

Orthogonal experiment and microstructure analysis on TiC-TiB₂ multi-phase ceramic coating prepared by SHS reactive spraying

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Abstract: Utilizing self-propagating high-temperature synthesis (SHS) reactive spraying technology, the feeding self-combustion agglomerated particles composed of Ti, B₄C and C powders, TiC-TiB₂ multi-phase ceramic coatings were prepared on the steel substrates. Orthogonal experiment was carried out to optimize the spraying parameters. The phase component and microstructure of the coating fabricated at the optimized parameters were studied by XRD and SEM. The reactive mechanism in flying agglomerated particles was discussed. The optimized conditions, spraying distance of 220 mm, powders delivering gas pressure of 0.3 MPa and preheating temperature of 240 °C to sprayed particles, were obtained from orthogonal experiment. For the coating, porosity of 2.5% and HV 1 595 are achieved under the optimized parameters. The coatings are mainly composed of TiC_{0.3}N_{0.7}, TiB₂ and a little TiO₂. The SEM analysis shows the morphology of TiC_{0.3}N_{0.7} matrix in which the fine granular TiB₂ crystals evenly disperse. It is concluded that, as solo reactive units, the agglomerated particles would finally form into the coatings after going through four successive stages in the flame, which are, respectively, pregnant reaction, flight combustion, collision and structure transformation and solidification. The solid diffusion and dissolution-precipitation are the two mechanisms to control the synthesis reaction.

Key words: TiC-TiB₂ ceramic coating; SHS reactive spraying; orthogonal experiment; reactive mechanism

1 Introduction

SHS (self-propagating high temperature synthesis) reactive spraying which is a comprehensive technology from SHS and traditional thermal spraying attracted many scholars concerns to produce the ceramic coatings in recent years. A number of self-propagating systems such as Ti-C, Ti-B, Mo-Si, Cr-C, Al-CuO, and Ti-B-N etc[1–4] have been developed. Different from the traditional thermal spraying, SHS reactive spraying process has an exciting characteristic of blazing chemical energy emission from in-situ reaction, by which the reactant particles and ceramic products can even be melted into the liquid droplets. Fused droplets can be atomized and sprayed onto the surface of substrate to form protective ceramic coating with higher density and binding intensity.

Titanium carbide-titanium boride multi-phase ceramic has promising applications for protective armors,

tool knife materials, shaping moulds and so on, due to high melting point, high micro-hardness, especially high performance and thermal stability at high temperatures[5–6]. As one of the surface coating material, TiC-TiB₂ composite also plays more and more important role in the field of re-manufacture to the mechanical subassembly or equipment[7–8].

Generally, TiC-TiB₂ multi-phase ceramic can be chemically synthesized by the reaction between Ti, B₄C and C[9]. In this work, taking Ti-B₄C-C as combustion system, TiC_xN_y-TiB₂ coating was fabricated on steel substrate by SHS flame spraying. The spraying parameters were optimized by orthogonal experiment. The properties of the coatings were tested. The phase component and microstructure were analyzed. Spraying procedure and reactive mechanism were discussed.

2 Experimental

The chemical purification Ti powders, B₄C powders

and graphite powders with particle size of less than 20 μm were chosen as reactive raw materials. After dried and sifted, Ti B₄C and C powders were mixed in the ball-grinding machine in proper proportion, and then prepared into agglomerated particles in proper size range. The substrate was 45 carbon steel flat sample with dimensions of 50 mm×50 mm×6 mm. The substrate was cleaned by grinding wheel to remove the rust. And then the surface was roughened and preheated before spraying. Ni-Al alloy powders were used as the intermediate.

High energy flame spraying gun was used to prepare coatings. The input energy was the mixture of oxygen and acetylene. The pressures of oxygen and acetylene were adjusted to 0.6 MPa and 0.11 MPa, respectively. During spraying, faint carbide flame was maintained. Nitrogen was used as carrier and sluggish gas. Powder delivering ratio was about 20 g/min.

Three key spraying parameters, namely spraying distance, delivering gas pressure and preheating temperature to agglomerated particles, were optimized by orthogonal experiment.

