Preparation of Ti(C, N)-based Cermets Powders with Double-core Ring Structure

Hui Yan1,2, Ying Deng1*, Shan Jiang1*, Qiaowang Chen, Shixiu Cao1, Bing Liu1
1 Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing, 402160, China
2 Faculty of Materials and Energy, Southwestern University, Chongqing, 400715, China
*Corresponding author’s e-mail: 397194810@qq.com and ShanJiang: 595820439@qq.com

Abstract. In this study, the microstructure of Ti(C, N)-based cermet was improved by adding β-cobalt (face-centered cubic) and (Ti, W, Mo, Ta)(C, N) solid solution powder to prepare micro-nano Ti(C, N)-based cermet powder. In order to improve the comprehensive properties of the material. Firstly, the Co powder with face-centered cubic structure was obtained by the solid-phase reaction of high-energy ball milling, and its plastic deformation resistance was higher than that of Co powder with dense hexagonal structure. Secondly, The powder of (Ti, W, Mo, Ta)(C, N) solid solution was obtained by mechanical alloying and high-temperature carbonization under the atmosphere of N2. And the two were applied to the micro-nano Ti(C, N)-based cermet powder, and finally the properties of cermet powder were compared with that of ordinary cermet powder. The results show that the microstructure of micro-Ti(C, N)-based cermet powder prepared in this study is a double-core rim structure, that is, the structure of black core white rim and gray core white rim. This structure can effectively prevent crack of the expansion. The strength and toughness of cermet materials are greatly improved, which is beneficial to the improvement of comprehensive properties of cermet materials.

1. Introduction
Ti(C, N)-based cermet material is prepared by powder metallurgy. It is a high strength and toughness metal matrix composite composed of ceramic hard phase and metal bonded phase[1]. In the composition of the cermet, the ceramic phase is an oxide or refractory compound having a high melting point, a high hardness, and the metal phase is mainly a transition element and its alloy[2]. Cermet not only maintains the ceramic high strength, high hardness, durable, high temperature resistance, anti-oxidation and chemical stability, but also has good metal toughness and plasticity[5]. However, there are still many deficiencies in Ti(C, N)-based cermet at present. The weakness of toughness is fatal, and the microstructure of cermet needs to be further improved[11]. It is urgent to optimize the microstructure of Ti(C, N)-based cermet materials.

This topic is about the preparation of micro-nano Ti(C, N)-based cermet powder. The combination properties of Ti(C, N)-based cermets can be improved by improving the composition of Ti(C,N)-based cermet powder, combined with high energy ball milling and spray drying. This study aims to improve the microstructure of the material by adding self-made face-centered cubic Co powder and (Ti, W, Mo, Ta)(C, N) solid solution powder to improve its overall performance. The experimental results are
verified by comparing it with the traditional Ti(C, N) based cermet materials. We have obtained more advanced Ti(C, N)-based cermet powder preparation formula and processing technology.

The innovation of this study is that the raw materials of Ti(C, N)-based cermet powder are prepared by the solid phase-thermal decomposition-reduction method in our laboratory. In general, Ti(C, N)-based cermet powders have a typical microstructure of core-ring structure, which will cause stress and segregation of composition and decrease the strength and toughness of the material. However, the Co powder with face-centered cubic structure prepared in this experiment has stronger ability to resist plastic deformation.[12], and the solution effect of (Ti, W, Mo, Ta)(C, N) solid solution is better. Therefore, the microstructure of Ti(C, N)-based cermet powder prepared in this study shows a double-core-rim structure, which effectively improves the stress and composition segregation.

2. Preparation strategy and experimental procedure

2.1. Preparation of Co powder
In this study, CoCl$_2$·6H$_2$O and Na$_2$CO$_3$ were used as raw materials, the precursor cobalt carbonate powder was prepared by solid-phase reaction of high energy ball milling, and the precursor powder was washed several times with deionized water and spray dried. Then the dried precursor powder is cracked at a high temperature (400-450℃). The whole process needs to be protected by nitrogen, and the air should be discharged to prevent oxidation as far as possible. Finally, the composition, structure and morphology of the powder were analyzed by XRD and SEM. And then compare it with commercial cobalt powder.

