Review

Development of TiCN-based cermets: Mechanical properties and wear mechanism

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ABSTRACT

In order to improve the performances of TiCN-based cermets, researchers have paid much attention directly towards developing various new spices of cermets. The present review will try to sum up the efforts in designing and tailing in compositions and microstructures of TiCN-based cermets in recent years aiming at enhanced cermet properties. The relationship between the cermet constituents and their mechanical properties and wear resistance, as well as the advances in the synthesis of TiCN powders and preparation of TiCN-based cermets were included. Special emphasis was paid on the preparation of ultrafine/nano TiCN-based cermets possessing enhanced hardness, mechanical strength, toughness and wear resistance, which has led to a very recent surge of interest in the development of TiCN-based cermets. In particular, it has been possible to obtain dense TiCN-based cermets with ultrafine- and/or nano-structures by means of fast sintering techniques, such as spark plasma sintering, microwave vacuum sintering and so on.

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1. Introduction

In recent few decades, although there have been some momentous advances in new forming techniques, machining is still a predominant industrial activity. In a machining system, cutting tools play a significant role for high cutting speed, namely for high productivity. With respect to a cutting tool, it has to withstand abrasion, chemical reaction, plastic deformation, and thermal shock during its application [1]. And it has been believed since a long time ago that adopting improved cutting tools would increase the speed and precision in machining, as well as prolong the tool life, or reduce the cutting cost thus the total cost in production.

Up to date, although numerous practical machining operations and several progresses have been made in various cutting tool materials, cermets have been considered as the most promising candidates due to their high-temperature hardness, low reactivity with steels and other metals, and specially high thermal conductivity. Since a high thermal conductivity of a cermet would lower the temperature gradient and lessen the stress and cracks resulting from the thermal shock during machining [2], so high speed cutting tool materials often give preference to those of high thermal productivity.

Compared to the conventional WC-based hardmetals, cermets can provide improved surface finishing, excellent chip and tolerance control, offer geometric accuracy in workpieces, increase the feeding speed as well as remain fixed in critical dimensions [3,4]. What is more, cermets are much competitive in both the price and the performance compared with the hardmetals, especially in high speed cutting and finishing operations [3,4].

Nowadays, in industry application, there are two kinds of cermets, namely TiC-based and TiCN-based cermets. Compared with TiC-based cermets, TiCN-based cermets have much higher high-temperature hardness, higher transverse rupture toughness, better resistance to oxidation, and much higher thermal conductivity (for details please check in Table 1). Moreover, due to the much finer grains of the hard phase in TiCN-based cermets, the resistance to high-temperature creep deformation of TiCN-based cermets is much better than that of TiC-based cermets. And during the machining with TiCN-based cermet cutting tools, it is much more difficult for the formation of oxidation layers, scaling, crescent depression and built-up edges, which is attributed to the higher enthalpy in formation of TiCN, as compared with TiC-based cermets. Considering all the above-mentioned facts, TiC-based cermets have been considered as the most promising candidates due to their high-temperature hardness, low reactivity with steels and other metals, and specially high thermal conductivity. Therefore, this paper has indeed put a special emphasis on the mechanical and properties of ultrafine/nano TiCN-based cermets, which are characteristic of at least one phase with grain size being typically smaller than 100 nm [5–7]. Such cermets have been confirmed in the majority of literatures that they possess improved physical, mechanical and tribological properties at ambient temperature and even elevated temperatures, thus they are more competitive and promising for rigorous engineering applications, when compared with their conventional counterparts [8,9].

Based on the previous experiences, applying nano-TiCN powders [10–12], adding nano-sized additives [13–17] into TiCN cermet matrix, and sintering TiCN-based cermets with fast sintering techniques [10,18–21] are three principle ways to prepare ultrafine and/or nano TiCN-based cermets. In order to synthesize nanosized raw powders, new techniques have to be developed, because the limited purity of the nanosized powders synthesized by traditional methods has imposed restrictions on the widespread commercial applications of TiCN-based cermets. To date, some modified and novel techniques have been developed and can solve this problem to some extent. For example, self-propagating high-temperature synthesis (SHS) can prepare nano-TiCN powders with a quite high purity and efficiency [22]. With respect to the sintering of nano-TiCN based cermets, the long sintering time in traditional processes makes it difficult to prepare nanosized TiCN cermets, and lacks efficiency in industrial production. Consequently, some fast sintering techniques, such as spark plasma sintering (SPS), bring us a promising prospect owing to its very short time in sintering [20,21,23].

However, even to date, the development of truly nano-structured TiCN powders on a commercial scale has not been achieved. Consequently, attempts are still being tried to develop appropriate ways to synthesize nano TiCN powders, which will play a great role in developing nano TiCN-based cermets. In the light of continuing study efforts aiming for ultrafine and/or nano TiCN-based cermets possessing further improved properties and enhanced applicability, all the important progresses in this aspect will be the vital part in the present review.

As for the content of the present review, at the beginning, the research backgrounds and development history of TiCN-based cermets will be primitively introduced. Then a brief description of microstructure and mechanical properties of bulk TiCN-based cermets will be given next, which will contain a critical analysis on the factors influencing the microstructure and properties of TiCN-based cermets. Following this, researches concerning with the wear mechanisms will be ticked off. Then the review sheds a light on the more recent attempts to develop ultrafine/nano TiCN-based cermets. Finally, few issues associated with the state-of-art in development and potential applications of such materials are raised.

The purpose of this review is to sum up the advance in preparation and properties of TiCN-based cermets during the past 20 years. Although there have been a couple of review literatures [2,4] which well summarized the processes and properties of TiCN-based cermets before, this paper has indeed put a special emphasis on the mechanical properties and wear mechanism of ultrafine/nano TiCN-based cermets, and coupled with a view of the guidance to the preparation of TiCN-based cermets with better performance and thus wider application.

