Investigation of preparation and properties of TiCN coatings by reactive plasma spraying

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Abstract. The TiCN coatings were successfully prepared by means of reactive plasma with spraying self-made composite powder prepared from 150°C to 350°C in the paper. Sucrose was used as a carbon source, using the means of Precursor body carbon, sucrose and titanium powder mixing at high temperature after the heat treatment furnace for carbonization. Finally, the titanium powder was wrapped by the carbon, so the composite powder was mixed more uniform and could react more fully. TiCN coatings could not be synthesized with the composite powder prepared the temperatures of 150°C and 250°C, because the sucrose was not carbonized totally and could not carbonize to synthesize TiCN with Ti and N in the process of spraying. TiCN coatings were prepared by spraying the composite powder under heat treatment at 350°C and which composed of Ti and C at a ratio of 1:3. The phase compositions, the morphologies, the hardness and the microstructures were analyzed. The results showed that TiCN coating was consisted of TiC$_{0.2}$N$_{0.8}$ phase and a few of TiN, the hardness of TiCN coating could reach 1000HV, the friction coefficient is about 0.45, the wear resistance of TiCN coating was lower compared with TiC coating because of the looser structure and the lower hardness.

1. Introduction

TiCN is a single compound TiC$_{1-x}$N$_x$, formed by the solid solution of TiC and TiN, and has both characteristics and advantages. It is used as a coating tool to improve the service life and the quality of processed products, because of the advantages of high hardness, good toughness, high bonding strength, small friction factor and stable chemical properties. However, TiN coating cannot be used in high-speed cutting extreme conditions. TiCN coating has excellent performance and hardness higher than TiN, but TiC is too brittle to collapse. The hardness of TiC$_{1-x}$N$_x$ coating decreases and toughness increases with the increasing of x. TiCN coating not only has a high hardness of cemented carbide, but also has high temperature performance of ceramic materials, leading to a wider application [1].

At present, the preparation methods of TiCN coating are mainly sintering and surface treatment. Sintering is namely mixing TiC and TiN in a certain proportion, keeping a certain temperature under nitrogen pressure to obtain TiCN solid powder [2-4]. However, it is difficult to prepare a complicated structural member. Surface treatment is generally based on plasma assisted chemical vapor deposition (PACVD) [5], physical vapor deposition (PVD) [6], chemical vapor deposition (CVD) [7-8], ion implantation and other surface treatment methods [9-11]. The low deposited rate, the poor binding of coating and matrix, and the expensive preparation equipment of above methods increase the preparation cost of TiCN coating and restrict the application of TiCN.

The powder used in the reactive plasma spraying is a high exothermic reaction system. The powder reacts with the reaction gas during the flight, and the reaction product particles are deposited on the
substrate to form the coatings [12-14]. The coating is synthesized by the hard phase in situ and has a typical layered structure. The superimposing of synthesis reaction heat and plasma arc heat is favorable for the melting of the hard phase with high melting point, which overcomes the shortcomings of arc uneven distribution, incomplete melting, and coarse tissue of the traditional plasma and improves the composite coating wear and corrosion resistance [13, 15]. A good combination of the hard phase and the matrix in the coating is helping to improve the wear resistance and corrosion resistance of the composite coating. The preparation of TiCN nanometer coating by reactive plasma spraying technology can greatly simplify the preparation process and reduce the cost of nanometer coating, which is a new method with application prospect.

It is of great significance not only to improve the production efficiency, reduce the cost and improve the quality of the products by reactive plasma spraying, but also to enhance the manufacturing level and develop of national defense cutting-edge technology. TiCN coating is prepared by reactive plasma spraying technique, and the preparation technology and wear resistance of TiCN coating are studied in this paper.

2. Experiment

45# carbon steel was used as substrate material. Rectangular specimens (10 mm×10 mm×12 mm) for coating deposition were fabricated and ground with SiC papers, followed by ultrasonically cleaning in acetone for 30 min. After that, NiAl adhesive layer with a thickness of 100μm was deposited on the specimens.

Ti powder produced by Beijing Research Institute of Nonferrous Metals was used in the test with a particle size of 30μm as shown in Figure 1. The carbon produced by C_{12}H_{22}O_{11} carbonization was the carbon source. A certain amount of Ti powder and the corresponding mass of C_{12}H_{22}O_{11} powder was weighed according to the 1:3 molar ratio of Ti:C and then grind the mixture, add deionized water, dry, and then put into the muffle furnace heating to prepare composite powder. The TiCN coating of about 300μm thickness was produced by spraying composite powder on NiAl adhesive layer. The ingredient of Al/Ni powder and Ti powder was listed in Table 1 and Table 2 respectively.

