Progress on Ti(C, N)-based Metal-ceramic Materials

Peng Zhang

The University of Shanghai for Science and Technology, Shanghai 200093, China

Abstract

This paper reviewed the research progress of Ti(C, N)-based cermet materials at home and abroad in recent years, and summarized the research results on the microstructure and properties of Ti(C, N)-based cermets. Firstly, the development of Ti(C, N)-based cermet materials and their microstructures were briefly introduced. Secondly, the influence of microstructure, sintering method and composition on the properties was analyzed, and the effects of different compositions on Ti(C, N)-based cermets were listed and in comparison. Then, the toughening methods of Ti(C, N)-based cermets were summarized and the development direction of the toughening of cermets was proposed. Finally, the future research directions of the new Ti(C, N)-based cermets were prospected.

Keywords

Ti(C, N); Metal Ceramic; Microstructure and Properties.

1. Introduction

Since the 21st century, with the development of cemented carbide industry, W, Co, etc., as strategic scarce resources, are decreasing year by year, which makes its manufacturing cost rise gradually, so that it is difficult to meet the demand of new difficult-to-machine materials processing. Metal ceramics have become an alternative to cemented carbide with their excellent red-hardness and high hardness, chemical stability, corrosion resistance, and oxidation resistance, and have received increasing attention from researchers [1].

Metal ceramics are mainly a material consisting of a ceramic hard phase and a metal (or alloy) binder phase, formed by the presence of ceramic grains (about 15%-85%) in a metal or alloy binder matrix [2]. Ti(C, N)-based cermet is a tool material that can be used for high-speed machining and semi-finishing of steel. It not only shows excellent high-temperature red-hardness and crescent wear resistance during high-speed cutting, but also improves the surface finish and dimensional accuracy of machined parts. Besides, it can realize "turning instead of grinding", reducing or eliminating the use of cutting fluid, greatly improving machining efficiency, saving costs, and realizing green machining.

The earliest TiC-Ni cermet appeared in 1929 and was mainly used to replace cemented carbide in cutting, but it was not widely used because of its brittleness [3-4]. Subsequently, during the decade 1956-1965, researchers found that the properties could be enhanced by adding some metals or metal compounds such as Mo, which greatly improved the strength of metal ceramics[5-7]. Later, researchers found that the addition of a certain amount of TiN to TiC cermets could improve their performance in all aspects. Since then, research on Ti(C, N)-based cermets has been growing. Cermet tools such as nano-cermet tools, coated cermet tools, and gradient cermet tools have started to emerge and are now gradually becoming one of the leading cutting tools. As shown in Fig. 1, the properties of cermets depend largely on their sintering method, composition and the microstructure, which are closely connected to each other. Therefore, this paper summarizes the factors influencing the performance of Ti(C, N)-based cermets and toughening methods in recent years based on the preparation method, composition and microstructure, and presents thoughts and prospects for the future development of cermets.

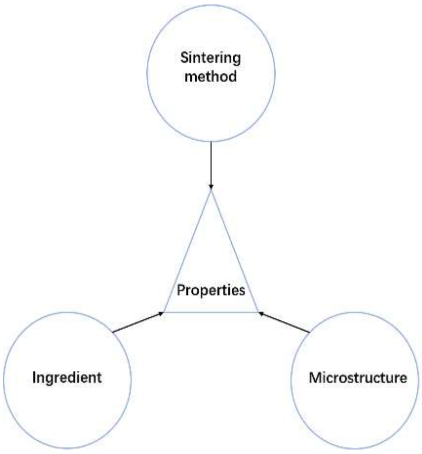

Fig. 1 Relationship between performance and sintering method, composition and microstructure.

2. Microstructure

Ti(C,N)-based cermets mainly consist of the hard phase TiN-TiC and the metal- binder phase. Many researchers also add different additives to the cermets to modify the properties of the cermets [6,8].

2.1 Binder Phase

A number of studies on the binder phase have also been conducted, and the traditional binder phase is usually used mostly such as Ni, Co, Cr, Fe, etc. As a binder phase, Ni mainly provides ductility, plasticity and flexural strength for cermets, however, it has poor wettability with hard phases such as TiC, which can result in brittle cermets. Co, as the binder phase, can improve the wettability of the hard phase and improve the performance of cermets to a certain extent, but it is not possible to replace the Ni phase completely, or it will lead to the degradation of the performance. Cr is used as a binder phase to enhance the oxidation and corrosion resistance of cermets. Fe as the binder phase has also attracted the attention of many researchers due to its wide source and inexpensive price, although the Fe binder phase has poor wettability and low mechanical properties of the prepared cermets [9]. The binder used alone has little performance improvement relative to cermets, and perhaps even causes performance degradation. As a result, a lot of researchers have worked to develop the overall performance of cermets by adding different metal composition compounds as binder phases, such as Ni-Al binder agents [10], Fe-Al binder agents [11], Ai-Ti binder agents [12], and high-entropy alloys [13] as binder agents. Other researchers have proposed the necessity of an in-depth study of Ti(C,N)-based cermets without binder phases, which could eliminate the conflict between the hard and binder phases [14]. In conclusion, the researches on binder phase have been an essential field of attention for investigators.

2.2 Hard Phase

The hard phase generally has a typical "core-rim" structure, with the core generally being TiC or Ti(C,N) and the rim generally being a solid solution structure formed by TiC or Ti(C,N) and metal additives such as W, Mo, V, Nb, Ta and other elements [5]. As shown in Fig. 2, the structure of Ti(C,N)-based cermets was researched in the literature [15], and this core-rim structure was produced due to the dissolution-reprecipitation process. The black core in the figure is the undissolved Ti(C,N) grains, and the gray rim is the solid solution of Ti(C,N) grains and carbides dissolved in the Ni-binder phase and deposited in the core after saturation. The structure of Ti(C,N)-based cermets investigated in the literature [16] is the same as the one described above, with a black core of undissolved Ti(C,N) particles and a gray rim of (Ti,La)(C,N) solid solution wrapped around the periphery of the core.

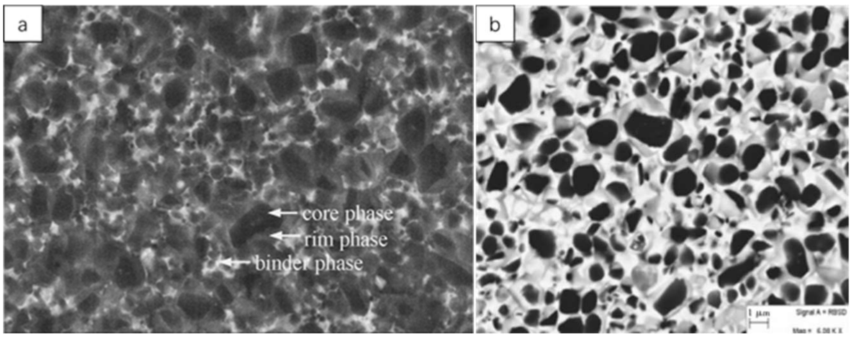

Fig. 2 Typical structure of Ti(C,N)-based cermets: (a) 10 wt% MoC added; (b) 0.35% solid solution of La element in (Ti,La)(C,N) [16].

