders) in which about 3% polyethylene glycol in weight was dissolved. Then they were dried in a vacuum drying oven at 90 °C for 2 h and then pressed in a rectangular beam-shaped die at a uniaxial pressure of 350 MPa. Finally, the green compacts were sintered in a MW-L0316HV type vacuum microwave oven with a frequency of 2.45 GHz at 1350–1550 °C for 30 min in argon

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and nitrogen environment, respectively. Hardness (HRA) of the sintering samples was measured on the Vickers hardness tester using 60 N for 10 s duration. Transverse rupture strength (TRS) was examined on test pieces with a dimension of 4.0 mm × 8.0 mm × 25.0 mm and the span was 20.0 mm. All the data was the average of five measured values. Microstructures of the materials were observed by scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis (EDX). As a comparison, the ultra-fine Ti(C,N) based cermets without the addition of nano-CBN particles was also prepared at the same condition.

3. Results and discussion

3.1. Mechanical properties

TRS and HRA of Ti(C,N) based cermet including 1.5% nano-CBN particles sintered at different temperature for different times in argon are shown in Fig. 1. It can be seen in Fig. 1(a) that TRS and HRA of the cermet increase with the increase of sintering temperature at first, then decrease over 1500 °C. Fig. 1(b) shows that TRS and HRA of the cermet reach the highest value when sintered at 1500 °C for 30 min. The metallurgical process of Ti(C,N) based cermets is usually considered as a liquid-phase sintering, during which the low melting or eutectic phase forms and assists in the densification process by infiltrating the porosity and inducing various mass

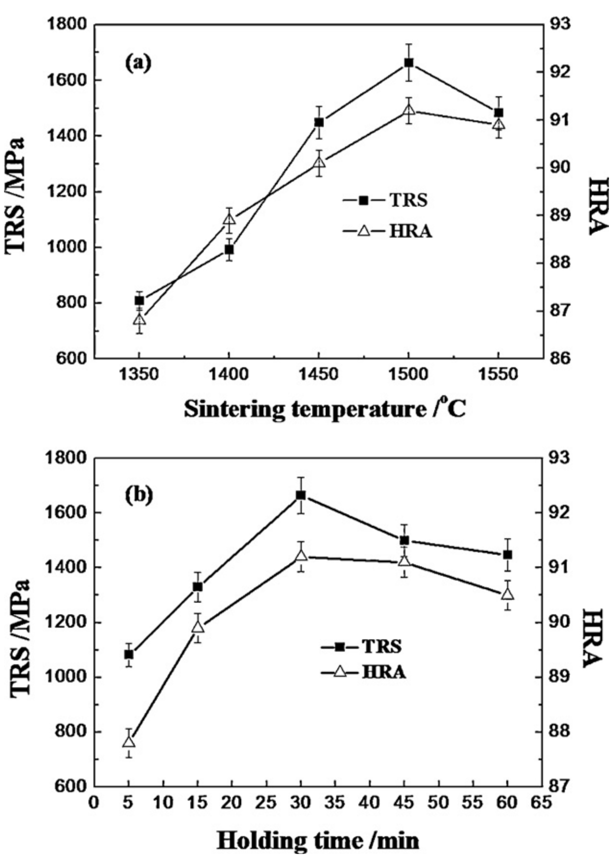

Fig. 1. Mechanical property of Ti(C,N) based cermet reinforced by 1.5% nano-CBN particles.

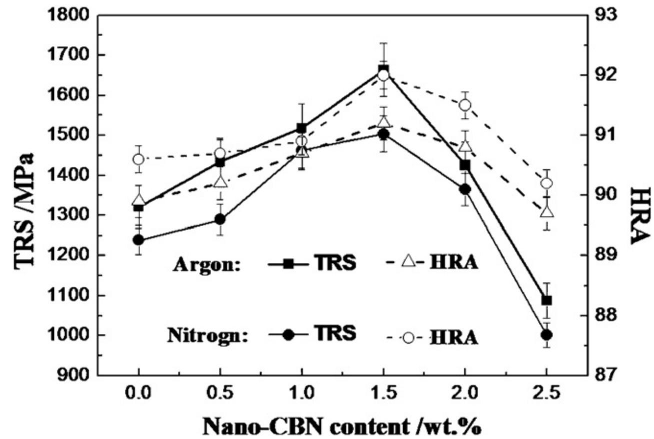

Fig. 2. Mechanical property of Ti(C,N) based cermets with different contents of nano-CBN particles.

transport mechanisms, such as dissolution, vapour-phase transport, and precipitation. When sintering temperature is lower than melting point of Co and Ni or holding time is too short to finish densification process, the cermet will have more porosity. However when the sintering temperature is too high (for example 1550 °C) or holding time is too long (for example 45 min), the growth of grains and pores will also reduce the compactness of this material. Therefore the cermet reinforced by 1.5% nano-CBN particles sintered at 1500 °C for 30 min in argon have the best transverse rupture strength and hardness in this experiment.