2. Development history of TiCN-based cermets

TiCN-based cermet was first developed in 1931 [24]. However, only until 1970s after the systematic work by Kieffer and coworkers [25], the research and industrial interest on it started to boom up. In Kieffer’s study, it was found that: adding TiN into TiC-Mo-Ni cermet could markedly improve its mechanical properties at room temperature and high temperature coupled with enhanced resistance to erosion and oxidation, which corrected the prejudice against nitrogen incluions in the full of the cermet. Following that, increasing researches have been carried out and sweeping industry products have been fabricated since 1980s. The developed industry nations of the world, especially Japan, took account of the major production of TiCN-based

<table>
<thead>
<tr>
<th>Cermets</th>
<th>Microhardness (1000 °C, kgf·mm−2)</th>
<th>Transverse rupture toughness (900 °C, MPa)</th>
<th>Weight gain (1000 °C, mg·cm−2·h−1)</th>
<th>Thermal conductivity (1000 °C, W·m−1·K−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-based cermet</td>
<td>500</td>
<td>1050</td>
<td>11.8</td>
<td>24.7</td>
</tr>
<tr>
<td>TiCN-based cermet</td>
<td>600</td>
<td>1360</td>
<td>1.6</td>
<td>42.3</td>
</tr>
</tbody>
</table>

Table 1: Comparison of high-temperature properties between a TiC-based cermet and a TiCN-based cermet [2].
cermets. Up to 1990s, TiCN-based cermet cutting tools occupied nearly 30% of the Japanese cutting-tool market [26]. Since the 1990s, the researches and applications of TiCN-based cermets in Asia and Europe increased sharply and dozens of patents in America and Europe were published [27–29]. To date, the preparation of TiCN-based cermets has made great strides along with the wide applications. The marked developments of TiCN-based cermets during the last two decades are listed in Table 2.

Today, TiCN-based cermets are mainly used as cutting tools. These tools are applied for high-speed finishing and semi-finishing of carbon steels and stainless steels [36]. They can also be utilized in machining and finish milling of alloy steels and cast irons as well as the normal carbon steels [4,37]. Owing to the excellent high-temperature properties and low density, TiCN-based cermets have been also applied as refractory parts of jet engines, turbine engines, civil gasoline engines and diesel engines [38,39]. Furthermore, in the field of oil and mining industries, TiCN-based cermets are used as not only drills and excavating tools, but also oil pipeline nozzles and throttles for their better practicability [40]. Additionally, on account of their excellent wear resistance, this kind of materials has been successfully used as gauges, hot working models like wire drawing dies, hot rolls and bearings, and even Si3N4 ceramics could not throw them into the shade when as bearing materials [38,40,41]. More encouragingly, surgical tools have even been made of TiCN-based cermets [42]. Other than the above-mentioned facts, TiCN could even be used as coating materials [43], functionally gradient materials [44], composites [45], and so forth.

3. Microstructure and mechanical properties of TiCN-based cermets

3.1. Microstructure and mechanical properties of the compound TiCN

So far, it was commonly accepted that, the compound TiCN (titanium carbonitride) is a kind of non-oxide material, and a sort of solid solution of TiC and TiN. Besides, TiCN has a FCC (face centered cubic) NaCl type structure, belonging to the Fm-3m space group, similar to TiC and TiN structures [46]. More details regarding the description of the microstructure of TiCN are beyond the present review and available elsewhere [47].

In some ways, it could be summarized that, TiCN could be formed by solid solution of TiC and TiN, with a structure that the C atoms in the Ti lattice could be occupied by N atoms in any proportion [2], due to the smaller unit cell parameters of TiN [35]. In other words, Model I as shown in Fig. 1 is nearly impossible to be present in the ceramic phase in TiCN structure. Thus, Model II and Model IV in Fig. 1 are the two principle structure models of TiCN. Moreover, when there are some vacancies of C and N atoms, the structure type of TiCN is of FCC structure, while with no vacancies the structure type is tetragonal [46].

However, according to Levi et al. [46], the existing structural model with a random occupation of all sites by Ti, C, and N was found to be incorrect. The correct description on its structure can be based on TiN structure with occupation of N sites by C, resulting in a FCC or tetragonal structure, which depends on how the substitution takes places. And, quite a few vacancies exist in the nonmetallic sub-lattice. While speaking of chemical ordering of C and N, there was no significant difference between the ordered and disordered states from the nonmetallic lattice. All these factors will have an important influence on the properties of TiCN.

As mentioned above, TiCN can be considered as a continuous solution of TiC and TiN. Thus the properties of TiCN vary with x, which means that they are dependent on the properties of both TiC and TiN. Commonly, with decreasing x, the unit cell parameter of TiCN decreased linearly, and the micro-hardness would drop down; yet the toughness would be enhanced on the contrary [48]. Table 3 lists the specific properties of TiC and TiN, from which one can judge approximately the properties of TiCN.

In conclusion, TiCN possesses both the properties of TiC [9,13]: high hardness, high melt point, good corrosion resistance, excellent wear resistance, good chemical stability, high thermal and electric conductivity, and so on. However, pure TiCN is much brittle due to its very low toughness and strength. So TiCN is often used as a hard phase in cermets or as composites for the wide demanding applications.

3.2. Core-rim structure of TiCN-based cermets

Commonly, cermets are composed mainly of three phases: hard phase, metal binder phase and surrounding phases. As is described in several literatures [50–52], in TiCN-based cermets, there is commonly a core-rim structure. And sometimes, the rim consists of two parts, which was called the outer rim and the inner rim, respectively.

Normally, the composition of the core in TiCN-based cermets, namely the hard phase, is believed to be TiCN or TiC, which was
deemed to be the residues of un-dissolved raw materials. And the rim, i.e. the surrounding phase, is a sort of complicated (Ti,W,..)(C,N) solution, which has a similar crystalline structure with the core but with much more heavy metal atoms than those in the core [50,51]. For this, it has been observed in SEM-BSE (back-scattering electron in scanning electron microscopy) images that, the rim is grey while, sometimes, the core is black. As it was known, the white brightness in SEM-BSE means a much higher content of heavy elements [52].

A typical microstructural schematic of a commercial cermet, imaged via SEM, is shown in Fig. 2.

