Microstructure evolution and sintering kinetics of Ti(C,N)-based cermet

S Q Xiao¹, M F Gong¹,²

¹School of Electromechanical Engineering, Lingnan Normal University, Zhanjiang Guangdong, China

Email: 576765637@qq.com

Abstract. In this paper, the grain growth behavior of Ti(C,N)-based cermet, including the microstructure evolution and sintering kinetics in the sintering process at different temperatures for different holding time, was studied experimentally and theoretically. A comprehensive grain growth model for Ti(C,N)-based cermet was established based on the experimental data. Furthermore, different influencing factors of microstructure evolution during sintering for Ti(C,N)-based cermet were investigated systematically by a scanning electron microscope. The results showed that the sintering temperature and holding time have a significant effect on the microstructure evolution of Ti(C,N)-based cermet. The grain growth rate was the fastest at the temperature range of 1300°C to 1400°C. The grain growth rate was reduced slightly at higher temperatures. A comprehensive sintering kinetics model of Ti(C,N)-based cermet during the sintering process was obtained based on the experimental results via nonlinear regression method.

Keywords: Sintering Kinetic; Ti(C,N)-based cermet; Microstructure evolution; grain growth

1. Introduction

Nowadays, Ti(C,N)-based cermet are considered to be the primary material in the field of high speed cutting, owing to its excellent hardness, strength, chemical stability, thermal deformation resistance, and oxidation resistance [1]. Compared with other hard metals, Ti(C,N)-based cermet can be employed in a cutting operation at a higher cutting speed. Hence, the application blank of cemented carbide and ceramic is filled.

Other paragraphs are indented (BodytextIndented style). It is known that the Ti(C,N)-based cermet consist of hard particles, i.e. carbonitride and various carbide additives, and binder phases including Ni, Co, and Ni-Co solid solution. The hard and binder phases affect the mechanical properties of Ti(C,N)-based cermet. The effects of various carbide additives (such as WC, Mo, TaC, NbC, and VC) on the microstructure and mechanical properties of cermet have been studied by various researchers [2–11], such as the ease of microstructure to become finer and the improvement of wettability between ceramic and metallic phases with the increase in molybdenum content. At the same time, many preparation routes and sintering processes in the fabrication of Ti(C,N)-based cermet have been researched. The conventional sintering methods used to prepare Ti(C,N)-based cermet are vacuum sintering (VS) [12–18], hot pressing (HP) [19, 20], and hot isostatic pressing (HIP) [21–24]. The emerging technologies used in the fabrication of cermet are spark-plasma-sintering (SPS) [25–27], self-propagation high temperature synthesis (SHS) [28,], and microwave vacuum sintering (MVS) [29, 30]. Among all the sintering methods, pressure, temperature, and holding time are the three vital parameters that contribute...
immensely to the transformation of green powders to sintered products. In most instances, temperature contributes immensely to the microstructure evolution and densification process, as well as final hardness and relative density properties of the sintered composites. As temperature increases, a substantial atomic diffusion of powder particles occurs inside the grains and across the grain boundaries. The influence of these parameters on the microstructure and mechanical properties of Ti(C,N)-based cermet can be obtained by establishing the sintering kinetic equation. Therefore, this is considered a worthy exploration by a lot of researchers.

In the 1990s, Sellars et al. [31] proposed a model of normal grain growth and used it to study the microstructure of C-Mn steel as in Eq. (1). Subsequently, Anelli et al. [32] also proposed a model of grain growth under isothermal sintering process with experimental data as in Eq. (2). Later on, a mount application for austenite grain growth of carbon steel was studied. All researched results proved that the two models can accurately describe the microstructure evolution of materials including grain growth.

\[ d^n = d_0^n + A t \exp(-Q / RT), \]
\[ d^n - d_0^n = B t^n \exp(-Q / RT), \]

where \( d \) is the final grain diameter (μm); \( d_0 \) is the original grain diameter (μm); \( t \) is the holding time (s); \( T \) is the heat treatment temperature (K); \( R \) is the gas constant (\( R = 8.314 \text{ J/mol·K} \)); \( Q \) is the grain growth activation energy (J/mol); \( A \) and \( B \) are experimental constants; and \( n \) is the growth index.