Fig. 2 shows the effect of nano-CBN particles content on the mechanical property of Ti(C,N) based cermets. It indicates that TRS and hardness increase firstly with the increase of the content of nano-CBN particles, but decrease rapidly when the content is over 1.5%. This means the appropriate addition of nano-CBN particles is 1.5%, where the TRS and hardness are improved to about 25.9% and 1.4%, respectively. The influence of sintering gas condition on mechanical property of Ti(C,N) based cermets is also shown in Fig. 2. The cermets sintered in nitrogen have higher HRA and lower TRS than in argon, which can be attributed to different microstructure.

3.2. Microstructures

All of the Ti(C,N) based cermets, which have been sintered with a liquid binder phase such as Ni and/or Co, show a typical microstructure consisting of hard phase with a core–rim type microstructure and binder phase [10]. Fig. 3 shows that the microstructure of Ti(C,N) based cermets with different nano-CBN particles contents. When sintered in argon, Ti(C,N) based cermets without nano-CBN particles exhibits a complex microstructure including lots of ‘‘white core–grey rim’’, and a little ‘‘black core–grey rim’’ as described in Ref. [16]. The black core is coarse and the thick grey rim is thick in Fig. 3(a). Fig. 3(b) shows there are lots of fine ‘‘black core–grey rim’’ and no ‘‘white core–grey rim’’ in the microstructure of the cermet reinforced by 0.5% nano-CBN particles. When the content of nano-CBN particles increases to 1.5%, a few of grey rims are divided into white inner rim and grey outer rim, and the size of