In contrast to the conventional core-rim structure, researchers have observed that the use of different sintering methods or additions also leads to changes in the microstructure. In the literature [17], it was discovered that different "core-rim" organizations are formed according to the different elemental distribution aggregates. For example, black core-gray rim organization formed by (Ti, Mo, W, Ta) (C, N) with lower content of Mo, W, Ta elements; black core-white rim organization formed by Ti(C,N) with lower content of Mo, W, Ta elements; white core-gray rim organization formed by (Ti, Mo, W, Ta) (C, N) with lower content of Mo, W, Ta elements precipitated on the solid solution with higher content of other heavy elements; and some larger particles without forming core-shell organization with no rim organization. A study in the literature [18] found that the addition of WC to Ti(C,N)-based cermets caused a gradual increase in the volume fraction of white nuclei and a gradual decrease in ceramic grain size as the WC content increased in a certain range.

In the same time, a new Ti(C,N)-based cermet with a single solid solution phase has been discovered by the researchers. In the literature [19], cermets with a microstructure of a single solid solution phase and uniform distribution were produced by mechanical activation and in situ carbon thermal reduction, as shown in Fig. 3a. These cermets lack the core-rim structure typical of conventional cermets, and thus can enhance their mechanical properties without large stress-strain resulting from the mismatch at the core-rim interface. Complete solid-solution cermets without core-rim structure were also fabricated by mechanical activation and in situ carbon thermal reduction in the literature [20], as shown in Fig. 3b. In this case, the complete solid solution phase and the adhesive Ni phase showed a semi-confluent state with high density dislocations, which significantly strengthened the flexural strength and fracture toughness of the cermets.

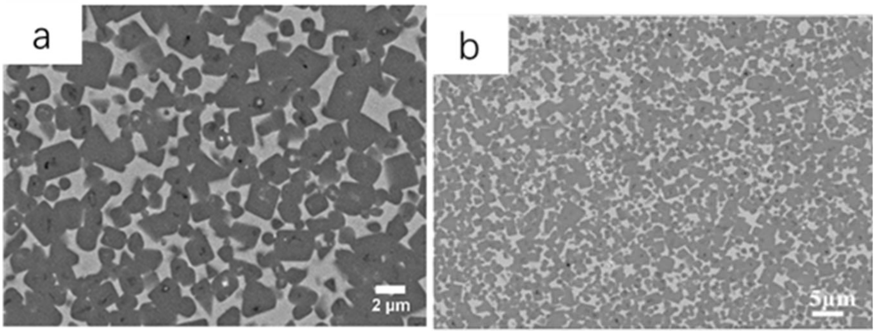

Fig. 3 Ti(C,N)-based cermets with a single solid solution phase [19-20].

3. Sintering Methods

Different sintering methods can affect the structure and properties of metal ceramics, and it is vital to select the appropriate sintering methods for different product applications.

3.1 Vacuum Sintering Method

Vacuum sintering is one of the traditional sintering techniques commonly used to prepare metal ceramics, and this method is performed in an environment of vacuum. The utilization of vacuum sintering can effectively isolate impurities in the air, prevent harmful substances from contaminating the raw material, facilitate the reduction of oxides during sintering and improve the wettability of cermets, moreover, at a lower cos [7]. The literature [17] investigated the evolution of the structure and properties of Ti(C,N)-based cermets during vacuum sintering and found that the critical densification temperature is approached at a temperature of about 1350°C and the densification mechanism converts to grain boundary diffusion, resulting in rapid densification of Ti(C,N)-based cermets. As it is increasing in temperature, the transition areas between the core frameless structure and the binder phase are expanding and reaching equilibrium at the final temperature to form the final microstructure. The literature [21] investigated the differences between vacuum and pneumatic sintering of Ti(C,N)-based cermets. Compared with vacuum sintering, pneumatic sintering obtained a homogeneous morphology and faster dissolution and precipitation rates. However, the ceramic grain size distribution widened and the number of coarse crystals increased, while a smaller pool of adhesive was observed in the vacuum-sintered samples.

3.2 Discharge Plasma Sintering Method

Discharge plasma sintering is a technology that generates high temperature using pulsed discharge by passing a pulse current between powder particles to form a discharge plasma. Discharge plasma sintering can achieve rapid sintering by causing the powder particles for sintering to fizzle and heat up to the sintering temperature quickly [8]. By using the discharge plasma sintering method, the temperature can be rapidly increased and the sintering temperature can be attained in a relatively short time, which is beneficial for the activation of the initial powder and the refinement of the crystalline grains of the cermet. Literature [22] prepared TiC metal ceramics by discharge plasma sintering method and discovered that Ti and C were not completely reflected at 1000 °C - 1100 °C and that the metal ceramics exhibited high porosity. At 1200°C, the reaction is basically completed, the densification of metal ceramics is greatly improved to 92%, and the hardness rises significantly. When the sintering temperature achieves 1300°C, the hardness is further increased to the maximum value due to the formation of skeletal structure between TiC, but the bending strength is reduced due to the evaporation of Ni-bonded phase at high temperature. The literature [23] compared Ti(C,N)-based cermets prepared by discharge plasma sintering with conventional sintering and found that the density of cermets sintered by discharge plasma could obtain 98.5% in a shorter period of time, while the density of cermets by conventional sintering was only 97% after 2h. Meanwhile, compared with conventional sintering after discharge plasma sintering, the cermet carbide size becomes more refined, and the hardness, fracture toughness, and Young's modulus appear to be higher than those of conventional sintering.

3.3 Self-propagating High-temperature Synthesis Method

Self-propagation high-temperature synthesis is a sintering technology that makes use of the chemical reaction heat released during reaction synthesis to complete the sintering process by self-heating and self-conduction. Self-propagating high-temperature synthesis methods are able to reach synthesis temperatures of 3000-4000°C, which are difficult to achieve with conventional sintering methods. Moreover, it is not necessary for external heating, and the equipment process is simple, with low energy consumption and low cost [24]. In the literature [25], the microstructural evolution of TiC-Ni cermets synthesized by self-propagation at high temperature from mixtures of Ti, Ni and C powders was investigated, and it was found that the self-propagation reaction could be described by a dissolution-precipitation mechanism. Starting from the formation of Ti-Ni solution, TiC particles precipitate out in Ti - Ni - C solution with the saturation of Ti - Ni - C solution, and the remaining liquid phase crystallizes in the TiN_3 and Ni matrix and combines with TiC particles. In the literature [26], the approach for the preparation of TiN-based ceramic powders by thermal reduction of self-propagating titanium nitride was investigated. In the titanium thermal reaction, solid nitrides are substituted for N_2 as the nitrogen source, resulting in higher conversion, more uniform microstructure and smaller grain size, which provides a new method for the synthesis of nitrides.