2.2. Preparation of (Ti, W, Mo, Ta)(C, N) solid solution
According to the composition (mass fraction, the same below), 30%MoO$_2$, 10%WO$_3$, 30%TiO$_2$, and 30%Ta$_2$O$_5$ were weighed and placed in a stainless steel vacuum metal can and an appropriate amount of alcohol was added. Ball milling on XQM planetary ball mill (The ball is made of metal ceramic ball, The mass ratio of ball to material is 10:1, rotation speed is 500r/min, ball milling time is 3h, 6h, 9h, 12h respectively). After ball milling, the slurry is sifted, cleaned, precipitated, spray dried. Finally, the sample and carbon powder were carbonized in vacuum tube furnace according to the process curve shown in the following diagram, using a nitrogen atmosphere (flow rate 600ml·min$^{-1}$, furnace pressure 0.1-0.2MPa), the carbonation temperature is 1200℃ and 1600℃, and the time is 5h.

Figure 1. (Ti, W, Mo, Ta)(C, N) solid solution of high-temperature carbonization process (1600℃).
2.3. Preparation of metal ceramic powder
The common commercial Co powder and the self-made Co powder were used in the experiment, and 50%Ti(C, N), 20%WC, 8%Mo2C, 5%TaC, 13%α/β-Co (β-Co)were weighed. Then add 3.5% of the total weight of paraffin and an appropriate amount of alcohol into a stainless steel vacuum metal can for ball milling (The mass ratio of ball to material is 5:1, rotation speed of 200r/min, ball milling time is 48h). The powder prepared by two groups of different Co powder was analyzed by SEM and XRD. Finally, the powder is sintered at high temperature according to the process curve shown below.

3. Results and Discussion
3.1. Structure and Morphology of Key Components of Cermet Powder
3.1.1. Analysis of Co Powder. The reaction equation that may occur during the preparation of the precursor is as shown in the following formula:

\[
\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{HCO}_3 \rightarrow \text{CoCO}_3 + \text{NH}_3 + 2\text{HCl} + 6\text{H}_2\text{O}. \tag{1}
\]

\[
\text{CoCO}_3 + \text{H}_2 \rightarrow \text{Co} + \text{CO}_2 + \text{H}_2\text{O}. \tag{2}
\]
The composition, structure and morphology of self-made Co powder and commercial Co powder were determined by XRD and SEM. Figure 4 is a comparison of the self-made β-Co powder (a) graph and commercial Co powder (b) graph by XRD and SEM. From Figure 4, we can see that the cobalt powder we prepared is a face-centered cubic structure, while the commercial cobalt powder is a dense hexagonal structure. Since the face-centered cubic structure has more slip systems than the dense hexagonal structure, the anti-shaping ability of the structure will be stronger than that of the dense hexagonal structure, which proves the superiority of our self-made cobalt powder from the crystal structure.

In contrast, (b) graph is the topography of commercial cobalt powder. It can be seen from the picture that the particles of commercial cobalt powder are not dispersed enough, and many of them are clustered in one piece and have irregular shape. (a) graph is a self-made cobalt powder. It can be seen from the topography that β-Co powder particles are uniformly dispersed and basically spherical. The dispersion and particle shape of the powder have a great influence on the flowability and loose density of the powder, and then directly affect the comprehensive properties of the final product. Obviously, our self-made cobalt powder with face-centered cubic structure is better than commercial cobalt powder in terms of crystal structure, dispersion degree or particle shape.

In this study, the mechanical solid-phase chemical method was used to distort the inner lattice of the material by high-speed grinding ball, increase the defect inside the lattice, and produce the thermal vibration energy of the lattice, thus increase the diffusion coefficient and decrease the activation energy of the reaction, so that the solid-phase chemical reaction to occur at low temperatures. The nucleation rate of the product is faster than that of the growth rate, resulting in the formation of nanoparticles. By ultrasonic spray, the particles were further dispersed and broken, and controlled by the nozzle, the morphology of the particles was changed under the action of surface tension, and the precursor of cobalt oxalate was changed from acicular to spherical, based on the heredity of the morphology. The spherical morphology of cobalt can be inherited from the final product. The formation energy of β-Co is higher than that of α-Co, and the mechanical effect of high energy ball milling enables the powder to reserve enough energy to ensure its thermal decomposition to form β-Co.