![Figure 1. Surface morphologies of the Ti powders.](image)

Table 1. The ingredients of Ni/Al powder in the experiment.

| Elements | Ni | Al | Others |
|----------|----|----|--------|
| wt.%     | 90 | Bal.| <1.0   |

A plasma spraying system (GP-80) produced by Taixing Yeyuan Spraying Machinery Factory equipped with power supply cabinet, plasma spray gun, gas supply system, circulating cooling system, powder feeder and working table was used for preparing the TiN coating. BT-1 plasma spray gun was used with the radial powder feeding method. The composite powder was prepared at 150°C, 250°C and 350°C respectively, according to the molar ratio of Ti:C was 1:3. The corresponding composite
powder was called composite powder I, composite powder II and composite powder III. The process parameters of NiAl and TiCN coating prepared by reactive plasma spraying were listed in Table 3.

**Table 2.** The ingredients of Ti powder in the experiment.

| Elements | Ti   | Fe | Si | Cl | C  | N  | O  | H  |
|----------|------|----|----|----|----|----|----|----|
| wt.%     | >99.4| <0.06| <0.01| <0.02| <0.04| <0.4| <0.02|

**Table 3.** Reactive plasma spraying parameters of NiAl and TiCN coating.

| Parameter                  | NiAl coating | TiCN coating |
|----------------------------|--------------|--------------|
| gas-flow rate/L·min⁻¹      | Ar 80        | 50           |
|                            | N₂ 30        | 50           |
| powder feeding rate /m³·h⁻¹| 0.5          | 3            |
| spraying power/Kw          | 28           | 28           |
| input voltage/A            | 400          | 400          |
| spraying distance/mm       | 120          | 100          |

The surface morphology of TiCN coating was observed by Philips XL30/TMP scanning electron microscopy, and the composite powder and coating were analyzed by energy spectrum. The coating was subjected to phase determination using a Philips X-Pert MPD X-ray diffractometer. The micro-hardness of the coating was measured using a digital micro-hardness tester. The prepared cross-section metallographic sample was placed on the microhardness tester and held 15 seconds for each load. Ring-block relative sliding and dry grinding wear method were used in friction and wear experiment, the experiment time was 60 minutes and dry grinding load was 100N.

3. Results and discussion

3.1. Morphology and composition of composite powders

From the energy spectrum analysis of composite powder I as shown in Figure 2, it can be seen that the Ti powder has been wrapped in sucrose. The energy spectrum analysis in Figure 3 shows that the composite powder I has a high content of carbon. The morphology and energy spectrum analysis of composite powder II was presented in Figure 2 and Figure 3, which illustrated that Ti powder was wrapped by sucrose more uniform and the carbon content increased slightly comparing with composite powder I. It can be inferred that the sucrose doesn’t decompose totally and only a part of the water evaporate at the temperature of 250°C. In comparison with composite powder I and composite powder II, it can be seen that fine particles precipitated at the surface of composite powder III as shown in Figure 2. Sucrose began to carbonize at 300°C according to the study on sucrose carbonization [1] and the carbon nanotubes were decomposed and crystallized after heating at 350°C. It can be seen that the carbon content of composite powder III was higher than the former two composite powders from the result of the energy spectrum analysis as shown in Figure 3, which provides a good condition for the subsequent reaction.

It can be seen that the composite powder particles are elliptical or round and the edges and fractions disappear gradually, indicating that the flow ability of the composite powder is better and it is beneficial to prepare a denser coating. The color of the composite powder particles is uneven when observed with the naked eyes to the, this phenomenon is more obvious especially use backscattered electron observation. The elements with different atomic numbers show different contrast according to the principle of backscattered electron image, and the backscattered electron signal is strong in the region with larger average atomic number and show a bright contrast on the backscattered electron image, while the area with smaller average atomic number is darker. Since each particle is mixture of Ti and C, the main reason for the difference in the content of the two elements in the different
composite powder particles may be the size of composite powder particles. The contact area of fine Ti particles in original powder and sucrose is larger leading to the composition of C on the surface of carbon particles after carbonization is higher, so the smaller particles show darker [16-17].