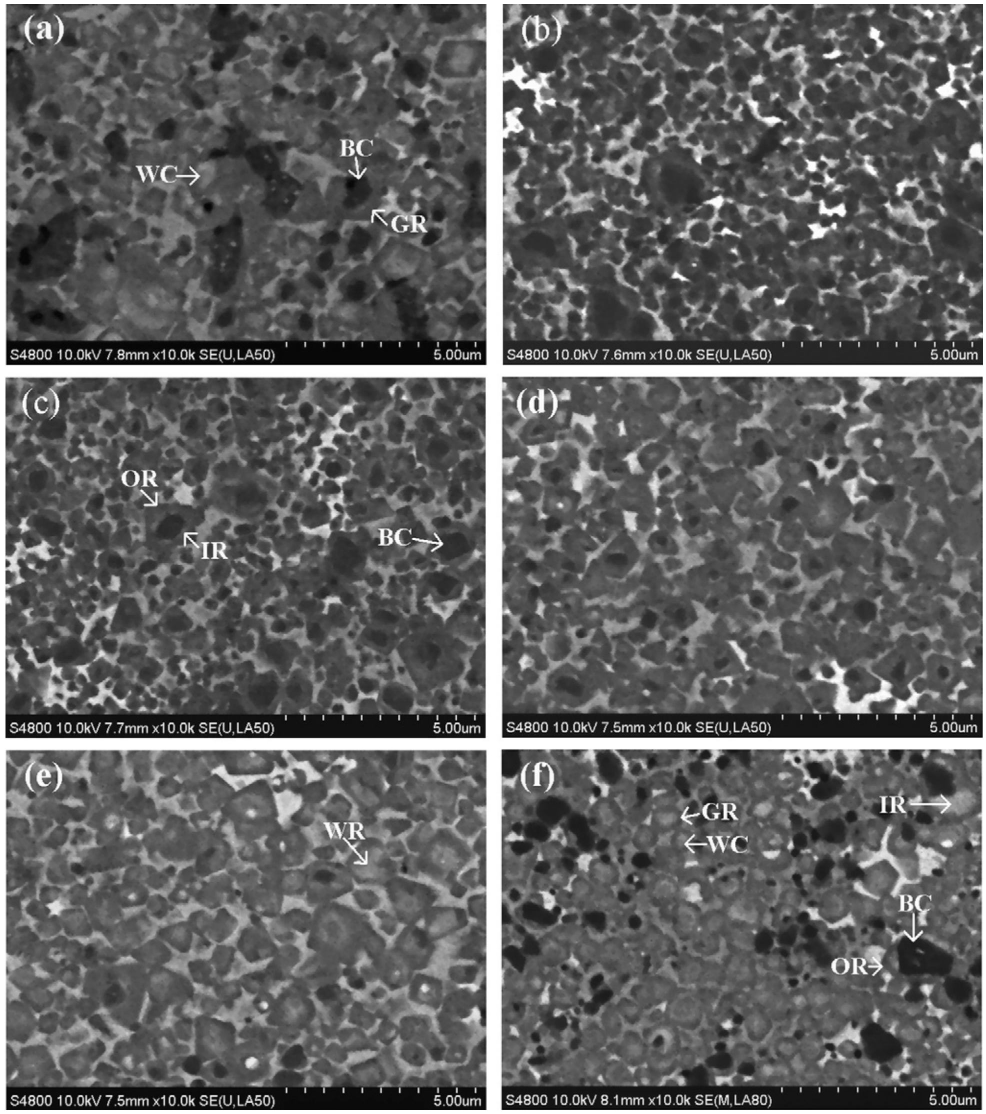

Fig. 3. SEM (BSE) micrographs of cermets with different content of nano-CBN particles. In argon: (a) 0%; (b) 0.5%; (c) 1.5%; (d) 2.0% and (e) 2.5%. In nitrogen: (f) 1.5%. BC, black core (Ti(C,N) core); WC, white core ((Ti,W, Mo) (C,N) core); IR, inner rim; OR, outer rim; GR, grey rim.

''black core–grey rim'' structure is lessening in Fig. 3(c), which improves TRS and hardness. However when the content of nano-CBN particles is over 1.5%, the size and number of white core increases as shown in Fig. 3(d) and (e), which results low TRS and hardness. It can be seen from Fig. 3 that the size of black core comes small until to disappear gradually with the increase of CBN content. This means the inhibition effect of nano-CBN particles on the dissolution of Ti(C,N) is weakened with the increase of CBN content, which may be because that the diffusion of carbides and Ti(C,N) is promoted.

Core–rim microstructure of Ti(C,N) based cermets is formed during liquid phase sintering through a dissolution and reprecipitation process. SEM–EDX analysis of the cermets reinforced by nano-CBN particles sintered in argon is shown in Fig. 4. It reveals that the metallic constitutes of black core are mainly titanium with little molybdenum and tungsten (in Fig. 4(a)). This is because that few amount of molybdenum and tungsten atoms can diffuse through dislocations and other crystal defects into Ti(C,N) cores. The grey rim (Ti,Mo,W)(C,N) phase is formed through Ti(C,N) particles firstly and dissolved in liquid binder and then it is precipitated on remaining Ti(C,N) core together with dissolved WC and Mo_2C. As a result, the high molybdenum and tungsten contents are found in grey rims (in Fig. 4(b)). Fig. 4(c) shows that more tungsten content is found in inter rim than that of titanium. It indicates more WC diffusing, solid-dissolving and precipitating in the inter rim around the black core. EDX of white core in Fig. 3(e) is shown in Fig. 4(d). It can be seen that W and Mo contents of white core are higher than that of black core, and the W content is even higher than Ti content. According to literature [17], for the extremely small particle size of Ti(C,N) at solid state sintering stage, the diffusion length between Ti(C,N) core and precipitated rim is significantly reduced. Then large amount of extremely small Ti(C,N) cores are completely consumed by counter diffusion of carbides and Ti(C,N), and the solid-dissolved (Ti,Mo,W)(C,N) core is formed. (Ti,Mo,W)(C,N) rim, which is relatively poor in Mo and W