3.4 Hot Isostatic Sintering Method

Hot isostatic sintering is a technique of sintering in which the powder is subjected to forces in all directions at high temperature and pressure, making the organization more homogeneous under uniform forces. In the literature [27], TiN coatings were deposited on Ti(C,N)-based cermets by hot isostatic pressing at 110 MPa N_2 pressure and 1000 °C. It was observed that hot isostatic pressing treatment could result in the formation of a diffusion interface at high temperature and pressure and improve the adhesion between the coating and the substrate. The hot isostatic press-treated coatings became tougher and had better properties than the untreated coatings. In the literature [28], the influence of hot isostatic pressing on the tissue properties of Ti(CN)-based cermets was investigated. It was discovered that the microhardness and toughness of TiN coating attached to the cermet surface using hot isostatic pressing significantly improved, and the tool life increased by 30% during turning and by 100% during milling.

3.5 Sol-gel Method

The sol-gel method is a technique in which compounds containing highly chemically active components are solidified in three steps: solution, sol-gel and gel, and then heat-treated to produce solids of oxides or other compounds. The material prepared by this method has good homogeneity and small powder particle size [7]. In the literature [29], Ti(C,N)-Mo_2C-Ni metal-ceramic composite powders were prepared by the sol-gel method at 1400 °C in combination with the carbothermal reduction method through a series of reactions such as hydrolysis, condensation, and cleavage/decomposition. The experimental results show that the cermet powders fabricated by sol-gel method have small grains, high purity and large specific surface area.

3.6 Microwave Sintering Method

Microwave sintering method is the application of microwave electromagnetic energy to increase the kinetic energy of molecules or ions inside the material, which makes the sintering activation energy decrease and the diffusion coefficient increase, and the temperature of microwave sintered material is uniform in all parts, which can densify the material in a shorter period of time. Compared with vacuum sintering, the sintering temperature is 50-100 K lower, hence the grains are not allowed to grow and can be used to generate ultra-fine grained materials [30]. In the literature [31], Ti(C,N)-based cermet tools were manufactured by an energy-efficient microwave sintering method, and it was shown that the addition of 5 wt% WC and 15% Mo_2C gave the best mechanical properties with a relative density of 97.2%, fracture toughness of 8.24 MPa $m^{1/2}$, and Vickers hardness of 17.54 GPa. The sintering temperature and holding time were reduced by 1.4-15.25% and 66.7-96.1%, respectively, compared to conventional sintering. At the same time, the hardness of cermets decreases with increasing sintering temperature and holding time. Longer holding time will generate some whisker-like material, which is beneficial to the fracture toughness. In the literature [32], Ti(C,N)-based cermets obtained by microwave sintering of chemically coated (Ti, W, Mo, V)CN powders were found to have finer grains and a more uniform microstructure than conventional mechanically sintered powders. However, the degree of densification obtained by microwave sintering is only 98.5%. If microwave sintering is combined with hot isostatic sintering, it is expected that densification will be accelerated in the final stage.

4. Influence of Composition on Organization and Properties

4.1 The Influence of Hard Phase on Mechanical Properties

The hard phases of Ti(C,N)-based cermets are mainly TiN and TiC, where the variation of the size and C/N ratio of the original powder particles has a strong influence on the organization and properties of the cermets. According to the study, with the decrease of the original powder particles to a certain extent, the comprehensive mechanical properties of cermets will be enhanced to a higher extent. It not only increases hardness, but also improves toughness and resistance to wear, corrosion and high temperature oxidation. In the literature [33], the influence of TiC/TiN powder size on the organization and mechanical properties of Ti(C,N)-based cermets was investigated. It was discovered that with the refinement of the original powder particle size, the microstructure of the prepared cermets was more homogeneous, the black cores in the cermets became finer, the gray rim thinner, and the white cores increased significantly. In addition, the transverse fracture strength of the finely powdered sintered cermets had a large increase, but the fracture toughness was slightly reduced. In the literature[34], the effect of particle size of pristine TiCN and WC powders on surface gradient formation and grain growth of cermets was discussed. As the original powder size decreased, the thickness of the gradient layer increased, but the number of anomalous WC grains grew. The thickness of the gradient layer obtained when nano-Ti(C,N) and ultrafine WC were employed was 36 um, and the average size of WC grains was 0.28 um.

The C/N content and ratio in the hard phase is also a significant factor affecting the organization and properties of cermets. The formation of free graphite, free TiN, and other impurity phases will occur with excessive or insufficient C content, while excessive N content will contribute to the denitrification of nitrides during high temperature sintering, thus sacrificing the densities of the cermets. All of the above phenomena result in a decrease in the strength and toughness of the cermets, so it is very important to choose the right C/N content and ratio. In the literature [35], the influences of nitrogen content on the organization of Ti(C,N)-based cermets were analyzed by a combination of scanning electron microscopy and transmission electron microscopy. As the N content of the original powder increased, it was observed that the thermodynamic stability of the hard phase at high temperatures increased, the proportion of insoluble raw materials increased, and the number of black-core gray-rim ceramic particles increased. Meanwhile, the size of ceramic grains gradually decreases with the increase of N content, and the flexural strength and fracture toughness present a trend of rising and then decreasing. Ti(C,N)-based cermets with different N/(C+N) ratios were fabricated in the literature [36], and the hardness, transverse fracture strength, fracture toughness and morphology were found to be closely associated with the nitrogen content. As shown in Fig. 4, When the N/(C+N) ratio was 30at%, the cermets showed the maximum fracture toughness as well as a high flexural strength. the finest grain can be obtained when the N/(C+N) ratio is 40at%, when the highest bending strength can be obtained, while the hardness increased slightly with the increase of N/(C+N) ratio.

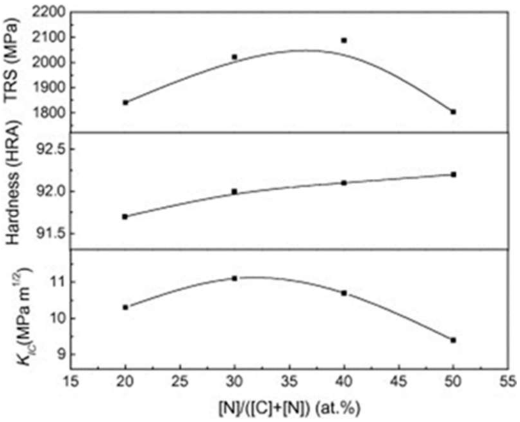

Fig. 4 Flexural strength, hardness and fracture toughness of cermets as a function of x(N)/x(C+N) ratio [36].