It is well known that the sintering kinetics of ceramic materials has been well established [33]. The grain growth kinetics of Ti(C,N)-based cermet during sintering, however, is yet to be systematically explored.

During the sintering process, temperature and holding time play very important roles in the kinetics of sintering. To understand the mechanism during different sintering stages, both the microstructure evolution and sintering kinetics of Ti(C,N)-based cermet should be understood. Therefore, this current study focuses on the effects of different sintering temperatures and holding time on the microstructure evolution of Ti(C,N)-based cermet in order to establish the grain growth model.

2. Experimental

A series of sintering experiments was performed to determine how the microstructure of Ti(C,N)-based cerments, sintering temperature, and soaking time are closely related. Experiments included the sintering of Ti(C,N)-based cermet compact sets at different temperature-time combinations.

| Starting powders | Ti(C_{0.5}N_{0.5}) | Co | Mo | WC | C |
|------------------|---------------------|----|----|----|---|
| Content (wt.%)   | 60                  | 15 | 12 | 12 | 1 |

Raw powder mixtures, with the addition of 2 wt.% wax, were mixed in a planetary ball-mill for 36 h at a speed of 300 rpm. The slurries obtained were dried at 60°C in an automatic constant temperature drying closet, and then sieved through 180 meshes. The Ti(C,N)-based cermet powder compacts were fabricated in two steps: first, the cylinders of powder compacts (30 mm diameter and 6 mm height) were prepared by uniaxial cold pressing with a typical load of 15 MPa; second, the powder compacts were pressed under a pressure of 200 MPa via cold isostatic pressing for 15 min. The green compacts were then sintered preliminarily for dewaxing at 600°C in a vacuum tube furnace (Beijing Sinat Co., Ltd., China) for an hour. The pre-sintered compacts were sintered in a high vacuum furnace under less than \( 10^3 \text{ Pa} \) vacuum, and the sintering temperatures were 1300°C, 1400°C, 1450°C, and 1500°C with a fixed
heating rate of 10°C/min, and a holding time of 0, 0.25, 0.5, 0.75 and 1 h, respectively. Microstructure analysis for the sintered cermet were performed on polished and fractured surface samples with a scanning electron microscope coupled to an energy dispersive microanalysis system (EDS). The grain size of the specimen for the SEM image was measured using Nano Measurer software. The relative density is measured using the Archimedes method.

3. Result and discussion

3.1. Starting powders morphology

The starting Ti(C,N)-based cermet powder mixtures were examined by scanning electron microscopy (SEM). Figure 1 shows the morphology of the starting Ti(C,N)-based cermet. The regular round shape of the powders in addition to fraction agglomerated large particles are evident, and their size is relatively uniform. The average particle size of the powders is 1.02 μm.

![Figure 1. Scanning electron microscopy micrograph of the starting Ti(C,N)-based cermet powders.](image)

3.2. Microstructure evolution at different temperatures

Generally, Ti(C,N)-based cermet sintering includes solid- and liquid-phase sintering. Zheng et al. [1] divided the process into four stages: solid-state heating, incipient liquid forming, dissolution-reprecipitation, and subsequent cooling. The experimental analyses in this study showed that the liquid phase occurred at a temperature greater than or equal to 1300°C. Hence, the SEM metallographic images at 1300°C–1500°C of Ti(C,N)-based cermet products were displayed for analysis. The fracture morphologies of sintered products were examined using backscattered electron SEM. The polished specimens of sintered Ti(C,N)-based cermet at different temperatures and holding time for a duration of 1 h under a scanning electron microscope in backscatter imaging mode are shown in Figure 2. A typical microstructure of black core-grey rim ceramic grains embedded into white binder was achieved, as shown in Figure 2.