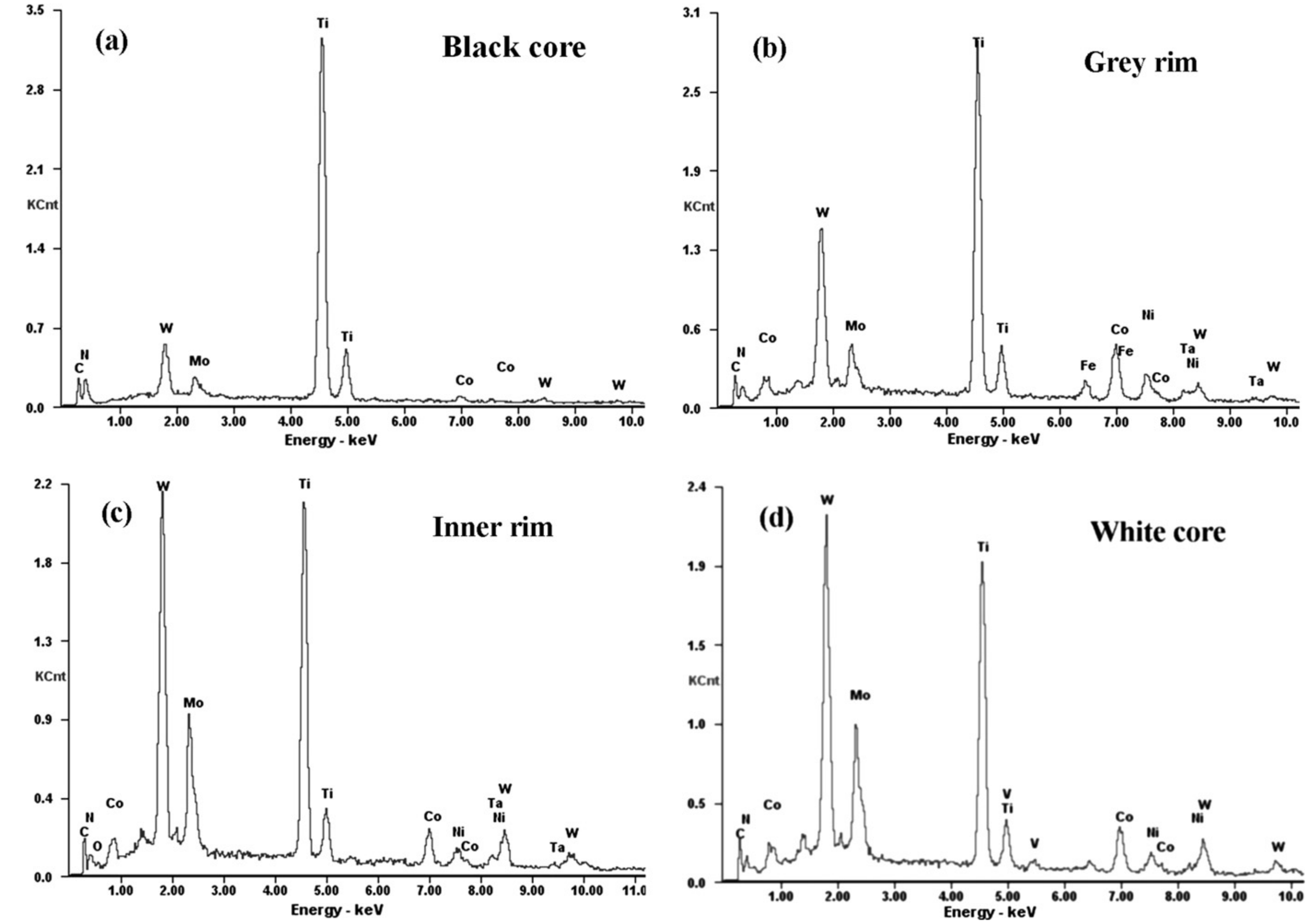

Fig. 4. The typical EDX spectrums of black core (a), grey rim (b), inner rim (c) surrounding the black core, and white core (d).

content, continues to precipitate around the previously formed (Ti,Mo,W)(C,N) core, which results in the ''white core–grey rim'' structure.

Microstructure of Ti(C,N) based cermet reinforced by 1.5% nano-CBN particles sintered in nitrogen is shown in Fig. 3(f). Compared with Fig. 3(c), it can be seen that the cermet sintered in nitrogen have many ''white core–grey rim'' structure in number, big black core and thin outer rim in size [14], which results in higher hardness and lower TRS than that of the cermet sintered in argon (in Fig. 2). Difference of above microstructure between sintering environment may be related to wettability of Co and Ni with carbides in argon and nitrogen, which will be carried out in further investigation.

4. Conclusions

Microstructure and mechanical property of Ti(C,N) based cermets including different content of nano-CBN particles have been investigated in this paper. They are clearly affected by the content of nano-CBN particles, sintering temperature and environment. The following conclusions can be drawn from the present investigations:

(1) When the content of nano-CBN particles is 1.5%, the Ti(C,N) based cermet sintered at 1500 °C for 30 min in argon has high TRS and hardness. Their values are improved to about 25.9% and 1.4%, respectively. It means the addition of nano-CBN particles has a good strengthening and hardening effect.

(2) Two kinds of core–rim microstructure, black core–grey rim and white core–grey rim, are found in Ti(C,N) based cermets with or without nano-CBN particles. The change of microstructure shows the inhibition effect of nano-CBN particles on the dissolution of Ti(C,N) is weakened with the increase of content of nano-CBN particles.

(3) Many fine black core–grey rims are found in the cermet reinforced by 1.5% nano-CBN particles sintered in argon. However the cermet sintered in nitrogen, the microstructure with many white core–grey rim structures in number and big black core and thin outer rim in size, results in high hardness and low TRS.

Acknowledgments

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