4.2 The Influence of Binder Phase on Mechanical Properties

The binder phase will also produce a strong influence on the organization and properties of Ti(C,N)-based cermets. The conventional binder phases are used mainly for Ni, Co, Cr, Fe, etc.

In the literature [37], metal ceramics with different Ni/(Ni+Co) mass ratios were prepared and the microstructure was observed to exhibit three structures of black core, gray rim and irregular binder phase. With the increase of Ni/(Ni+Co) mass ratio, the size of the black core gradually reduced, the rim part gradually became thicker, and it facilitated the dissolution of Mo_2C and WC in the liquid binder phase. Compared with pure Co or pure Ni, the Ni-Co binder phase can accelerate the formation of the edge phase and avoid the inhomogeneous dispersion of the binder pool. As shown in Fig. 5, with Ni/(Ni+Co) mass ratio of 0.5, the alloy had the finest grain size, uniform adhesive dispersion, little difference in composition between cores and rim, and minimal lattice mismatch. It exhibited coherent characteristics and was possible to achieve the best mechanical properties, with a Vickers hardness of 1670 (HV30) Kgf/mm^2, a bending strength of 1970 MPa and a fracture toughness of 8.94 $MPa.m^{0.5}$. The effect of partial Cr substitution for Ni on the densification, organization and properties of Ti(C,N)-Ni-based cermets was investigated in the literature [38]. The addition of Cr was discovered to reduce the complete densification temperature, and the densification temperature gradually decreased with increasing Cr content until the addition amount reached 9.6 wt%. At the same time, the addition of Cr had no impact on the dissolution of Ti(C,N) and WC, but would have an influence on the dissolution of Mo_2C. Above 1000°C, Cr in the Ni phase with Cr content of 6.4wt%-9.6wt% would diffuse into the insoluble Mo_2C and form (Mo, Cr)C. As the sintering temperature was raised to 1410°C, a portion of (Mo, Cr)C was still undissolved. Therefore, with the increase of Cr content in the Ni bonding phase, the binder phase hardened and the hardness of the cermet increased, but the flexural strength decreased, as shown in Fig. 6. The literature [39] studied the effect of Fe on the wettability of Ti(C,N)-based cermets. Fe was discovered to be extremely soluble for TiC, but almost insoluble and with zero wettability for TiN. This indicates that the wetting of Ti(C,N) by Fe was not transient and was the result of two different wetting behaviors. The addition of a small amount of Ni could significantly improve the wettability of Fe to Ti(C,N) since Ni showed good wettability to both TiC and TiN. It was demonstrated that the addition of 15 wt% Ni to the Fe binder phase could reduce the contact angle of the liquid phase to reach a contact angle close to that of Ni alone, which offers the possibility of replacing Ni with Fe as the binder phase.

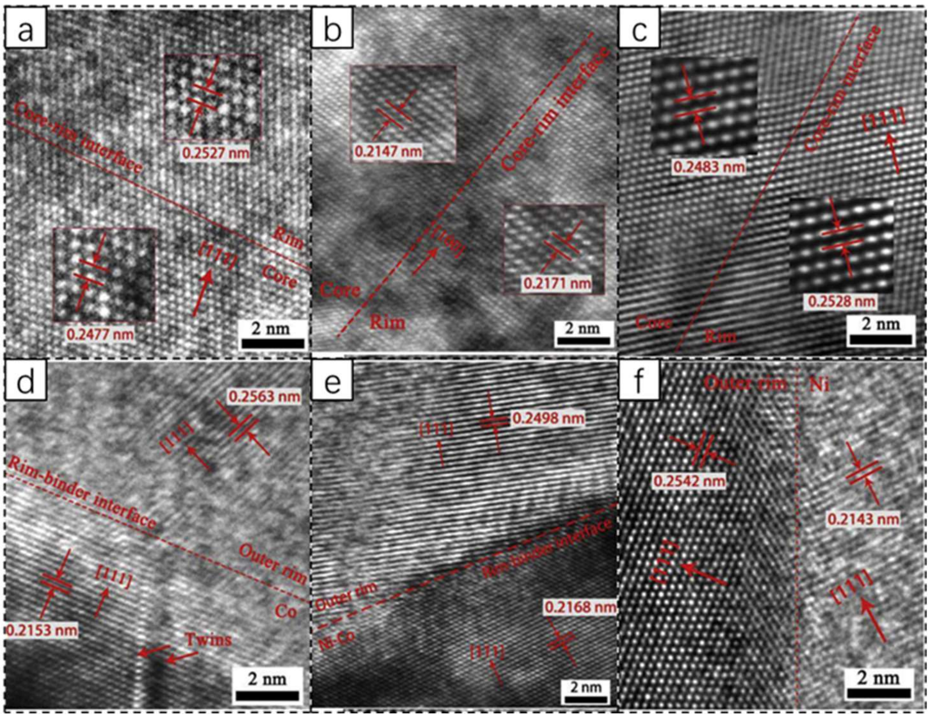

Fig. 5 HRTEM images of Ti(C, N)-based cermets with different binders: (a,b,c) HRTEM images of the core-rim interface containing 16 wt% Co, 8 wt% Co-8 wt% Ni, and 16 wt% Ni binder phases, respectively; (d,e,f) HRTEM images of the rim-binder phase interface containing 16wt%Co, 8wt%Co-8wt%Ni, and 16wt%Ni bonded phases, respectively [37].

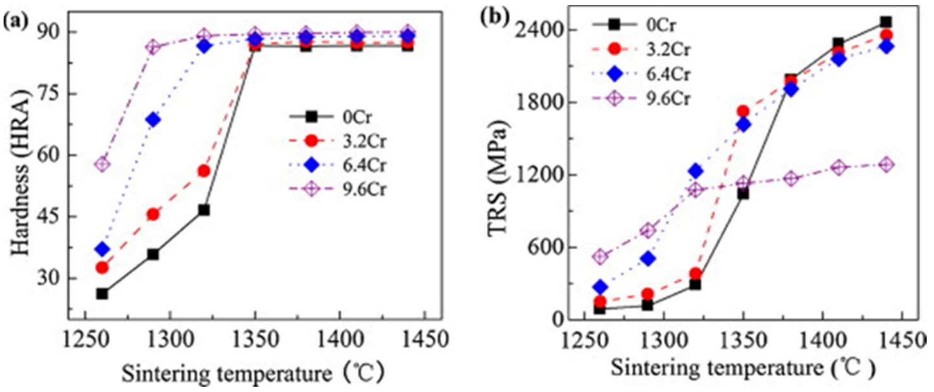

Fig. 6 Variation of hardness and bending strength with temperature for cermets with different Cr contents [38].

In recent years, intermetallic compounds NiTi, Fe-Al, Al_3Ti, Ni_3Al and high-entropy alloys have also been applied by researchers as binder phases to improve the properties of cermets. The high entropy alloy as the binder phase of the cermet might theoretically enhance the overall toughness of the cermet by virtue of its superior mechanical properties.