In general, the rim of TiCN-based cermets is grown on the basis of the core by the way of oriented attachment mechanism, which means that the structure of the core-rim interface would not change but the constituents varied due to the dissolved elements during sintering [53]. And as mentioned about the two rims, it was generally considered that, the inner rim was a solution originated from the diffusion of W, Mo and other atoms during the solid sintering, and the core was all surrounded by the inner rim. However, the outer rim was a similar solution as the inner rim but just with less W, Mo and other heavy elements originated from the dissolution-precipitation through the liquid sintering. In a word, the components of both the inner and outer rims of TiCN-based cermets are the same, only a matter of that, their contents are different [50–52,54].

A number of studies [33] suggest that the typical core-rim structure of TiCN-based cermets was formed by means of Ostwald dissolve-precipitation mechanism. According to thermodynamic principles, the solubility of the smaller hard phase grains in the liquid was much higher than that of the bigger ones [54]. Consequently, when the smaller atoms have reached the saturation point, the bigger ones still have a long way to go yet. It has been suggested that [55], smaller TiCN grains dissolved in the liquid continually and the dissolved ones kept precipitating on the undissolved bigger ones. At the same time, other additives like metal carbides also precipitated in the form of complicated solution of (Ti,W,M)(C,N) (M represents for the metal element added in the cermets) surrounding the undissolved particles. Besides, with the temperature elevating, the N atoms derived from the decomposition of TiCN would replace partial C atoms, turning the external solution of (W,Mo,M)(C,N) into (W,Mo,M)(C,N), thus forming the outer rim.

3.3. Relationship between the core-rim structure, constituent and mechanical properties of TiCN-based cermets

There have been a variety of papers [56,57] concerning the influence of core-rim structure to the properties of TiCN-based cermets. Most of them believe that, the present of surrounding phase could improve the wettability of the hard phases with the binders and bond the two phases well, thus enhancing the toughness of the cermets [56]. Moreover, the surrounding phase would inhibit the approaching of TiCN particles with each other, hindering the growth and conglomeration of TiCN grains. For this reason, the hard phase grains would be fine and disperse evenly. As referred to Ref [57]: a much complete surrounding phase would strengthen the bonding between the hard phase and binder phase, thus suppressing the crack propagation in the cermets. As a result, the bending strength of the cermets would be improved. However, the rim phase was actually a kind of quite brittle phases, and when the thickness of the rim was larger than 0.5 μm, the strength would turn to decrease sharply.

Because the core-rim structures of TiCN-based cermets depend on their different constituents, which include in C, N, binder metals (Ni, Co, Mo, etc.), secondary carbides, and/or sometimes other additives, the following text will focus on the relationship between the core-rim structure, constituent and mechanical properties of TiCN-based cermets.

3.3.1. Influence of C or N on TiCN-based cermets

In the light of previous studies [28,30–32], it can be concluded that: after the addition of small amount of C (no more than 0.5 wt.%) into the raw materials for preparing TiCN-based cermets, the η phase (Ni3Ti) and TiO phase, remained by incomplete deoxidization, would be formed, thus deteriorating the bending strength and toughness of the cermets. Moreover, in this case, the binder phase could not thoroughly wet the hard phase, which would induce the grain growth of TiCN, thus reducing the cermet toughness. After the addition of medium amount of C (in a range of 1–1.5 wt.%), the solid solubility of heavy metal elements in the binder phase increased and the wettability of the hard phases in the cermets was improved along with the thickness of the rim decreased. As a result, the bending strength increased while the hardness presented a decrease. When the addition of C in the cermets is beyond its saturation (about 2.5 wt.%), the dissociative carbon phase appeared along with more pores and looser microstructure in the cermet matrix, which would result in decreasing bending strength and hardness. The appropriate amount of C addition may be 1 wt.% [58].

In a similar note, N also plays an important role in both ambient-temperature and high-temperature mechanical properties of TiCN-based cermets. Since that, bringing N into the cermets would be always crucial. However, the added N should be in the form of TiN, TiN or some other solutions [59,60].

Bunches of researches tended to add TiN into the cermets, given that TiN has a similar FCC structure with TiC, and TiN can resolve in TiC infinitely [61]. In addition, with the addition of TiN, the core size became finer and the thickness of the rim turned out to be thinner. Accordingly, both the strength and hardness of the cermets increased. However, when the addition amount of TiN exceeded a certain amount, maybe 12 wt.% [62] or 15 wt.% [63], the wettability of the
hard phase in the cermets was deteriorated, the rim structure became imperfect and the core size grew up, which would lead to deteriorated mechanical properties. Furthermore, it has been observed that the TiCN-based cermets modified by TiN would possess a higher thermal shock resistance than the ones without TiN [64].

3.3.2. Influence of binder metals on TiCN-based cermets

In most TiCN-based cermets, the binder phase is mainly composed of Ni or Co, and the solid solution hardening of binder phase plays a vital role in the application of cermets. In TiCN–Ni–Mo cermets [65,66], an increased addition of Ni would result in increased bending strength and decreased hardness. Nevertheless, the addition of Co into TiCN-based cermets would result in a higher toughness and resistance to oxidation, owing to the higher toughness of Co than that of Ni and the improved wettability to hard phase in the cermets. However, the resistance to corrosion of TiCN-based cermets with Co is inferior to that of cermets with Ni.

The atom radius of Mo is much larger than that of Ni; hence, after the addition of Mo as binder into TiCN-based cermets, the solid solubility of Ti in Ni will be reduced, resulting in a much stable carbonitride [67] and a rim of (Ti,Mo)C or (Ti,Mo)(C,N)-rich Mo, which can hold up the growth of TiCN grains and suppress the re-crystallization [68]. In consequence, the relative density, the resistance to plastic deformation as well as the strength of the cermets would increase [54,69]. However, the optimal Mo content is still an open question, because too much addition of Mo will lead to a sharp decrease in the fracture toughness and bending strength of cermets [70].

Except for the above-mentioned three binder metals, some efforts have been made on the addition of rare earth metals into TiCN-based cermets in recent few years. The literatures reported that, the addition of rare earth metals, that is, secondary additives like WC, NbC, TaC, Mo2C and used NbC in TiCN-based cermets also improve the wettability of the hard phase in the cermets. Moreover, the introduction of Mo into TiCN-based cermets can also improve the wettability of the hard phases, and it could dissolve in the binder phase, precipitating on the larger TiCN cores. So both the hardness and strength of the cermets increase. However, excessive addition of Mo (may be 15 wt.%) will result in an increased rim thickness. As a result, both the hardness and strength of the cermets decrease.