Figure 2 shows the typical core-rim structure including ceramic hard particles and metal binder phase. Generally, the core phase is composed of residual undissolved Ti(C,N) particles. The rim structure is composed of (Ti,Mo,W…) (C,N) during the liquid sintering stage. And the binder phase is mainly a metal (Ni or Co, or Ni+Co, etc.) solid solution. To verify the composition of these phases, EDS spot-scan results of the microstructure in Ti(C,N)-based cermet are shown in Figure 3. Figure 3(b) and (c) showed that the hard-phase composition of Ti(C,N)-based cermet (black core section) appeared as titanium carbon-rich, while the binder phase (grey section) was dominated by tungsten, molybdenum, and carbon.
Figure 2. SEM (BSE) metallographic images of Ti(C,N)-based cermet products sintering at different temperatures and holding time for 1 h. (a) 1300°C; (b) 1400°C; (c) 1450°C; (d) 1500°C.

Figure 3. Representative microstructure: (a) EDS profile for spectrum1; (b) EDS profile for spectrum2.

An evident difference can be found from Figures 2 (a) to (d). The amount of the black core phase and the grain size continuously increased with the increasing sintering temperature. The rim phase formed by (Ti,W,Mo)(C,N) could inhibit the core-phase growth depending on the dissolution and re-precipitation of W, Mo, resulting in well-distributed grains. The decrease in small grains and the continuous growth of large grains in the liquid-phase sintering stage was consistent with Ostwald ripening. There are many gray phases as opposed to fewer black phases, as seen from Figure 2(a). The grain sizes are small and yet to grow since it is still under the transitional period from solid-state to liquid-state sintering at 1300°C. Particles diffused accelerate, and solid solutions occurred at this temperature. A complex solid solution can be formed gradually, since the Ti atom in Ti(C,N) had been replaced by a part of metal elements. The gray phase shown in Figure 2(a) is rich (Ti,W,Mo)C. However, the majority of the coarse Ti(C,N) particles in the raw powders remained undissolved. The black core-grey ring structure then formed gradually. The black core phase increased and grew more gradually than
it did before, as seen from Figure 2 (b) to (d). On the one hand, the particles rearranged, the green body shrinkage intensified due to the action of smaller wetting angle and surface tension at temperature 1400°C. On the other hand, Ti - based carbonitride complex solid solutions with less W or Mo precipitated on the coarse TiCN particles and fine (Ti, Mo, W)C particles, resulting in core-rim structures. The pores were slowly eliminated with two or more small pores connecting to form a large pore. The liquid phase increased and the cermet compacts started to densify and reached the full density at 1450°C (Figure 2(c)). The small particles continued to dissolve in the liquid phase and precipitates from the surface of the large particles at the sites of the solubility saturation. It appears that the black core phase grows significantly, but the distribution is not uniform. Figure 2(d) indicates the grain growth and the distribution is relatively uniform. Furthermore, it shows that the lipostomous formed were removed due to the phase plastic flow strengthening. The wettability of Mo reached the maximum while the contact angle reduced, such that most of the small pores between the crystal grains were filled by the liquid phase. The composition of the core was observed to be undissolved Ti-rich Ti(C,N) nuclei, because of the higher solubility of TiC in the liquid metal compared to the low solubility of TiN.

As discussed above, it can be concluded that the temperature is a key factor in the formation of core-rim structure of cermet from Figure 2. Increasing the heating temperature can significantly enhance the tendency to form a typical core-rim phase proportion of Ti(C,N)-based cermet, which may also increase the amount of the liquid phase and accelerate the formation of the rim phase.

3.3. Microstructure evolution in different holding time at various temperatures

To research the changes in Ti(C,N)-based cermet microstructure during sintering at different holding times (0, 0.25, 0.5, 0.75, and 1 h), the fracture SEM (BSE) metallographic of Ti(C,N)-based cermet was used. The difference in the microstructure evolution between the holding time of 0.5 and 1 h can be made out by observing the fracture SEM/BSE images (Figure 4). The other specimen data is shown in Figures 5 and 6.