The literature [40] researched the impact of adding NiTi on the organization and properties of Ti(C,N)-based cermets. The grain size of cermets was detected to become finer with the increase of NiTi powder content without reaching 16wt%. Moreover, a new ceramic phase with a gray core, a continuous black inner rim, a discontinuous white inner rim and a continuous gray outer rim structure was identified. The gray core is the initial undissolved NiTi binder phase, the black and white inner rim are TiC and (W,Mo,Ti)C, respectively, while the gray outer edge is (W,Mo,Ti)C or (W,Mo,Ti)(C,N). As the NiTi powder content increased, the crack closure effect and microcracking caused by martensitic phase transformation caused a significant improvement in both fracture toughness and flexural strength of the cermets, but the hardness showed an opposite trend. In the literature [41], the organization and properties of Ni3Al-bound Ti(C,N)-based cermets with different temperatures and contents were investigated. After the addition of Ni_3Al alloy, the cermets presented two grain structures, black core-gray rim organization and black core-white inner rim-gray outer rim organization, and the grains had abnormal growth and tended to be slate-like. The bending strength of metal ceramics raises with increasing alloy content and sintering temperature, reaching 1131 MPa at 1450°C, and the hardness of the metal ceramics also reaches its peak at this time. The fracture toughness also tended to increase with the alloy content, with a peak of up to 16.1 $MPa.m^{1/2}$ for a Ni_3Al content of 30 wt%.The literature [42] prepared cermet using CoCrFeNiCu high-entropy alloy as the binder phase. The CoCrFeNiCu binder phase was discovered to be more advantageous than the Ni binder phase in inhibiting the growth of core-rim grains and forming a nucleation-free structure, with certain enhancement effect in terms of toughness. High hardness of prepared cermets due to the maximum solid solution strengthening effect of CoCrFeNiCu binder phase. At high temperatures, the high entropy effect of CoCrFeNiCu facilitates the bonding of cermets as well as the lubricating effect, which improves the wear resistance. The high temperature wear rate and intersteel friction coefficient of conventional Ti(C,N)-Ni-based cermets are 1.4-2.4 times higher than those of cermets with high entropy alloys. In the literature [12], Ti(C,N)-based cermets were prepared with CoCrFeNiAl and Ni/Co as the binder phases, respectively, and the results indicated that the cermets with high-entropy alloys as the binder phases formed a continuous and dense external oxide layer with good oxidation resistance. In further, the high-temperature hardness of cermets prepared from high-entropy alloys at 1000°C could achieve 993.7 HV_{20}, while the high-temperature hardness of cermets prepared from Ni/Co bonded phases at the same temperature was only 668.1 HV_{20}. The literature [42] prepared TiC-CoCrFeNiMo cermets and revealed that the flexural strength of the cermets exhibited a tendency to increase and then decrease with the rising of the sintering temperature. The flexural strength at 1290°C could attain 2358.1 MPa, while the hardness keeps increasing, reaching 67.6 HRC at 1370°C.

4.3 The Influence of Additives on Organization and Mechanical Properties

Many researchers have studied the relationship between the addition of different additives to metal ceramics, however, only some valuable results and basic laws have been obtained, and there is still no mature system for this.

The addition of carbides has received a lot of attention from researchers, and a large number of carbides have been applied to cermets to improve their properties. For example, Mo_2C, WC, NbC, TaC, VC, Cr_3C_2, ZrC, etc. The effect of secondary carbides (Mo_2C, WC, NbC, TaC) on the organization and properties of Ti(C,N)-based cermets was investigated in the literature [43]. It was demonstrated that due to the high solubility and dissolution rate of Mo_2C and WC in the Ni-binder phase can inhibit the dissolution-precipitation process of Ti(C,N), which obviously refines the ceramic grains and improves the bending strength, fracture toughness and hardness of the ceramics. While the solubility of TaC and NbC in the Ni phase was smaller, the size of the core of the prepared cermets decreased, the grain size of the brittle shell phase became coarser, the thickness increased. Compared to the cermets with Mo_2C and WC, their mechanical properties were to some extent reduced in order. At the same time, the refinement of the core and rim grains increased the crack resistance of the ceramic phase, so that the performance of the anti-corrosion properties was consistent with the mechanical properties, and Mo_2C had the best anti-corrosion properties. The effect of WC content on the organization and properties of Ti(C,N)-based cermets was examined in the literature [44]. Since the solubility and dissolution rate of WC in Ni phase was higher than Ti(C,N), the ceramic particles transformed from a completely solid solution state to a partial solid solution containing a small amount of core-rim structure. As shown in Fig. 7, with the growth of WC content, the crystal size gradually decreased and the grain shape gradually changes from multifaceted to round. However, the grain size tended to increase when the WC content increased to 12 wt%. At this point, the bending strength of the cermet also increased with the addition of WC content, and the hardness also gained slightly at a lower WC addition, which is the result of solid solution strengthening and fine grain strengthening. The cermets with different WC contents all show high fracture toughness. It was attributable to the reduced core-rim phase interface area at 0wt%-3wt% WC compared to conventional ceramics, which significantly reduces the interfacial strain. The toughness of the cermets gradually improved at WC contents of 6wt%-12wt%, which was caused by the superb co-grid relationship between the black core grey rim and the binder phase (Fig. 8A(a)). There is a semi-coherent lattice relationship between the solid solution particles, but no apparent coherence between the white-core gray-rim particles and the binder phase is noticed (Fig. 8B(a)). This is similar to the findings in the literature [18]. The binder phase outside the black core has a smooth interface with the outer rim, and both are completely coherent (Fig. 8A(b)). While the adhesive phase outside the white core shows a rough interface with the rim and no obvious orientation relationship (Fig. 8B(b)). In the literature [37], VC and Cr_3C_2 were added to Ti(C,N)-based cermets and V was detected to be present mainly in the whole ceramic grains, and Cr is mainly present in the edge phase and Ni binder phase. The influence of VC and Cr_3C_2 on cermets is basically the same, which can refine the grain size of cermets and exert a significant influence on the mechanical properties of cermets. The addition of VC increased the porosity of the alloy and reduced the plasticity of the alloy. The addition of Cr_3C_2 enhanced the plasticity and interfacial bonding strength of the edge phase of the alloy, thus improving the alloy properties. The bending strength and fracture toughness of the cermets with the addition of 1.5 wt% Cr_3C_2 achieved 3054 MPa and 17.3 $MPa.m^{1/2}$, respectively. The effect of ZrC on the organization and properties of Ti(C,N)-WC-NbC-Co-Ni cermets was presented in the literature [46]. The findings indicate that the addition of ZrC could serve to inhibit the dissolution-repigmentation process, thus refining the grain size of the cermets. With the increase of ZrC content, the oxidation resistance of cermets continued to improve. The flexural strength and fracture toughness of cermets with the addition of 1 wt% ZrC were up to 2549 MPa and 13.0 $MPa.m^{1/2}$.