Due to the continuous solid solution of NbC and TaC in the hard phase, their volume fractions in the inner rim would become larger, thus the plastic deformation and hot-hardness of the cermets would increase. However, too much addition of NbC and TaC (normally more than 10 wt.%) into TiCN-based cermets will lead to more pores in the cermets, which is harmful to improve the bending strength and hardness of the cermets [74,78,79,50]. Especially, adding medium amount of NbC (about 5 wt.%) could lower the sintering temperature [80].

While the solubility of Cr3C2 and VC in the hard phase is limited, few Cr3C2 or VC can dissolve in the hard phase, and partial of them can dissolve in the binder phase, leading to an improved plasticity of the rim and enhanced bending strength, and the others in the cermets would disperse at the interface, which would inhibit the core growth, thus resulting in a higher hardness [81–83]. However, too little addition of Cr3C2 (lower than the solubility of Cr3C2 in TiCN) will slightly affect the grain size; specifically speaking, it could increase the core size and decrease the rim thickness [81], thus the bending strength of the cermets decreases. Here listed some examples in Table 5.

4. Wear mechanism of TiCN-based cermets

Nowadays, with the property improvement of TiCN-based cermets, they can be applied under various conditions. And the service lifetime during machining, commonly, depends on the wear resistance of the cermets applied. So, it is imperative to discuss the wear mechanism and behaviors of TiCN-based cermets in this section. Generally, during machining with TiCN-based cermets, there are fretting wear, sliding wear, erosive wear, crater wear, creep and so forth. A comprehensive study of these diverse wear behaviors may contribute to a deeper understanding of the performance attainable by a cermet material and how to design its composition and even microstructure so as to enhance some required properties.

In order to improve the high-temperature machining performance of TiCN-based cermets, most of the ongoing efforts are to select the cermet composition, that is, secondary additives like WC, NbC, TaC, HfC and Al2O3 have to be added into TiCN-based cermets to enhance their high-temperature strength and hardness. While the microstructure characterization of this important class of materials has been reported to a great extent, the tribological study has not been dealt

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Mechanical properties of TiCN-based cermets with different secondary carbides of optimal amount addition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary carbides</td>
<td>Optimal amount</td>
</tr>
<tr>
<td>WC</td>
<td>15 wt.%</td>
</tr>
<tr>
<td>20 wt.%</td>
<td>91.6 HRA</td>
</tr>
<tr>
<td>10 wt.%</td>
<td>91.2 HRA</td>
</tr>
<tr>
<td>15 wt.%</td>
<td>16.3 GPa (HV)</td>
</tr>
<tr>
<td>Mo2C</td>
<td>5 wt.%</td>
</tr>
<tr>
<td>10 wt.%</td>
<td>93.5 HRA</td>
</tr>
<tr>
<td>NbC</td>
<td>3 mol%</td>
</tr>
<tr>
<td>TaC</td>
<td>7 wt.%</td>
</tr>
<tr>
<td>Cr3C2</td>
<td>7 wt.%</td>
</tr>
<tr>
<td>VC</td>
<td>1 wt.%</td>
</tr>
</tbody>
</table>

3.3.3. Influence of secondary carbides on TiCN-based cermets

Commonly, a better wetting between the binder phase and hard phase is quite necessary to a better binding of chemical bonds. Typically in TiCN-based cermets, in order to improve the wetting, several carbides have to be added into TiCN-based cermets. The most commonly used secondary carbides included WC, VC, NbC, Cr3C2, TaC, Mo2C and the similar. It is worth mentioning that, good wetting between the hard phase and binder phase is dependent on low stability of the secondary carbides, which can be judged from the formation enthalpy of the carbides.

As seen from Table 4, the addition of Mo2C and WC could greatly improve the wetting between the binder phase and hard phase. Additionally, NbC and TaC have the same cubic structure as TiCN, so they will readily form a uniform solid solution with TiCN. VC and Cr3C2 have much higher solubility in the binder phase, thus they could inhibit the growth of the hard phase [core] [73].

With addition of medium amount of WC (10–20 wt.%), the wettability between the hard phase and binder phase can be improved, the carbonitride grains would become finer and the core-rim structure would be readily formed as well. In consequence, the fracture toughness, bending strength and hardness of the cermets increased. Whereas, when the addition amount of WC is too much, the hardness of the cermets will decrease, while their bending strength would increase slightly [74–77]. Similarly, the introduction of Mo2C into TiCN-based cermets can also improve the wettability of the hard phases, and it could dissolve in the binder phase, precipitating on the larger TiCN cores. So both the hardness and strength of the cermets increase. However, excessive addition of Mo (may be 15 wt.%) will result in an increased rim thickness. As a result, both the hardness and strength of the cermets decrease.

Table 4

<table>
<thead>
<tr>
<th>Carbides</th>
<th>TaC</th>
<th>NbC</th>
<th>VC</th>
<th>Cr3C2</th>
<th>WC</th>
<th>Mo2C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation enthalpy (KJ/mol)</td>
<td>–</td>
<td>–183.7</td>
<td>–142.3</td>
<td>–126.4</td>
<td>89.7</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Table 5

The formation enthalpy of typical carbides at 298 K [2].
with considerably. In the present review, the main attempt is tried to discuss the relationship between the secondary carbides and wear mechanism of this kind of cerments. And the influence of hard phase like TiCN on the wear behavior of the cerments is also discussed. However, it is known that the wear performance of the cerments is of close connection with experimental conditions, such as impact angels, the value of applying load, the load cycle and so on. But, due to the length limit, all these factors will not be discussed in the present review.

4.1. Relationship between fretting wear and secondary carbides

Fretting is a type of wear phenomena that is characterized by the removal of materials from two contacting surfaces due to friction resulting from minute oscillations [84]. During fretting wear, it is assumed that, at first the domain wear mechanism is abrasive; and then, due to the friction heat, it was confirmed that tribolayers were formed, which contained oxides rich in Ti and Fe; with minimum transition metals, however, as the working temperature was elevated, there also existed mutual transfer between the ratings and the cerments, accompanied with brittle fracture of the tribolayers [85–88]. In some cases, the nature of the oxide which was formed from cerments containing various carbides plays great influence on the stability of the tribocochemical layer [86].