The microstructure evolution of the Ti(C,N)-based cermet exhibits two main characteristics as the temperature or holding time increases: the variation of porosity and the change of grain homogeneity. In Figures 4 (a) and (A), a significant amount of pores was found in the samples sintered at heating temperature 1300°C. The volume fraction of pores in Figure 4(A) is more than that in Figure 4(a). Meanwhile, there were small liquid-phase parts that started to appear (found in Figure 4(A) but not in Figure 4(a)). The compositions such as Mo2C, WC, and Ti(C, N) mutually diffused faster and solid-solved to form a fine solid solution (W, Mo, Ti) (C, N) at this stage, resulting in the composite particles presenting a phenomenon of particle agglomeration. It indicates that the holding time had an effect on the appearance of the liquid phase and the volume fraction of pores. The amount of liquid phase increased with the rising temperature (1400°C). Dissolution of the smallest particles and the increase in total number of particles occurred during the liquid-phase sintering stage. In the meantime, many small pores were eliminated slowly or connected to become a larger pore. Compared with Figure 4(B), the pores were larger and the porosity is higher in Figure 4(b). The microstructure densified and did not loosen, from Figure 4(a) and (A). These changes induced a trend towards decreasing porosity, owing to the prolongation of holding time that can reduce the wetting angle between hard phase and binder phase while accelerating closing or removal of pores. This phenomenon continued until 1450°C. From Figure 4(c) and (C), the densification of Ti(C,N)-based cermet increases as the holding time prolonged. We can infer that the densification of Ti(C,N)-based cermet was almost complete at 1450°C, since most of pores disappeared and became denser in this stage. However, the densification in Figure 4(C) is distinctly much higher than that in Figure 4(c) (the relative density was 95.6% and 98.4%, respectively). Two micrographs of the samples in Figure 4(d) and (D) revealed the completely dense cermet irrespective of the holding time (0.5 or 1 h), while their relative density had already reached 99.3% and 99.8%, respectively. In spite of that, some characteristics, including the homogeneity of small pits of the hard phase, the degree of plastic deformation of the bonding phase, and the level of developed tearing edge (as shown in Figure 4(D)), were better than those exhibited in Figure 4(d).
Therefore, the holding time remarkably affects the microstructure features and evolution. In terms of the microstructure, the thickness of rim structure and ceramic grain distribution, whether uniform or not, probably influenced the product densification during sintering. However, the formation of the rim structure and the distribution of grain were closely associated with the holding time during different sintering stages. A reasonable holding time extension (which ensured the increase of binder liquid phase and would benefit the particle coalesce resistance) resulted in inhibiting crystal grain abnormal growth and uniform ceramic grain distribution. Consequently, the holding time was another key factor for the microstructure evolution of Ti(C,N)-based cermet. However, Yan and Zheng et al. [34] had found that the holding time had seriously affected the mechanical properties of the material if it was kept too long. Therefore, the holding time must be controlled in a suitable range. Otherwise, it is not beneficial for the mechanical properties of cermet, if kept for a long time.

3.4. Effect of heating temperature and holding time on grain size

To further investigate the relationship of the microstructure evolution affected by heating temperature and holding time during sintering, a curve chart was drawn with the average grain size sample data measured by Nano Measurer software (shown in Figure 5 and 6). Figure 5 presents the heating temperature dependent variation in the average grain size of Ti(C,N)-based cermet during different holding times, while Figure 6 presents the effects of holding time and sintering temperature on relative average grain size of Ti(C,N)-based cermet.