Figure 2. Surface morphologies of the composite powders (a) I (b) II (c) III.

Figure 3. The energy spectrum analysis of the composite powders (a) I (b) II (c) III.

3.2. The surface morphology of coatings
Figure 4 shows the surface morphology of coating I, coating II, coating III which was produced by spraying composite powder I, composite powder II and composite powder III, respectively. The surface of coating I was not flat, the structure was loose and a large number of pores existed on the surface, the reason was that smelting of molten particles was uneven during the spraying process. Comparing with the coating I, the coating II was smoother, the pores reduced, and the bonding performance between the particles increased. Otherwise, some micro-cracks existed in the surface coating II, because of the thermal stress due to the high temperature and slow heat dissipation of the sample during spraying. The typical lamellar structure can be seen in coating III and the distribution of
particles was more uniform comparing with the former coatings, but there were still a small number of holes.

![Figure 4](image1.png)

**Figure 4.** The surface morphology of coatings (a) I (b) II (c) III.

3.3. XRD analysis of the coatings

The XRD patterns of the coatings are presented in Figure 5. The result shows that the main phase of coating I and II is Ti, and TiCN phase is not detected. The main phase of coating III is TiC\textsubscript{0.2}N\textsubscript{0.8}, and a small amount of TiN phase is also included, indicating that composite powder III reacted in the flame flow.

![Figure 5](image2.png)

**Figure 5.** The typical XRD pattern of the coatings (a) I (b) II (c) III.

Only Ti phase was detected in coating I, because the water contained in sucrose had not completely evaporated at 150°C and the Ti powder was completely wrapped in sucrose, part of the energy was used to remove moisture from the sucrose and then carbonized it when the composite powder I sprayed into the plasma flame. The composite powder I has reached the substrate surface when the
sucrose had not fully reacted for the high rate of plasma flame flow, which not only prevented the reaction of Ti and C, but also hampered the reaction of Ti and N.

No TiCN phase was detected in coating II, but TiO phase appeared. Although the Ti powder particles in composite powder II were wrapped in sucrose, some sucrose decomposed for the high heating temperature, and part of the Ti powder was oxidized during spraying process.

TiCN phase appeared in coating III, indicating that the sucrose has been carbonized during preparation the composite powder III, but the carbonization was not complete and Ti powder could not fully react with N. Therefore, the TiN phase appears in the coating. Further study should be carried out on sucrose carbonization process, so that the composite powder can fully react in the flame flow.

3.4. The hardness of the TiCN coating

Table 4 shows the micro-hardness of the three coatings. It can be seen that coating III has the highest hardness which is close to the micro-hardness of the coating prepared using the reaction chamber. The hardness of coating III can reach 1000HV indicating that the sucrose in the composite powder III decomposed into C, and Ti reacted with C and N into TiCN. But the micro-hardness of TiCN coating was not high enough compared with TiN coating prepared by reactive splama spraying [16], because the uncompleted reaction induced the loose coating, and the experimental process need to be further optimized.

| No. | coating I | coating II | coating III |
|-----|-----------|------------|-------------|
| Hardness HV(100g) | 390 | 690 | 945 |
|     | 410       | 750        | 932         |
|     | 370       | 690        | 911         |
|     | 450       | 680        | 980         |
|     | 435       | 730        | 1010        |
| Average HV(100g) | 411 | 708 | 956 |

Figure 6. The relationship of wear coefficient and time of coating III.
3.5. The wear resistance of TiCN coating

Large studies show that the composition, thickness and process conditions have a great influence on the performance of the coating, and the working condition is the main factor affecting the friction and wear performance. The friction coefficient and time curve of coating III is presented in Figure 6. The friction coefficient is about 0.45 which is belonging to the normal range, but the larger friction coefficient illustrating the wear resistance was poor of coating III under dry grinding conditions. The friction coefficient was up to 0.43 at the initial stage of wear experiment, because the surface particles was peeled off due to the loose structure, some of the hard TiCN particles were abrasive and the grinding action of the abrasive grains would stimulate the attenuation of the coating.

From the surface morphology after abrasion of coating III as shown in Figure 7 the TiCN coating was brittle and had some defects. Large deformation occurred inside coating III under load and the loose coating structure resulting in cracks and holes produced in the weak place, and even brittle fracture or layered peeling occurred.