As in the researches on the fretting wear behavior of TiCN-based cerments, it could be observed that, each of the carbides plays a quite different role in the wear resistance of the cerments as shown in Tables 6 and 7. From the two tables, it could be presumed that: compared with the TiCN–20Ni cerments without any carbide, the addition of WC or NbC will lead to a decrease in the wear resistance of TiCN-based cerments, while TaC has a limited influence on the resistance to plastic deformation [85]. However, there still exists a controversy over the effect of the addition of HfC. Some believe that the addition of HfC will deteriorate the toughness of TiCN-based cerments, and the wear resistance will be reduced in turn [86]. Others suggest that the formation of harder HfO2 could enhance the wear resistance of HfC-containing TiCN–Ni cerments via forming a thick tribolayer on the counter surface [85]. Besides, the abrasion resistance of the cerments decreases with the addition of carbides, which can be seen from the COF (coefficient of friction) [85,87].

More specifically, as observed from Fig. 3, the addition of WC deteriorates the wear resistance and abrasion resistance of TiCN-based cerments as well, which may be due to the volatilization of tungsten oxides and their following diffusion through the tribolayer in the cerments, resulting in a severe increase in abrasion [85,87]. Additionally, the wear mechanism of the TiCN-Ni cerments was mainly micro-cracking induced spalling and abrasive wear. And as the addition amount of WC increased, it turned to be adhesive and tribocochemical wears [87].

In a similar note, Manoj Kumar et al. [88] found that, TiCN–20Ni cerments with addition of 5 wt.% NbC obtained a lowest steady-state COF in the same series of cerments, as listed in Table 8, and showed a better wear resistance than the other investigated TiCN-based cerments, as shown in Fig. 4. Furthermore, after the addition of NbC, the predominant fretting wear mechanisms transferred from abrasion and spalling into abrasion and tribo-oxidation. And a large amount of NbC addition (25 wt.%) may cause further tribo-oxidation and ejection of debris during fretting. As a result, the wear of the investigated cerments will become much severer [88].

4.2. Relationship between crater/sliding wear and secondary additives

With regard to TiCN-based cerment cutting tools, in order to exploit their tribological potential and extend long service time, it is important to evaluate and understand the crater wear or sliding wear properties of TiCN-based cerments [89].

With a view on the common facts about the addition of WC, as reported in Ref [90] about evaluating the dominant crater wear mechanisms of TiCN-based cerments, responsible for the material removal on the rake face of the cerments, it could be observed that, as shown in Fig. 5, the increase in WC addition into TiCN–20Ni cerments (<10 wt.%) was of benefit to improve the wear resistance of the cerments. What is more, when the addition amount of WC was less than 10 wt.%, tribocochemical wear determined the tool life of TiCN–Ni cerments, while it was above 10 wt.%, mechanical abrasion and pull-outs dominated the machined surface of the cerments.

In the investigation on the tribological behavior of TiCN–Ni–Mo cerments at elevated temperatures [91], it could be concluded that the addition of Al2O3 would lessen the wear loss of TiCN–Ni–Mo cerments at lower temperature (<600 °C). The dominant mechanism of sliding wear was tribo-oxidation together with the formation and destruction of tribo-layer for all the TiCN-based cerments with or without Al2O3, while the worn surfaces of TiCN–Al2O3–Ni–Mo were relatively smoother than those of TiCN–Ni–Mo cerments, which might be attributed to the hardening arising from the addition of Al2O3.

In the investigation on load-dependent sliding wear and friction properties of TiCN–20Ni–xWC (where x = 5–25 wt.%) cerments [89], it could be concluded that: the stability of the tribolayer appears to be the predominant factor for the friction behavior; at a given load the volumetric wear loss of TiCN–Ni cerments increased with increasing addition of WC, as shown in Fig. 6, which may be attributed to the grain detachment; the dominant wear mechanisms at lower loads (<5 N) were identified to be abrasion and mild tribo-oxidation, and dense

| Table 6 |

Summary of friction and wear data, measured when the as-investigated TiCN-based cerments were fretted against commercial SAE 52100 bearing steel at 550 °C with a load of 20 N at 6 Hz oscillating frequency and 0.1 mm linear stroke for 4 h 37 min [85].

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Steady-state COF</th>
<th>Wear rate of cerments (×10^-6 mm³/Nm)</th>
<th>Wear rate of steel ball (×10^-3 mm³/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN–20Ni</td>
<td>0.46</td>
<td>3.0</td>
<td>7.1</td>
</tr>
<tr>
<td>TiCN–20Ni–10WC</td>
<td>0.46</td>
<td>5.0</td>
<td>14.1</td>
</tr>
<tr>
<td>TiCN–20Ni–10NbC</td>
<td>0.46</td>
<td>5.2</td>
<td>16.9</td>
</tr>
<tr>
<td>TiCN–20Ni–10TaC</td>
<td>0.43</td>
<td>3.5</td>
<td>12.4</td>
</tr>
<tr>
<td>TiCN–20Ni–10HfC</td>
<td>0.43</td>
<td>3.8</td>
<td>6.5</td>
</tr>
</tbody>
</table>

| Table 7 |

Average steady-state COF values and profilometry measurements of the wear scars on the as-investigated TiCN-based cerments under different loads [86].