3.1.2. Analysis of the results of (Ti, W, Mo, Ta)(C, N) solid solution. Fig 5 is the result of XRD composition analysis of (Ti, W, Mo, Ta)(C, N) solid solution powder) at 1600℃ and 1200℃, from the figure we can see that after 1600℃ high temperature carbonation obtained MoC, WN, Ti2N, MoC, Mo9Ti4 compounds, but after 1200℃ high temperature carbonization is Mo, WN, TiW1-x in contrast, the solid solution effect of (Ti, W, Mo, Ta)(C, N) solid solution obtained at 1600℃ high temperature carbonization is better than that at 1200℃. This can also be explained from the thermal analysis data.
Figure 5. XRD images of two different carbonization temperatures.

Figure 6. TG-DSC curves of (Ti, W, Mo, Ta)(C, N) solid solution powders.

Figure 6 is TG-DSC curves of (Ti, W, Mo, Ta)(C, N) solid solution powders. It can be seen from the diagram that several endothermic peaks appear continuously at 200°C, and the powder begins to carbonize at 800°C. After 1500°C, DSC tends to calm down and the reaction is stable. This indicates that the (Ti, W, Mo, Ta)(C, N) powder is still in the reaction stage before 1500°C, and then tends to be stable at 1500°C, and the solid solution tends to be completed. This also verifies the XRD results in Figure 5. It is only at 1600°C (Ti, W, Mo, Ta)(C, N) that the solid solution is complete.
Figure 7. The morphology of (Ti, W, Mo, Ta)(C, N) powders obtained by SEM.

a: ball mill 3h b: ball mill 6h c: ball mill 9h d: ball mill 12h.

Fig 7 shows four images of the SEM morphology of the powder at four different milling times (Ti, W, Mo, Ta)(C, N). It can be seen from the figure that the particle size of (Ti, W, Mo, Ta)(C, N) powder decreases with the increase of milling time. However, the particle size of the powder after 9h and 12h ball milling has not changed much, indicating that the effect of ball milling for 9h has been very good. This provides a theoretical basis for the final selection of the ball milling time of 9h and the carbonization temperature of 1600℃.

Figure 8. The morphology of (Ti, W, Mo, Ta)(C, N) solid solution obtained by SEM.

Figure 8 shows the topography and energy spectrum of (Ti, W, Mo, Ta)(C, N) solid solution powder which was finally carbonized at high temperature. It can be seen from the topography that (Ti, W, Mo, Ta)(C, N) solid solution powder has a good morphology and is spherical. The energy spectrum shows that the solid solution is very good, and the final product is (Ti, W, Mo, Ta) (C, N) solid solution. It shows that the process design of high temperature carbonization at 1600℃ is feasible when milling time is 9h.
3.1.3. Phase analysis. Fig 9 is a XRD comparison between A and B groups of cermet samples. It can be seen from the figure that the crystal structure of the Co powder of Group A is close to hexagonal, and the crystal structure of Group B Co powder is a face-centered cubic structure. And if we look closely at the peaks (111) and (200) of groups A and B in figure 9, we can see that the ratio of I(111)/I(200) in group B is higher than that in group A. The relative strength of solid solution phase of cermet sample in Table 1 can also be seen. The value of I(111)/I(200) in group A was 1.08, while the value of I(111)/I(200) in group B was 1.35. Because a large number of heavy metal elements are solidly soluble on (111) peaks, such as W, Mo, Ta, the higher the I(111)/I(200) value, the better the solution effect is. This shows that the solution effect of group B is better than that of group A. In addition, it is not difficult to see from Table 1 that the relative strength of the solid solution phase of group B cermet is obviously higher than that of A. This also proves that the strength of the cermet in group B is better than that in group A.