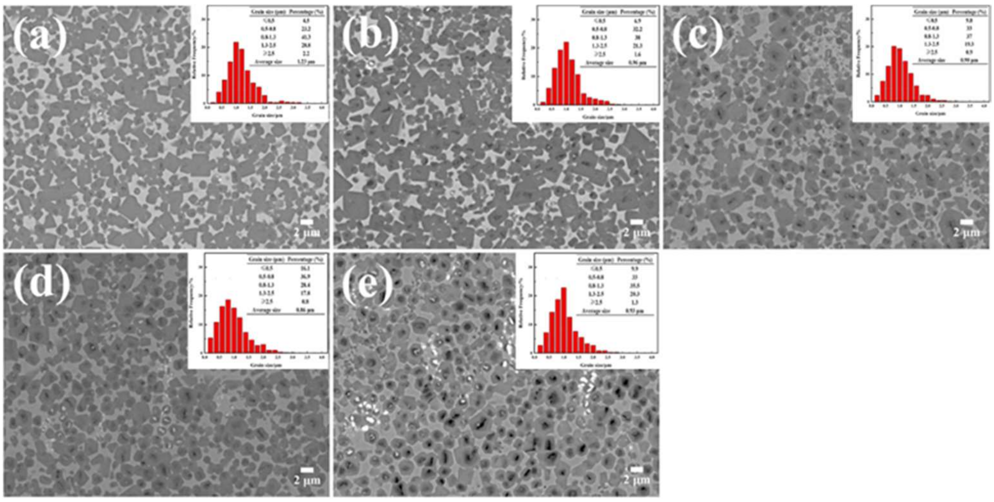

Fig. 7 Average particle size of sintered cermets with different mass fractions of WC addition: (a) 0 W C, (b) 3 W C, (c) 6 W C, (d) 9 W C, (e) 12 W C [44].

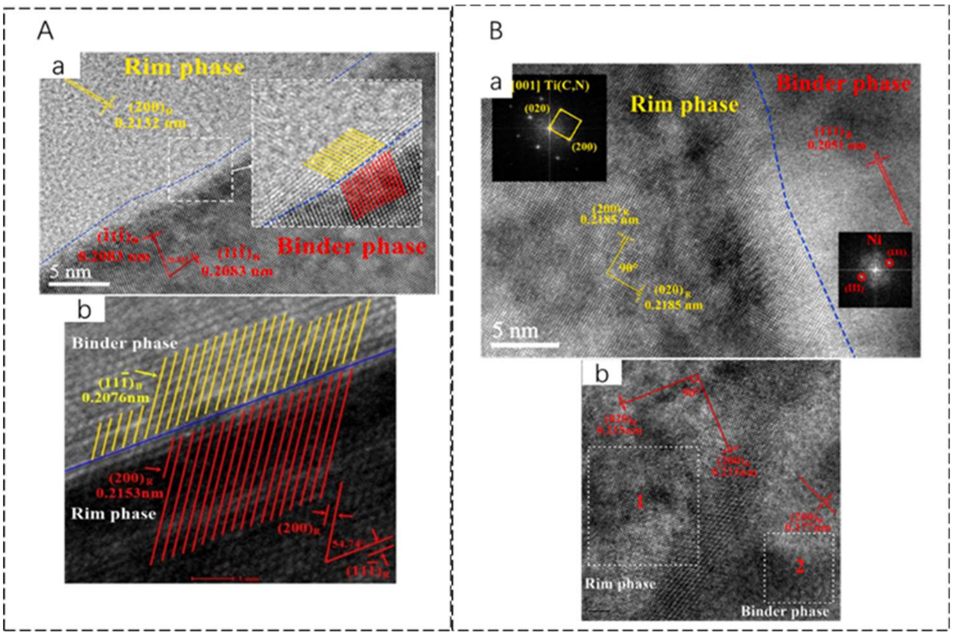

Fig. 8 HRTEM images of metal-ceramics with different core-rim structures: Figure A(a,b) shows the HRTEM images of the interface between the binder phase and the black core-gray rim; Figure B(a,b) shows the HRTEM images of the interface between the binder phase and the white core-gray rim [18,46].

From the mentioned above, it is obvious that the addition of carbide has a significant effect on the organization and properties of cermets. Besides carbide, numerous researchers have attempted to add some other substances to cermets, such as metal monomers and oxides, rare earth elements, whiskers, carbon nanotubes, etc. These have a significant impact on the organization and properties of cermets. The literature [47] investigated the organization and properties of ultrafine Ti(C,N)-based cermets with different Cu contents. Cu could enter the binder phase to form solid solution and hinder the growth of hard phase grains by inhibiting the dissolution-precipitation process, which is consistent with the effect of Ru addition on cermets [48]. The results indicated that the hardness and fracture toughness of 1 wt% Cu cermets added were 92.5 HRA and 10.7 MPa.m$^{1/2}$, respectively. The hardness, flexural strength and fracture toughness of the cermets with the addition of 1 wt% Ru achieved 92.6 HRA, 2806 MPa and 9.11 MPa.m$^{1/2}$, respectively. The effect of carbon addition on the organization and properties of Ti(C,N)-based cermets was investigated in the literature [49]. The incorporation of carbon enabled the rearrangement of Ti(C,N) particles in the liquid phase and the densification process of metal ceramics. Ti(C,N) particles were gradually and uniformly distributed in the tissue with the increase of carbon content, which substantially improved the mechanical properties of the cermets, as shown in Fig. 9A. This was similar to the results in the literature [50]. The addition of carbon had a significant influence on the sintered cermets at 1400°C. The outcomes demonstrated the excellent mechanical properties of the cermets with 1 wt% carbon sintered at 1400 °C. The literature [51] added different contents of diamond to Ti(C,N)-based cermets. An increase in diamond content within a certain range was observed to lead to diamond graphitization, triggering higher carbon activity and thus promoting the production of more white core structures. And it enabled a uniform tissue distribution, which was favorable to improve the performance of cermets. The bending strength and fracture toughness with the addition of 0.6 wt% diamond were 2026 MPa and 12.95 MPa.m$^{1/2}$, respectively. The literature [52] explored the variations in the organization and properties of Ti(C,N)-304ss-based cermets by adding different contents of rare earth Y . The in situ formation of Y2O3 in the form of heterogeneous cores was found to refine the organization of cermets and inhibit the growth of hard phases, thus enhancing their mechanical properties. The hardness and bending strength of the cermet with the addition of 0.3 wt% Y were up to 91.7 HRA and 1527 MPa. Ti(C,N)-based cermets with SiC whisker addition were prepared in the literature [53]. It was identified that the addition of SiC can affect the grain size of ceramics. Ceramics with 1 wt% SiC added have the smallest grain size, uniform organization, and moderate edge phase thickness. Compared with the cermet without SiC addition, the bending strength and fracture toughness were increased by about 24% and 29%, reaching 2279 MPa and 17.7 MPa.m$^{1/2}$, respectively. The literature [54] investigated the impacts of different additions of surface-modified carbon nanotubes on the organization and properties of Ti(C,N)-based cermets. The addition of carbon nanotubes was observed to reduce the dissolution of tungsten, titanium and molybdenum in the binder phase. The cermets with 0.5 wt% carbon nanotubes added had the smallest grain size, the most homogeneous organization, and the largest volume fraction of binderphase, with the highest bending strength of 2181 MPa and fracture toughness of 14.9 MPa.m$^{1/2}$.