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Under a load of 2 N</th>
<th></th>
<th></th>
<th>Under a load of 10 N</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>Wear volume (×10^-4 mm³)</td>
<td>Wear rate (×10^-6 mm³/Nm)</td>
<td>CF</td>
<td>Wear volume (×10^-4 mm³)</td>
<td>Wear rate (×10^-6 mm³/Nm)</td>
<td></td>
</tr>
<tr>
<td>TiCN–20Ni</td>
<td>0.33</td>
<td>1.33</td>
<td>3.33</td>
<td>0.36</td>
<td>3.49</td>
<td>1.75</td>
</tr>
<tr>
<td>TiCN–20Ni–10WC</td>
<td>0.44</td>
<td>1.34</td>
<td>3.31</td>
<td>0.39</td>
<td>3.26</td>
<td>1.63</td>
</tr>
<tr>
<td>TiCN–20Ni–10NbC</td>
<td>0.39</td>
<td>1.35</td>
<td>3.38</td>
<td>0.36</td>
<td>3.52</td>
<td>1.56</td>
</tr>
<tr>
<td>TiCN–20Ni–10TaC</td>
<td>0.42</td>
<td>1.23</td>
<td>3.07</td>
<td>0.38</td>
<td>3.32</td>
<td>1.66</td>
</tr>
<tr>
<td>TiCN–20Ni–10HfC</td>
<td>0.47</td>
<td>1.42</td>
<td>3.55</td>
<td>0.42</td>
<td>3.99</td>
<td>1.99</td>
</tr>
</tbody>
</table>
tribo-oxide layer formation at higher loads ($\geq 20$ N); and a simple wear map of TiCN–Ni–WC cermets sliding against steel at different loads was proposed as in Fig. 7.

4.3. Relationship between erosion wear and secondary additives

Erosion of brittle materials have been described by a combination of plastic deformation in the impact zone with the formation and quasi static growth of lateral cracks which may cause a subsequent removal of chips of target materials by eroding particles [91–93].

Apart from the influence of mechanical impact, such as orthogonal or oblique impacts [94], the composition of TiCN-based cermets and their mechanical properties definitely play important roles in the resistance to erosive wear for cutting tools applied in interrupted cutting processes.

According to the formula, $E = C K_1^{m} H_v^n$, where $E$ is the erosion rate (E) of the brittle target materials, $C$ is a proportionality constant; $K_1$ and $H_v$ are the fracture toughness and Vickers hardness of the target materials; and $m$ and $n$ are constants, which are 1.3 and 0.25, respectively [95]. From the formula, it can be seen that the wear resistance of cermets mainly depends on their mechanical properties such as hardness and toughness [96]. However, in another interesting work, the hardness was not observed as a major factor influencing the erosion wear resistance of cermets; instead, the fracture resistance and modulus of elasticity of the cermets were observed as important material properties affecting the erosive wear resistance of the cermets [97,98].

From the point of view on compositions, it is interesting to note by Refs [99,100] that the content of TiCN is responsible for the insert resistance to flank wear, and the addition of NbC as well as TaC is of slight influence on anti-erosion wear properties of the cermets [95,99,100], while the addition of WC results in an increase in erosion wear resistance of TiCN–20Ni cermets [100]. Additionally, the dominant wear mechanism is the binder phase extrusion and smearing as well as the de-cohesion or pullout of brittle carbonitride grains in the cermets [100].

4.4. Relationship between creep and compositions of TiCN-based cermets

Given the high speed performance of cermets, it is imperative to grasp a better understanding of the deformation mechanisms operating at elevated temperature. Among the previous studies, it has been stated that, during high speed cutting with increasing temperature, there are three dominant mechanisms concerning the deformation: brittle, tough with limited plasticity and creep behaviors [101]. However, it seems that the deformation is controlled by the carbonitride phase deformation [102,103]. Whereas, there is quite a need in the data about the creep behavior of TiCN-based cermets.

In a recent research about TiC–xN–CoTi cermets with two additives, W and WC, Morales-Rodríguez et al. indicated that no remarkable differences in their mechanical properties at high temperatures were recorded; TiCN phase also controlled the plastic deformation, which evolved from diffusion creep to grain-boundary sliding as the strain rate increased; both the two deformation mechanisms...
were rate-controlled by the carbon self-diffusion in the TiCN phase [104].

5. Advance of ultrafine/nano TiCN-based cermets

According to Hall-Patch formula, materials with ultrafine or nano structure possess better mechanical properties. It was well-known that grain refining would enhance the hardness, bending strength and toughness of engineering ceramics. Consequently, increasing efforts have been made to produce nano-modified TiCN-based cermets or ultrafine TiCN-based cermets with improved mechanical properties catering to their demands for much harsher applications.

5.1. Synthesis of ultrafine/nano TiCN powers

As the very beginning of preparing ultrafine/nano TiCN-based cermets, the synthesis of nano or ultrafine raw powders is of great significance. To sum up, there are five main ways to achieve such TiCN powders: (1) synthesis by high-temperature solid-state diffusion from TiN–TiC, TiN–C, TiC–Ti powder blends, which is the most conventional way and the details could be referred to elsewhere [3,105]; (2) carbothermic reduction synthesis; (3) self-propagating high-temperature synthesis (SHS) and mechanically-induced self-sustaining reaction (MSR); (4) mechanical alloying; (5) chemosynthesis. Now considerable researches commit to synthesize ultrafine/nano TiCN powders using the ways except the first one. So the following text will roughly elaborate each way except the first one.

5.1.1. Carbothermic reduction synthesis

In this way, the methods usually use TiO2 and C powders as raw materials to synthesize TiCN powder in N2 at high temperature. The carbothermic reduction synthesis has been largely recognized as a low-cost way for the synthesis of non-oxide ceramic powders, for example, carbides, nitrides and carbonitrides, with a fairly simple processing set-up, wide range of C/N ratios and potentially mass-scale production [106,107]. Ultrafine TiCN powers with a particle size of no more than 100 nm can be produced by this way [108,109]. However, there are still limitations in this way, including the presence of residual oxides and the use of excess carbon, and high combustion temperature. Hence, much attention has been paid on overcoming the shortcomings of such methods, in which sol–gel process [110] may be a promising one. As in a recent study [110], ultrafine TiC$_1$–$_x$N$_x$ powders with $x=0.2$–0.8 of particle sizes less than 100 nm as well as of high purity could be successfully synthesized by sol–gel process.