![Figure 9. The structure of solid-solution phase of cermet samples detected by XRD.](image)

| sample | (Ti, W, Mo, Ta)(C, N) | Co |
|--------|-----------------------|----|
|        | (111) | (200) | I(111)/I(200) | (111) fcc | (200)fcc | (101) hcp |
| A      | 291  | 269   | 1.08          | 57         | 19       | 29        |
| B      | 312  | 230   | 1.35          | 83         | 42       | -         |

3.1.4. Microstructure analysis. Fig 10 shows the microstructure of two groups of cermet samples under backscattering scanning electron microscopy. We can obviously see the "core-shell" structure of cermet in the diagram, the complex core-ring structure appears in figure A, the interface is complex and easy to produce stress, and the double core ring structure of black core-white ring and gray core-white ring appears obviously in figure B. Although it is still a core ring structure, there is no complicated core ring structure, and the present research is not to eliminate the core ring structure, but to reduce the lattice difference between the cores and rings. The double-core ring structure in B diagram can improve the strength and toughness of the matrix.
4. Conclusions

(1) The Co powder with face-centered cubic structure obtained by solid state reaction of high energy ball milling has higher dispersion, stronger ability of plastic deformation resistance and closer to spherical shape than that of Co powder with dense hexagonal structure.

(2) (Ti, W, Mo, Ta)(C, N) solid solution can be prepared by high energy ball milling and high temperature carbonization (heating temperature 1600°C in N₂ atmosphere).

(3) The powder morphology of Ti(C, N)-based cermet was spherical by adding cobalt powder with face-centered cubic structure and (Ti, W, Mo, Ta)(C, N) solid solution, combined with high energy ball milling and spray drying. The crystal structure of solid solution phase is face-centered cubic structure. The physical and chemical properties of cermet are higher than those of ordinary cermet.

Acknowledgments
The authors acknowledge the financial support to this work from the Chongqing Research Program of Basic Research and Frontier Technology cstc2017jcyjBX0051, cstc2016jcyjA0567 and cstc2015jcyjA70014.

References
[1] Chen, W.L. (2007) Research on Ultra-fine Ti(C, N)-Based Cermet Cutter and Its Cutting Behavior[Dissertation]. Hefei: Hefei University of Technology.
[2] He, X., Ye, J.W., Liu, Y. (2009) Preparation of Ti(C, N) powder by carbothermal method open system[J]. China Academic Journal Electronic Publishing House, 5(40): 771
[3] Peng, Y., Miao, H.Z., Peng, Z.J. (2013) Development of Ti(C, N)-based cermets: mechanical properties and wear mechanism[J]. Hard Mater, 39: 78-89
[4] Zhang, D.Y., Shi, Z.M. (2012) Effect of chemical composition on the sinterability and mechanical properties of Ti(C, N)-based cermets[J]. Powder Metallurgy Technology, 30(02): 88
[5] Yan, L., Ning, L. (2008) Microstructure and Mechanical Properties of Fine-Grained Ti(C, N)-Co Cermets[J]. Transactions of Materials and Heat Treatment, 29(1): 1-4
[6] Zhou, Z.S., Wang, S.Q., Wang, W.S. (2007) Phase composition changes during sintering of nano-Ti(C, N)-based cermets[J]. Journal of Central South University: Natural Sciences, 38(3): 404-408
[7] Zheng, Y., You, M., Xiong, W.H. (2003) Valence electron structure and properties of main phase in Ti(C,N)-based cermets[J]. Materials Chemistry and Physics, 82(3): 877-881.
[8] Lays, Hamar-Thibault, S., Lacknera, (2002) Location of VC in VC, Cr3C2 codoped WC-Co cermets by HREM and EELS[J]. International Journal of Refractory Metals & Hard Materials, 20(1): 61-69
[9] Mari D, Bolognini S, Feusier G. (2003) TiMoCN based cermets part: morphology and phase composition[J]. International Journal of Refractory Metals & Hard Materials, 21(1/2): 37-46
[10] Wang, H.P., Yin, Z.M. (2003) Research on Ti(C, N)-based cermet inserts[J]. Cemented Carbide, 20(3): 133-137
[11] Liu.B, Zhang.Q, Chen.H. (2015) Study on the Effect of Sub-micro SiC Particle on the Properties and Microstructure of Ti(C, N)-based Cermet[J]. Powder Metallurgy Technology, 33(03): 170

[12] Zhang.X.B, Liu.N. (2008) Microstructure, mechanical properties and thermal shock resistance of nano-TiN modified TiC-based cermets with different binders. International Journal of Refractory Metals and Hard Materials, vol. 26, no. 6, pp. 575–582.

[13] A.Jain, S.R.Agnew. (2007) Modeling the temperature dependent effect of twinning on the behavior of magnesium alloy AZ31B sheet. Materials Science and Engineering A, vol. 462, no. 1-2, pp. 29–36.