The ceramic coating sample prepared at optimized conditions was incised along the cross section, and was polished for observation. The phase structure of the coating was investigated by X-ray diffraction (XRD) on a Dmax diffractometer with Cu K α (40 kV, 20 mA, $\lambda=0.154\ 06\ \text{nm}$) radiation with the 2θ angles ranging from 10° to 80° in steps of 0.02°. The surface morphology was observed with a JEOL JXA-840 scanning electron microscope (SEM) under 25 kV. Optical microscope was used to quantitatively analyze the porosity of the coatings. The micro-hardness of the coating was tested with MT-4 micro-hardness machine.

3 Results and discussion

Table 1 lists the schedule of the orthogonal test in which the key parameters including spraying distance (A), delivering gas pressure (B) and preheating temperature to agglomerated particles (C) are selected as three factors. And every factor has four levels to be optimized. The porosity and micro-hardness of the coatings are taken as the index points to evaluate the coatings performance under different factors and levels.

Detailed spraying conditions and the property results tested are listed in Table 2. From the mathematical processing of the data, some results can be concluded as follows. First, the factor of delivery gas pressure shows the most notable influence on whichever index point. Then preheating temperature is the relatively remarkable factor comparing with spraying distance. Second, coating with the lowest porosity and the highest micro-hardness would be prepared when 0.3 MPa, 240 °C and 220 mm were selected, respectively, for

delivering gas pressure, preheating temperature and spraying distance. Moreover, 2.5% porosity and HV 1 595 micro-hardness were achieved under the optimized spraying parameters.

Table 1 Factors and levels selected for orthogonal experiment

Level	A: Spraying distance/mm	B: Delivery gas pressure/MPa	C: Preheating temperature/°C
1	160	0.3	150
2	180	0.4	180
3	200	0.5	210
4	220	0.6	240

Table 2 Detailed scheme of orthogonal test and property results of sprayed coatings

Series No.	Level of A	Level of B	Level of C	Porosity/%	HV _{0.2}
1	1	1	1	6.7	1 248
2	1	2	2	7.8	1 287
3	1	3	3	8.7	1 070
4	1	4	4	9.6	982
5	2	1	2	6.0	1 304
6	2	2	1	4.2	1 379
7	2	3	4	6.5	1 281
8	2	4	3	8.3	1 171
9	3	1	3	6.0	1 341
10	3	2	4	5.7	1 451
11	3	3	1	7.5	1 230
12	3	4	2	13.8	927
13	4	1	4	2.5	1 595
14	4	2	3	2.8	1 550
15	4	3	2	9.3	1 035
16	4	4	1	9.7	998

XRD analysis was used to distinguish phase structure of the coating sprayed at the optimized condition. As shown in Fig.1, the diffraction pattern indicates that the coating is mainly composed of TiC_{0.3}N_{0.7} and TiB₂ as well as a little TiO₂.

Accordingly, Fig.2 gives the morphology of the microstructure. From Fig.2(a), dense coating with low porosity can be seen. As shown in Fig.2(b), phase distribution can be clearly observed that numerous irregular black TiB₂ particles evenly immerse into grey TiC_{0.3}N_{0.7} matrix.

In SHS reactive flame spraying, chemical combustion and phase transformation synchronously occur and mutually affect with physical process. Once agglomerated particles are fed and dispersed into the

flame, acting as solo reactive units, they would finally form into the coatings after going through four successive stages in the flame, which are, respectively, pregnant reaction, flight combustion, collision and structure transformation and solidification.

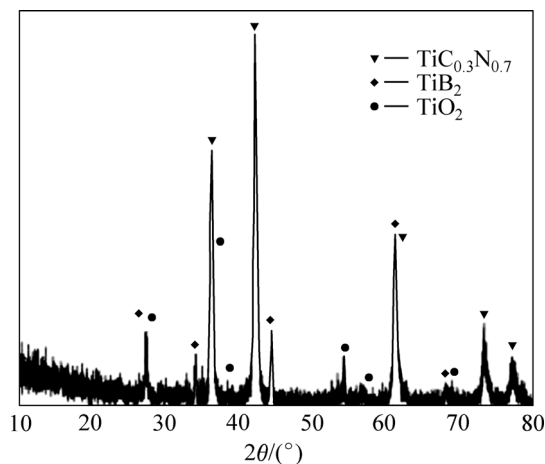


Fig.1 XRD patterns of multi-phase ceramic coating prepared at optimized parameters