The bumps between the two contact surfaces bear the load deformation under the action of the load, and the actual contact surface expenses until the bumps is no longer deformation under the load. The bonding point is cut off at a certain distance from the interface when the two surfaces are relatively sliding, namely the adhesive wear occurred. The coating is under the friction contact stress as adhesive wear time extended and micro-cracks form and gradual expanse in the local high concentration of stress, which leads to the coating peel off eventually. Moreover, the exfoliation of hard TiCN particles as abrasive grinding will lead to accelerate the strength of the coating and accelerate the wear of the coating.

![Figure 7. The surface morphology after abrasion of coating III.](image)

4. Conclusions

The composite powder was prepared by carbonizing sucrose as precursors, and TiCN coating was prepared by reactive plasma spraying. The phase composition, microstructure and micro-hardness of the coatings were studied by XRD and SEM. The wear resistance of the coatings was also studied. Some conclusions can be drawn as follows:

1) TiCN coatings could not be synthesized with the composite powder prepared the temperatures of 150°C and 250°C. The main phase of coating III which was prepared by spraying the composite powder heating at 350°C was TiC₀.2N₀.8, and a small amount of TiN phase was contained.

2) TiCN coating prepared by spraying the composite powder heating at 350°C had the highest hardness which was close to the micro-hardness of the coating prepared using the reaction chamber.

3) The looser structure of TiCN coating and the lower hardness of the TiCN coating resulted in the poor wear resistance.

References

[1] Peida Tang, Qing Gao and Xiaoyu Jiang 2005 Research on performance and influence factors of TiN,TiC and Ti(C,N) coatings Journal of Material Protection 38 3

[2] Ji Xiong, Yakun Zhang and Baoluo Shen 2003 The preparation and performance of superfine TiCN cermet Journal of Powder Metallurgy 21 2
8

[3] Dike Yan, Houan Zhang and Jiyong Yi 2010 Study on preparation and microwave sintering process of Ultra-fine TiCN matrix cermet Material & Heat Treatment 39 20
[4] C Morant, P Prieto and A Forn 2004 Hardness enhancement by CN/TiCN/TiN multilayer Films Surface and Coatings Technology 180
[5] E S Puchi-Cabrera, M H Staia and D T Quinto 2007 Fatigue properties of a SAE 4340 steel coated with TiCN by PAPVD International Journal of Fatigue 29 3
[6] Di Wu 2011 Research progress and application of physical vapor deposition technology Machinery Manufacturing and Automation 4
[7] Xi Yang and Yuhua Yang 2008 Research progress and application of chemist vapor deposition technology Water Resources and Hydropower Technology in Gansu Province 44 3
[8] Qicheng Liu, Peiying Liu and Ye Tao 2000 Investigation on TiN Coating by CVD and PCV methods Journal of Materials Engineering 12
[9] Bo Liang and Chuanxian Ding 2005 Phase composition of nanostructured zirconia coatings deposited by air plasma spraying Surface and Coatings Technology 191 2
[10] Yi Zeng and S W Lee 2002 Atmospheric plasma sprayed coatings of nanostructured zirconia Journal of the European Ceramic Society 22 3
[11] P Huber, D Manova and S Mandl 2003 Formation of TiN, TiC and TiCN by metal plasma immersion ion implantation and deposition Surface and Coatings Technology 174
[12] Zhengyong Cheng, Zhengcui Cheng and Jiangsu Li 2003 Hot Spraying Technology and Ceramic Coating Journal of Heat Treatment 18 1
[13] Xin Ji, Yiming Mi and Xiying Zhou 2009 Research Progress of Preparation Technology, Properties and Application Development of TiN Thin Film Journal of Hot Working Technology 38 4
[14] S J Bull, D G Bhat and M H Staia 2003 Properties and performance of commercial TiCN coating. Part 2: tribological performance Surface and Coatings Technology 163-164
[15] Changhong Song, Yaran Zhang and Shiming Li 2017 Research Progress on Fabrication of Ceramic Coatings by Plasma Spraying Technology Thermal Spray Technology 9 4
[16] Wenyan Qi, Fang Ye and Siwei Fu 2017 The Crystallization Mechanism of Reactive Plasma Spraying Journal of Ceramics 38 1
[17] Baoyan Liang, Yanli Zhang and Wangxi Zhang 2017 Synthesis of Carbide by Spark Plasma Sintering with Carbon Nanotubes as Carbon Source Journal of Ceramics 38 1