It is well known that the mean grain size can play a crucial role in the mechanical properties of materials. Figure 5 shows a similar trend, that is, the average grain size of Ti(C,N)-based cermet increased with the heating temperature. The same rule applies to the holding time. The average grain size curve initially showed a rapid grain growth of Ti(C,N)-based cermet between 1300°C and 1400°C, and then the grain growth rate reduced slightly after 1450°C. The average grain size and heating temperature nearly have a linear relationship when the heating temperature is below 1450°C. However, it was interesting to note that the holding time curve at 0 h was evidently different from the four other curves (Figure 5). The main reason for this phenomenon is the lower apparent activation energy, resulting in a difficulty to provide sufficient driving force to drive the sintering and cooling down with the furnace when the heating temperature just reached the predetermined value. However, if the heating temperature reaches the predetermined value and maintains for some time, it may provide sufficient time for the sintering process to continue. In addition, the phenomena is associated with two factors; an increase of particle diffusion solid solution in the composite material, and an increase in the liquid phase
at high temperature. Experimentally, Mo\(_2\)C and WC particles begin to dissolve between the temperature range 1300°C and 1400°C (small particles diminished and gradually disappeared, while large particles gradually become larger than before). The presence of the liquid phase at 1400°C will contribute to the dissolving of each component in the liquid phase Co, including (Ti,Mo,W)C, (Ti,Mo)C, (Ti,W)C, (Ti,W)C, and (Ti,Mo,W)(C,N) that are generated by the previous reaction. As the amount of liquid phase increases, the grain growth rate reduces. Because it has been proved that Mo\(_2\)C and WC can improve the wettability of Ti(C,N) during the sintering process, but the core/rim structure can also suppress the growth of grains. Although Mo\(_2\)C and WC improved the wettability of Ti(C,N) and the rim-core structure could also concurrence inhibit the growth of grains.

![Figure 5. Change in average grain size of Ti(C,N)-based cermet with heating temperature.](image1)

![Figure 6. Average grain size - holding time curve.](image2)

To analyze the relationship between microstructure evolution and holding time of materials under different sintering temperature, Figure 5 can be transformed to Figure 6. The average grain size increased significantly when the holding time increased from 0 to 15 min. The average grain size increased gradually and flattened out as the holding time increased further. The curves shown in Figure 6 can be divided into two groups: (a) heating temperature at 1300°C, the average grain size of the samples change irrespective of the holding time; (b) heating temperature greater than or equal to 1400°C, the heating temperature and holding time have a significant effect on the change of average grain size. More precisely, a careful analysis of Figure 5 and 6 reveals that the average grain size increased as the heating temperature increases at the same holding time. Likewise, the average grain size increased as the holding time increases at the same heating temperature, with the maximum change of grain growth reaching 122.5%. As seen from Figure 2, the particle diffusion of Ti(C,N)-based cermet tends to be uniform and the grain boundaries spontaneously migrated outwards, which
increased the possibility of growth and uniform distribution of grains with the increasing temperature, resulting in a stable shape and size of the crystal grains. This is consistent with the law of slow growth rate of grains during liquid phase sintering.

Combined with the aforementioned result, it was further proven that heating temperature and holding time were the two key factors affecting the microstructure evolution. Some characteristics of cermet microstructure such as grain size, rim structure and thickness, and porosity would change with the two key factors.

3.5. Sintering kinetic
To accurately describe the microstructure evolution behavior of Ti(C,N)-based cermet during sintering, Sellars and Anelli models were used to establish sintering kinetic for Ti(C,N)-based cermet. A new comprehensive model was established in this paper (Eq. (3)), based on Sellars and Anelli models in order to study the microstructure evolution of Ti(C,N)-based cermet.

\[ d^n - d_0^n = A t^m \exp(-Q / RT) \]  
\[ (3) \]

To determine the model constant, the logarithm is taken on both sides of the above equation. Then,

\[ \ln(d^n - d_0^n) = \ln A + m \ln t - Q / RT \]  
\[ (4) \]

In Eq. (4), n, m, A, and Q are four constants (but the values for the sintering process are different for different materials). Therefore, these values must be determined to obtain the accurate sintering kinetics model of Ti(C,N)-based cermet. These four constants were obtained using the nonlinear-fitting method with the experimental data. The sum of the squares of the above parameters was used as a function of n. The minimum of the sum of the squared regression errors is taken as the optimal target to obtain the value of n.