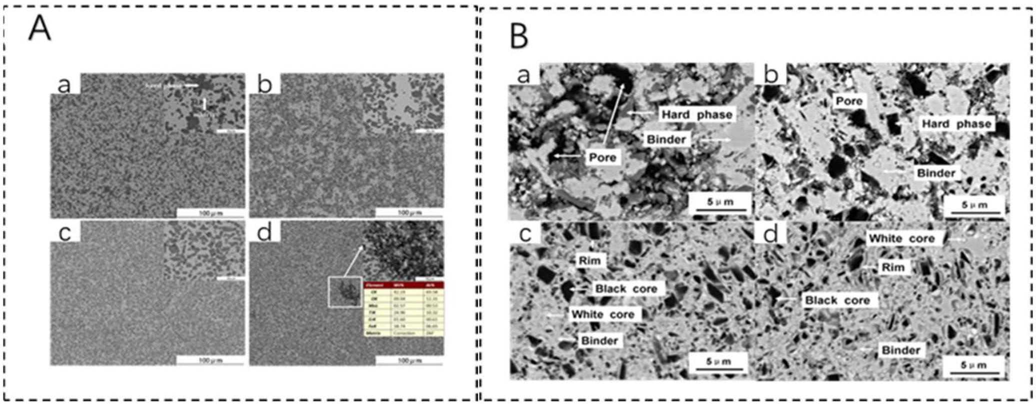

Fig. 9 Microstructure of cermets at different carbon additions and sintering temperatures: Fig. A (a,b,c,d) SEM images of sintered Ti(C,N)-Fe metal ceramics with 0wt%, 0.5wt%, 1.0wt%, and 1.5wt% carbon additions, respectively; Fig. B(a,b,c,d) shows the BSE images of 1.0wt% carbon addition sintered at 1240°C, 1280°C, 1340°C and 1400°C for 1h, respectively [52].

In summary, the addition of carbides, rare earth elements, whiskers and carbon nanotubes to Ti(C,N)-based cermets will improve the organization of the cermets and significantly enhance their mechanical properties, as shown in the following table. These additions provide a great combination of properties that enable cermets to be even better tool materials.

Table 1. Effect of additives on Ti(C,N)-based cermets

Additives	Effects	Influence
Mo/Mo_2C	An essential ingredient to improve wettability and promote sintering densification.	Within a certain range, the mechanical properties are enhanced as the content increases; in excess, the properties decrease.
WC	Similar to Mo/Mo_2C, it is favorable to the formation of ring phase; directly related to the formation of white nuclei, it can inhibit grain growth and refine grain organization.	The hardness, flexural strength and fracture toughness improve as the content increases within a certain range; the performance decreases in excess.
TaC/Cr_3C_2/VC	It can improve wettability, inhibit grain growth, refine grains, etc.	The appropriate amount can improve fracture toughness, flexural strength, red-hardness, thermal shock resistance, and oxidation resistance.
NbC	Similar to TaC and also decreases the sintering temperature.	Within a certain range, it can reduce the sintering dimension and improve all mechanical properties, and in excess, the properties are degraded.
ZrC	Ceramic grains can be refined by a dissolution-redeposition process.	Necessary content can provide improved strength, fracture toughness and oxidation resistance, and the performance decreases in excess.
C	Reduction of adsorbed oxygen; Ensuring the generation of Mo2C; Avoiding brittle and free graphite phases.	The best mechanical properties are obtained by adding 1 wt%.
Rare earth elements	Purifies the interface; Improves wettability; Reduces porosity and facilitates sintering densification.	The addition of the right amount can promote the mechanical properties.

5. Toughening Methods

Despite the many advantages of cermets, their inherent low fracture toughness has affected their development and restricted their applica Therefore, in recent years, an increasing amount of literature has focused on the study of cermets in terms of fracture toughness, and a variety of methods for toughening cermets have been proposed.tions.

5.1 Whisker Toughening

Researchers have realized that by adding a certain amount of whiskers, carbon nanotubes and other fibrous substances to metal ceramics, not only can the self-wetting properties of metal ceramics be improved, but also can make them consume more strain energy during crack expansion and thus promote their toughness. The influences of ZrO2 whiskers on Ti(C,N)-based cermets were analyzed in the literature [56], and it was discovered that the fracture toughness showed an increasing trend with the increase of ZrO2 whisker content. It is due to the phase change of ZrO2 during the temperature change which inhibits the crack expansion and compensates the natural defects of the dispersed whiskers. The literature [57] incorporated carbon nanotubes in cermets, the mechanisms of strengthening and toughening were identified as crack deflection, bridging effect and pull-out effect of carbon nanotubes. It was consistent with the above mentioned ZrO_2 whisker toughening at that time. The fracture toughness of the cermets with 5% carbon nanotubes added increased from 10.2 MPa.m$^{1/2}$ to 15.9 MPa.m$^{1/2}$.

5.2 Phase Change Toughening

Phase change toughening is also one of the significant toughening methods for cermets, of which ZrO_2 toughening is typical. As mentioned above, the phase transformation of ZrO2 inhibits the crack extension, and in the modification of Ti(C,N)-based cermets, phase transformation toughening is employed to provide a stress-induced quadratic ZrO_2 martensitic phase transformation to improve the toughness of the material. And this martensitic phase transformation leads to shear shielding and lattice expansion at the crack tip, and the generated residual compressive stress forms a crack closure effect. The microcrack in front of the main crack is allowed to expand and consume energy, resulting in a smaller stress field intensity factor at the crack tip than in the far field, further improving the fracture toughness of the material, as shown in Figure 10a. In addition to ZrO2, the literature [40] researched the effect of martensitic phase transformation of NiTi alloys on the organization and properties of cermets. The transformation of NiTi alloys from austenite to martensite also contributed to the formation of residual compressive stresses thereby reducing the stress field strength factor at the crack tip. Meanwhile, crack deflection of small particles (Fig. 10b) and crack bridging of large particles (Fig. 10c) also consumed large amounts of energy and improved the fracture toughness of the cermets.