5.1.2. SHS and MSR

SHS or combustion synthesis with the advantages of saving time and energy has been recognized as a promising alternative to the conventional methods to produce carbonitride [22]. In addition, it is widely
acknowledged that the products prepared by this process are of high purity and low cost [11,111]. Based on new milling process and SHS, MSR has been realized. It has been demonstrated to be an appropriate method for preparing the pre-reacted hard components as raw materials for the fabrication of TiCN-based cermets [12]. Recently, MSR has allowed the synthesis of TiCN powder in a short time with nanometric characteristics and good stoichiometric control by adequately adjusting the milling parameters and the metal-to-carbon atomic ratio in the starting mixture [18].

5.1.3. Mechanical alloying

Commonly, mechanical alloying is a dry and high energy ball milling process for producing composite metallic powders with a well controlled microstructure [19]. However, there are still some limitations during powder synthesis due to its small-scale production and serious contamination from milling balls and jars [112]. Recently, it has been assumed to be a simple and cost-effective process when combined mechanical alloying with carbothermal reduction. For instance, by the method of mechanical alloying with carbothermal reduction, TiCN powders with average size of below 100 nm were successfully achieved in a shorter reaction time (about 10 h) under a lower reaction temperature (about 600 °C) [113]. Besides, nanocrystalline (Ti,M)(C,N)–Ni and (Ti,M₁,M₂)–(C,N)–Ni powders in a size of about 30 nm were successfully synthesized by this method with lower oxygen content (<0.5 wt.%)[108].

5.1.4. Chemosynthesis

This process is easily controlled and the reaction temperature is pretty lower than those in other synthesis methods for TiCN. It has been reported [113–115] that, TiCN powders can be synthesized by polymer-to-ceramic transformation of metal-organic precursors, which can be seen in Table 9. However, the problem of this method is that the manufacturing procedure is complicated and of quite a high cost. Hence, concerns are always about its innovations. On one hand, a plenty of novel precursors have been prepared to the synthesis of TiCN powders, including a novel refluxing-derived precursor [116]; on the other hand, combination with other synthesis methodology may show the outstanding, such as by using a combination of carbothermic reduction and chemosynthesis [117]. However, the manufacturing process parameters need to be set up more precisely, which may not be accomplished easily. So it is imperative to do much effort on their innovations and reformations.

5.2. Sintering process of ultrafine/nano TiCN-based cermets

As is well known, sintering is a key process for the preparation of TiCN-based cermets. And in preparing ultrafine or nano TiCN-based cermets, the commonly applied sintering processes include vacuum sintering (NS), hot isostatic pressing sintering (HIP), SPS, microwave vacuum sintering (MVS), and so on. Table 10 lists the properties of ultrafine and/or nano TiCN-based cermets via different sintering processes.

Vacuum sintering is a very traditional way to sinter TiCN-based cermets. It is easy to control the procedure; however, it also easily leads to the occurrence of de-nitration and pores. HIP is founded on the basis of pressure sintering, which could manufacture fine cermets and cemented carbides with improved mechanical properties [119,120]; however, HIP still presents its limitations due to the excessive grain growth during sintering and high cost [122]. SPS has been increasingly used for preparing ultrafine and/or nano TiCN-based cermets in the recent two decades, for its advantages of

Table 9

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Particle size</th>
<th>Synthesis reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>(nm)</td>
<td>Refs</td>
</tr>
<tr>
<td>TiC₀.7N₀.3</td>
<td>600</td>
<td>&lt;30</td>
</tr>
<tr>
<td>TiC₀.2N₀.8</td>
<td>420</td>
<td>13</td>
</tr>
<tr>
<td>TiC₀.4N₀.6</td>
<td>450</td>
<td>66</td>
</tr>
<tr>
<td>(Ti,W,Mo)C(N,C)</td>
<td>–</td>
<td>10-100</td>
</tr>
</tbody>
</table>

Fig. 6. (a) volumetric wear and (b) wear rate of the as-investigated cermets with varying WC contents sliding against commercial AISI 52100 grade steel under different loads [89].

Fig. 7. Wear map of TiCN–Ni–WC cermets with varying WC contents sliding against commercial AISI 52100 steel under different loads [89].
low sintering temperature and short sintering time owing to synergetic combination of electrical energy and mechanical pressure, fast heating rate, the integrity of starting microstructure remained without grain coarsening, in-situ cleaning of oxide surfaces generating cleaner materials with high consolidated densities, and so forth [10]. It is assumed to be a promising method promoting the cost-effective fabrication of bulk nanocomposites. Despite of the advantages that SPS offers, the porosity of the as-sintered cermets is still comparatively high, and the shape of the sintered cermets is so limited, which is not of benefit to the mass industrial production. Besides, the mechanism of sintering remains to be not so clear and needs to be exploring. However, it has been recently demonstrated that using multi-stage sintering scheme in SPS can minimize the non-uniform temperature distribution for some conducting ceramics as well as non-conducting ceramics [123,124]. Maybe such a novel processing scheme extended towards the sintering of nanostructured TiCN-based cermets would lead to improved properties and microstructure for the cermets.

MVS is a novel sintering method, which could obtain a sintered material with little internal heat-stress in a short time under a low temperature, which is economically and environmentally friendly [125]. Furthermore, microwave vacuum sintering is a very promising way to produce ultrafine and/or nano TiCN-based cermets [13,123,125], but it is still at laboratory exploration stage.

5.3. Nano-additives and mechanical properties of ultrafine/nano TiCN-based cermets

With the advance of technology, there has been increasing interest in nano-modified TiCN cermets. In a nano-strengthening, the nuclei concentration of TiCN increased, its grain size was quite well distributed and the bending strength of the cermets enhanced after the addition of nano-additives [126]. Conventional nano-additives include nanopowders, nano-whisker, carbon nano-tube (CNT), and the similar, as listed in Table 11.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Hardness (max)</th>
<th>Bending strength (max)</th>
<th>Toughness (max)</th>
<th>Optimal amount</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>90.9 HRA</td>
<td>2180 MPa</td>
<td>14.7 MPa·m^{1/2}</td>
<td>0.5 wt.%</td>
<td>[14]</td>
</tr>
<tr>
<td>SiC whisker</td>
<td>~92.0 HRA</td>
<td>1820 MPa</td>
<td>13.5 MPa·m^{1/2}</td>
<td>10 wt.%</td>
<td>[127]</td>
</tr>
<tr>
<td>Nano TiN particle</td>
<td>~92.0 HRA</td>
<td>~1800 MPa</td>
<td>~2.0 wt.%</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Si₃N₄ powder</td>
<td>91.8 HRA</td>
<td>~1600 MPa</td>
<td>~10 wt.%</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Nano TiCN powder</td>
<td>92.3 HRA</td>
<td>~1800 MPa</td>
<td>~10 wt.%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As referred in Ref [14], medium addition (about 0.5 wt.%) of CNTs could bring into the effect of fine-grain strengthening, crack bridging toughening, pull-out toughening and crack deflection toughening mechanism, which may contribute to the higher toughness and hardness as well as the strength of TiCN-based cermets. On a similar note, appropriate addition of SiCw (SiC whisker) could also toughen the TiCN-based cermets via crack deflection, crack bridging and whisker pulling out mechanisms as well [15].