a) If the holding time is constant, the partial derivative of 1/T in Eq. (4) is as follows in Eq. (5):

\[ Q = -R \left[ \frac{\partial \ln(d^n - d_0^n)}{\partial (1/T)} \right] \]  
\[ (5) \]

In the Eq. \( l = \frac{\partial \ln(d^n - d_0^n)}{\partial (1/T)} \), the regression can be performed by the least squares method. The relationship curve \( \ln(d^n - d_0^n) \) with 1/T is obtained. The average value of the slope is \( l \).

b) If the heating temperature is constant, the partial derivative of \( \ln t \) in Eq. (4) is as follows in Eq. (6):

\[ m = \frac{\partial \ln(d^n - d_0^n)}{\partial (\ln t)} \]  
\[ (6) \]

Using the linear relationship of \( \ln(d^n - d_0^n) \) and \( \ln t \), m can be found (which is the average value of the slope).

The optimal values for n, A, m, and Q were calculated by nonlinear regression using the (3) model and experimental data. A few different n values were taken (n = 0.5, 1.0, 2.5...6.0) to calculate the sum of squared the error as a function of n, as shown in Figure 7. The minimum of the squared sum of the fitted errors was n = 2.82.

Substituting \( n=2.82 \) into Eq. (3):

\[ A = 2.75 \times 10^{23}; m = 1.373; Q = 493.67 \text{ kJ/mol} \]

Consequently, the sintering kinetic model for grain growth of Ti(C,N)-based cermet can be obtained as follows:

\[ d^{2.82} = d_0^{2.82} + 2.75 \times 10^{23} t^{1.373} \exp(-493670 / RT) \]  
\[ (7) \]

where \( d \) is the final grain diameter (\( \mu \)m); \( d_0 \) is the original grain diameter (\( \mu \)m); \( t \) is the holding time (s); \( T \) is the heat treatment temperature (K); \( R \) is the gas constant (\( R = 8.314 \text{ J/mol·K} \)); \( Q = 493.67 \text{ kJ/mol} \) is the grain growth activation energy; \( A = 2.75 \times 10^{23} \) is experimental constants; and \( n=2.82 \) is the growth index.
4. Conclusions
In the current study, the microstructure evolution of Ti(C,N)-based cermet were investigated and a mathematical model was proposed using Sellars and Anelli models to quantitatively describe the sintering kinetics of Ti(C,N)-based cermet. The experimental part on the sintering behavior of Ti(C,N)-based cermet and kinetic sintering can be concluded as follows.

(1) The microstructure of Ti(C,N)-based cermet exhibited the typical core-rim structure. The core phase is formed by residual undissolved Ti(C,N) particles. The rim structure is formed by (Ti,Mo,W…)(C,N) during the liquid sintering stage, and the binder phase is formed by metal (Ni or Co, or Ni+Co, etc.) solid solution.

(2) The microstructure evolution of Ti(C,N)-based cermet exhibits two main characteristics as the temperature or holding time increases: the variation of porosity and the change of grain homogeneity.

(3) The heating temperature and the holding time are the two key factors for Ti(C,N)-based cermet sintering. They have a significant effect on the microstructure evolution of Ti(C,N)-based cermet. The longer holding time is not beneficial for their mechanical properties.

(4) The grain growth rate of Ti(C,N)-based cermet increased rapidly between 1300°C to 1400°C, and then slowed down slightly after 1450°C. The average grain size and the heating temperature have a near-linear relationship when the heating temperature is below 1450°C.

(5) In terms of the microstructure, the formation of rim structure and the distribution of grains were closely associated with the holding time at different sintering temperatures. In turn, the temperature and holding time affected the thickness of rim structure and ceramic grain distributions.

(6) The apparent activation energy of Ti(C,N)-based cermet during sintering is \( Q = 493.67 \text{ kJ/mol} \), and the kinetic equation of grain growth is

\[
\frac{d^{2.82}}{dt^{2.82}} = \frac{d_{0}^{2.82}}{2.75 \times 10^{21} t^{1.373}} \exp\left(\frac{-493670}{RT}\right)
\]

So the kinetic equation for grain growth of Ti(C,N)-based cermet can be used to control the production process and predict the product quality by calculating the size of the microstructure.