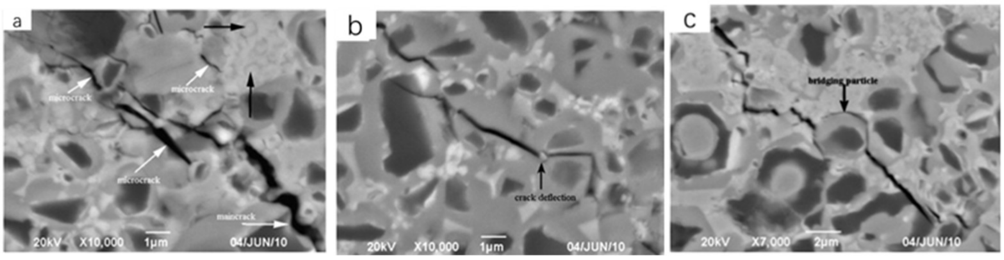

Fig. 10 SEM-BSE images of metal-ceramic microstructures: Fig. a shows the microcrack before the main crack; Fig. b shows the crack deflection in the cermet; Fig. c shows the crack bridging in the cermet [40].

5.3 Nanophase Toughening

Currently, modification by adding nano-phase to metal ceramics to improve the toughness of metal ceramics is also one of the methods. TiC, TiN, and nanophases such as carbon nanotubes and nitrogen nanotubes have been attempted to modify cermets. In the literature [58], carbon nanotubes were inserted into Ti(C,N)-based cermets. The incorporation of carbon nanotubes produced crack deflection as well as bridging effects, which can effectively crack deflect and thus substantially improve the fracture toughness of cermets. Based on the experiments, the fracture toughness of the incorporated carbon nanotube cermets attained 15.9 MPa.m$^{1/2}$, but the hardness would decrease to some extent. The influence of nano-Ti(C,N) phase was investigated in the literature [33] and it was observed that the incorporation of nano-Ti(C,N) phase could inhibit the grain growth. As shown in Fig.11, the finest and homogeneous metal-ceramic tissue was achieved at the addition amount of nano-Ti(C,N) phase content of 10%. Fine grains would develop intergranular fracture, which could consume more energy during fracture and increased fracture toughness.

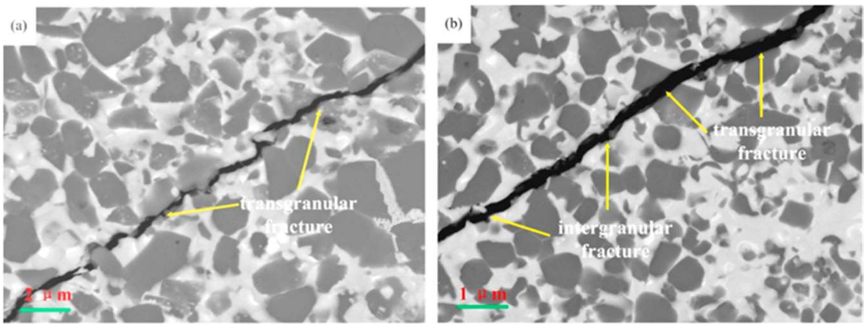

Fig. 11 SEM micrographs of the crack extension path: (a) Ti(C,N)-based cermet without Ti; (b) Ti(C,N)-based cermet containing 10 wt% of Ti [58].

5.4 Gradient Toughening

Gradient toughening is performed by causing a gradient change in the composition of the material, which results in a gradient change in its properties as well. Compared to traditional metal ceramics, gradient ceramics show their unique advantages. In the literature [59], self-diffusing gradient cermet tool materials were prepared and it was revealed that as the sintering temperature increased, the adhesive diffusion coefficient increased and diffused more easily. At a sintering temperature of 1500°C, a holding time of 40min was sufficient to complete the sintering of the self-diffusing cermet. Excessive holding time would cause the Ni content to decrease, the thickness of Ni layer to decrease, and the metal matrix to be too hard and brittle, which is not conducive to its mechanical properties. And it was noticed that a Ni-rich sub-surface layer with a thickness of about 20um was successfully prepared between the surface layer and the base layer at 30min of sintering. This sub-surface layer strengthens the effect of grain pull-out, absorbs energy during crack expansion, and improves the fracture toughness of ceramets.

In Addition to the above toughening methods, there are also particle dispersion toughening, pre-solid solution treatment, dual structured ceramets and other ways to toughen ceramets. Toughening of cermets is also a current hot topic of concern for researchers. At present, the main development of metal ceramics is towards multi-phase multi-layered composites, nano-ceramics and synergistic toughening in the homogeneous way.

6. Prospects and Outlook

In recent years, with the demand for aerospace, high-end equipment and a variety of difficult-to-machine materials, the performance requirements for cutting tools are increasingly high. The application of Ti(C,N)-based cermets as cutting tool materials can effectively overcome these challenges. This article reviews the researches and developments of cermets in recent years, but the problems faced by cermets also require further in-depth consideration. A number of achievements have been made by domestic and foreign scholars to explore the improvement of the tissue properties of Ti(C,N)-based cermets. There have been significant advances in research on preparation methods as well as performance enhancement.

Despite the unique advantages of cermets in terms of red-hardness, oxidation resistance and wear resistance. The insufficient toughness is still an urgent problem for researchers to overcome. A great deal of progress has been made in the attempts to toughen ceramets with respect to different sintering methods, refinement of the structure and improvement of additives. Based on the research status at home and abroad, the research direction of new Ti(C,N)-based ceramets will be reflected in the following aspects.

1) Complete and optimize the sintering technology and explore the basic theory and process control. And a combination of one or even several sintering techniques is deployed to prepare ceramets.

2) Further establish the intrinsic connection between sintering methods, compositions, microstructures and properties. Development of cermet system based on existing experience. To clarify the interrelationship between different sintering methods, composition content and microstructure and their effects on the properties of cermets, and to achieve precise control of the properties of cermets.

3) The reinforced toughening aspect of metal ceramics will also be the emphasis of research on Ti(C,N)-based metal ceramics, which is also a serious challenge for metal ceramics all the time. At present, the major direction of metal-ceramic reinforced toughening is to refine the grain, towards the technology of adding nanomaterials. This will be the direction of research for the next period of time. In addition, the development of new additives, improvement of interfacial structure and wettability will also become the main methods to enhance the toughening of metal ceramics.

4) Establish a material genome database with the core of metal-ceramic system. The application of computational simulation technology to simulate the production preparation process is also imperative to shorten the cycle time and reduce costs. The advancement of computer technology will certainly promote the development of cermet research.

5) Ecological and environmental protection is a vital part that should not be ignored. Achieving green processing, energy saving and recycling will also be hot spots for future studies on metal ceramics.

Due to the decrease in scarce resources such as W and Co, it has also become imperative to replace scarce resources with resource-rich materials. Therefore, the development of Ti(C,N)-based cermets has become the focus of research, and the study of cermets will certainly bring a bright future for the cutting field.

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