According to partial of the previous researches, the addition of nano-particles or nano-powders will lead to the decrease in the solubility of hard phase in binder phase, and refining of the grains of hard phase, due to the ready solution and diffusion of the nano-additives in the binder phase and the inclination of locating in grain boundary as well [16,17,127]. As a result, the hardness and the toughness of the cermets increase in the meantime. However, there still exist some limitations, due to the ready agglomeration of the nano-additives, which may make it hard to sinter fully dense cermets, resulting in cermets with worse mechanical properties. For this reason, it is necessary to take measures to avoid or reduce the agglomeration of the nano-additives via developing some high-efficiency dispersing methods.

6. Conclusions and outlook

The researches over the last two decades have unambiguously established the superiority of ultrafine/nano TiCN-based cermets over its conventional counterparts, with respect to their toughness and strength. It is believed that the use of ultrafine/nano TiCN-based composites is more likely to result in improved performances in the demanding applications, and by using an advanced methodology through an optimized processing procedure with some appropriate additives, ultrafine/nano TiCN-based cermets could be fabricated with excellent performances.

However, ultrafine/nano TiCN-based cermets have not yet penetrated into commercial market. The primary hindrance is related to the processing challenges, in spite of the advent of synthesis techniques like SHS [22] and MSR [11,12], and commercially available TiCN nano-powders. Furthermore, although SPS and microwave vacuum sintering have been proved to be promising sintering techniques for the preparation of ultrafine/nano TiCN-based cermets, such processes are not yet applied commercially, due to the high expediencies involved and limitations on the shapes/sizes of the components they can prepare.

Another point of concern for ultrafine/nano TiCN-based cermets is that in most cases, a reduction in TiCN grain size to ultrafine/nano regime adversely affects the hardness of cermets [127,17], because of the decrease of bonding force between the hard phases and binder, due to the more oxygen and other contaminates attached at the surfaces of raw powders.

In addition, there are strong demands in detailed investigations on the elevated temperature properties of ultrafine/nano TiCN-based cermets. And even though nanocomposites usually show superior strength with respect to their conventional counterparts at room temperature, it still needs to make sure if such behavior is also true at elevated temperatures.

We believe that the presence of ultrafine/nano TiCN-based cermets is likely to affect the field of cutting tool materials. In fact, nano-TiCN-based cermet cutting tools exhibited better wear and oxidation resistances, and even a longer service life, with respect to its counterpart with coarser grains [127,17], which render such kind of materials much more suitable for various engineering applications. Such preliminary researches have undoubtedly opened up new vistas for further investigation and development of novel TiCN-based materials for improved performance, increased durability and the use in more demanding applications.

Table 10
Properties of ultrafine and/or nano TiCN-based cermets via different sintering processes.

<table>
<thead>
<tr>
<th>Sintering process</th>
<th>Hardness (max)</th>
<th>Fracture toughness (MPa)</th>
<th>Bending strength (MPa)</th>
<th>Grain size (μm)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS 11.2–12.3 GPa (HV)</td>
<td>12.6–13.2</td>
<td>~0.0030–0.1</td>
<td>[5]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NS 14.7 GPa (HV)</td>
<td>10.1</td>
<td>2210</td>
<td>0.5–1</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>NS 14–15 GPa (HV)</td>
<td>8–10</td>
<td>~&lt;0.3</td>
<td>[118]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP 93.0 HRA</td>
<td>1740</td>
<td>~7</td>
<td>[7]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP 91.5 HRA</td>
<td>1740</td>
<td>0.2</td>
<td>[23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP 92.6 HRA</td>
<td>295</td>
<td>&lt;0.3</td>
<td>[10]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP 92.8 HRA</td>
<td>295</td>
<td>&lt;0.3</td>
<td>[20]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPS 89.9 HRA</td>
<td>840–920</td>
<td>0.5–1</td>
<td>[21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPS 91.0 HRA</td>
<td>295</td>
<td>&lt;0.4</td>
<td>[19]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPS 91.2 HRA</td>
<td>295</td>
<td>0.2</td>
<td>[23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVS 90.6 HRA</td>
<td>1547</td>
<td>~0.2</td>
<td>[10]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVS 91.6 HRA</td>
<td>1547</td>
<td>&lt;1</td>
<td>[13]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 11
Mechanical properties of TiCN-based cermets with various nano-additives.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Hardness (max)</th>
<th>Bending strength (max)</th>
<th>Toughness (max)</th>
<th>Optimal amount</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>90.9 HRA</td>
<td>2180 MPa</td>
<td>14.7 MPa·m^{1/2}</td>
<td>0.5 wt.%</td>
<td>[14]</td>
</tr>
<tr>
<td>SiC whisker</td>
<td>~92.0 HRA</td>
<td>1820 MPa</td>
<td>13.5 MPa·m^{1/2}</td>
<td>10 wt.%</td>
<td>[127]</td>
</tr>
<tr>
<td>Nano TiN particle</td>
<td>~92.0 HRA</td>
<td>~1800 MPa</td>
<td>~2.0 wt.%</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Si₃N₄ particle</td>
<td>91.8 HRA</td>
<td>~1600 MPa</td>
<td>~10 wt.%</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Nano TiCN powder</td>
<td>92.3 HRA</td>
<td>~1800 MPa</td>
<td>~10 wt.%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Acknowledgments

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References