Acknowledgements
This work was supported by Talent Introduction Special Project of Lingnan Normal University (Grant No. ZL2021006).

References
[1] Zheng Z P, Lin N and Zhao L B 2018 Fabrication and wear mechanism of Ti(C,N)-based cermets tools with designed microstructures used for machining aluminum alloy, Vacuum. 156 30-8
[2] Shi Z M, Yin D Zh and Zhang D Y 2017 Characterisation of Ti(C,N)-based cermets with various nitrogen contents studied by EBSD/SEM and TEM, J. Alloys & Compounds 695 2857-64
[3] Wang S W, Zheng Y and Zhang G T 2019 Effect of NbC addition on the microstructure,
mechanical properties and thermal shock resistance of Ti(C,N)-based cermets, *J. Mater. Res. Express* 6 1-8

[4] Zheng Q, Yao W X and Lin L C 2016 Ostwald ripening and grain growth in Ti(C,N)-based cermets during liquid phase sintering, *Int. J. Refract. Met. & Hard Maters.* 58 1-7

[5] Kim S, Zuo J M, Kang S 2010 Effect of WC or NbC addition on lattice parameter of surrounding structure in Ti(C0.7N0.3)-Ni cermet investigated by TEM/CBED, *J. Eur. Ceram. Soc.* 30 2131–8

[6] Xu Q, Zhao J, Ai X, Qin W, Wang D and Huang W 2015 Effect of Mo2C/(Mo2C + WC) weight ratio on the microstructure and mechanical properties of Ti(C,N)-based cermets tool materials, *J. Alloys Compd.* 649 885–90

[7] Xiong J, Guo Z, Shen B and Cao D 2007 The effect of WC, Mo2C, TaC content on the microstructure and properties of ultra-fine TiC0.7N0.3 cermet, *Mater. Des.* 28 (5) 1689–94

[8] Wan W, Xiong J, Li Y, Tang Q and Liang M 2017 Erosion-corrosion behavior of Ti (C, N)-based cermets containing different secondary carbides, *Int. J. Refract. Metals Hard Mater.* 66 180–7

[9] Wang J, Liu Y, Zhang P, Ye J and Tu M 2009 Effect of VC and nano-TiC addition on the microstructure and properties of micrometer grade Ti (CN)-based cermets, *Mater. Des.* 30 (6) 2222–6

[10] Liu C, Lin N, and He Y H 2016 Influence of Mo2C and TaC additions on the microstructure and mechanical properties of Ti (C, N)-based cermets, *Ceram. Int.* 42 (2) 3569–74

[11] Dong G, Xiong J, Chen J, Guo Z, Wan W, Yi C and Chen H 2012 Effect of WC on the microstructure and mechanical properties of nano Ti (C, N)-based cermets, *Int. J. Refract. Metals Hard Mater.* 35 159–62

[12] Liu A J and Liu N 2016 Effect of WC-Co granules on mechanical properties and microstructure, *Ceramics Int.* 42 15274–84

[13] Zhao Y J, Zheng Y and Zhou W 2017 Microstructure and performance of functionally gradient Ti(C, N)-based, Materials Chemistry and Physics cermets fabricated by low-pressure carburizing treatment during liquid phase sintering. *Ceram. Int.* 43 1956–62

[14] Xiong H W, Wu Y X and Li Z Y 2018 Comparison of Ti(C, N)-based cermets by vacuum and gas-pressure sintering Microstructure and mechanical properties, *Ceram. Int.* 44 805-13

[15] Xiong H W, Wu Y X and Gan X P 2018 Strengthened Ti(C, N)-based cermets using high-energy ball-milled NiTiC binders: Microstructure and mechanical properties, *Ceram. Int.* 45 19113–22

[16] Yun H, Zou B and Wang J 2017 Effects of sintering temperature and nano Ti(C,N) on the microstructure and mechanical properties of Ti(C,N) cermets cutting tool materials with low Ni-Co, *Mater. Sci. Eng. A* 705 98-104

[17] Chen M, Zhuang Q M and Lin N 2017 Improvement in microstructure and mechanical properties of Ti(C,N)-Fe cermets with the carbon additions, *J. Alloys Compd.* 701 408–15

[18] Dios M, Kraleva I and González Z 2018 Mechanical characterization of Ti(C,N)-based cermets fabricated through different colloidal processing routes, *J. Alloys Compd.* 732 806–817

[19] Chicardi E, Gotor F J and Medri V 2016 Hot pressing of (Ti, Mt)(C, N) –Co-Mo2C (Mt= Ta, Nb) powdered cermets synthesized by a mechanically induced self-sustaining reaction, *Chem. Eng. J.* 292 51-61

[20] Xu Q, Ai X and Zhao J 2015 Comparison of Ti(C,N)-based cermets processed by hot-pressing sintering and conventional pressureless sintering, *J. Alloy. Comp.* 619 538-43

[21] Lin N, Zhao L B and Zou J C 2019 Improvement in densification process and properties of Ti(C,N)-based cermets with vanadium carbide addition, *Ceram. Int.* 45 2692–700

[22] Lin N, Zheng Z P and Zhao L B 2019 Influences of ultrafine Ti(C,N) additions on microstructure and properties of micron Ti(C,N)-based cermets, *Materials Chemistry and Physics.* 230 197–206

[23] Kang X Y, Lin N and He Y H, Influence of ZrC addition on the microstructure, mechanical
properties and oxidation resistance of Ti(C,N)-based cermets, *Ceram. Int.* **44** 11151–9

[24] Zhao L B, Lin N and He Y H 2018 Improvement in microstructure and properties of Ti(C,N)-based cermets with Ruthenium additions, *Ceram. Int.* **44** 17553–61

[25] Shankar E, Balasivanandha Prabu S 2017 Microstructure and mechanical properties of Ti (C, N) based cermets reinforced with different ceramic particles processed by spark plasma sintering, *Ceram. Int.* **43** 10817–823

[26] Yin Z B, Yuan J T and Xu W W 2019 Improvement in microstructure and mechanical properties of Ti(C, N) cermet prepared by two-step spark plasma sintering, *Ceram. Int.* **45** 752–8

[27] Vasanthakumar K, Ghosh S, Koundinya NTBN, Ramaprabhu S, Bakshi S R 2018 Synthesis and mechanical properties of TiCx and Ti(C,N) reinforced Titanium matrix in situ composites by reactive spark plasma sintering, *Ceram. Int.* **759** 30–39

[28] Zhou W, Zheng Y and Zhao Y J, Zhang G T, Ke Z and Yu L X 2018 Study on microstructure and properties of Ti(C,N)-based cermets with dual grain structure, *Ceram. Int.* **44** 14487–94

[29] Yin Z B, Yan S Y and Xu W W 2018 Microwave sintering of Ti(C, N)-based cermet cutting tool material, *Ceram. Int.* **44** 1034–40

[30] Yin Z B, Yuan J T and Cheng Y 2016 Microstructure and mechanical properties of Al2O3/Ti(C, N) ceramic tool materials by one-step and two-step microwave sintering, *Mater. Sci. Eng. A* **670** 159–65

[31] Devadas C, Samarasekera I V and Hawbolt E B 1991 The thermal and metallurgical state of steel strip during hot rolling: part iii. microstructural evolution. *Metallurgical Transactions A*, **22** 335-49

[32] Anelli E 1992 Application of mathematical modelling to hot rolling and controlled cooling of wire rods and bars. *ISIJ International*, (32) 440-9

[33] Yan Y L, Zheng Y and Liu W J 2008 Study on sintering process of Ti(C, N)-based cermets, *Mater. Eng. (Chinese)*, **1** 49–53