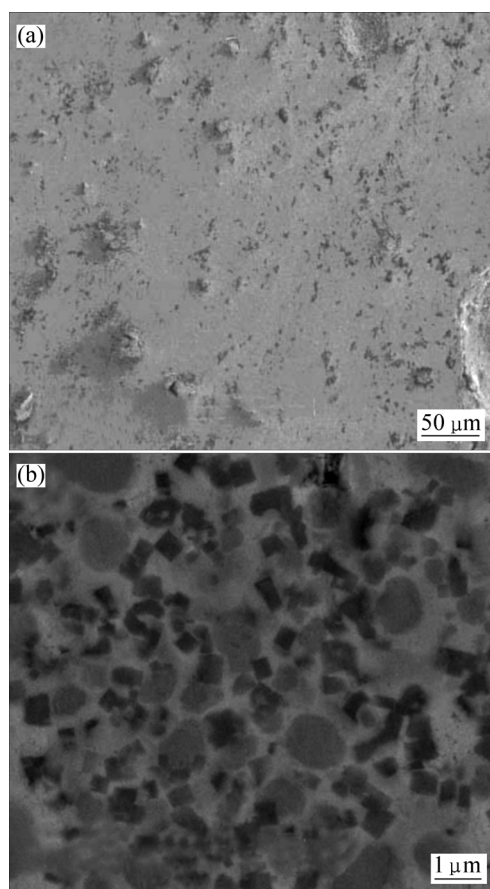


Fig.2 SEM microstructures of multi-phase ceramic coating observed under different magnifications

First of all, the state of fed particles is crucial for spraying process. In-situ SHS reaction between Ti and

B₄C powders merely occurs in an agglomerated particle. Fig.3 shows the morphology of agglomerated particles.

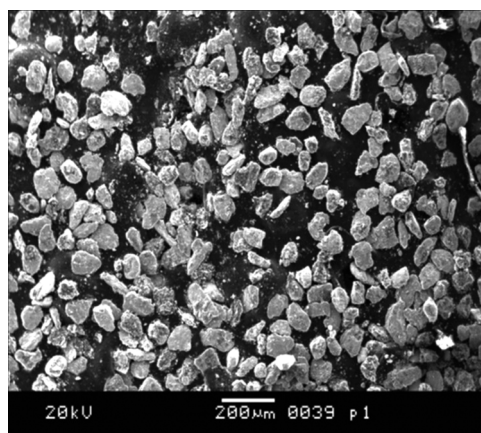


Fig.3 SEM morphology of agglomerated particles

At the beginning of the flight, SHS chemical reaction would be ignited at the moment when the particles are heated to the critical temperature due to the rapid energy accumulation. SHS combustion synthesis takes place as described in Eqns.(1) and (2).



The adiabatic temperature of this reaction is about 3 200 K calculated from thermodynamics. The exothermic reaction with the accessory flame energy can melt the particles into liquid droplet, which are very helpful to produce high performance multi-phase coating with low porosity and good component dispersion between various phases. So from Fig.2 even and homogenous coating shows great variation from the lamella-like structure obtained by traditional thermal spraying.

Water quenching method, which was initially used to study the structure transformation by ROGACHEV et al[10], was carried out to observe the change and state of the particles in flight. Fig.4 gives the morphology of the particles water quenched at the flight distance of 220 mm. It clearly indicates that the original particles are almost melted and become spherical.

The phase transformation and solidification perform with the propagating of combustion wave.

Two modes exist in the ignition of reactive agglomerated system and the spread of the combustion wave. One is self-propagating mode and the other is thermal explosion mode. Self-propagating mode often takes place in particles with smaller size. And thermal explosion occurs intensively in bigger particles at an instant due to energy accumulation.

Two mechanisms, solid diffusion and dissolution-precipitation, respectively, control the synthesis reaction.

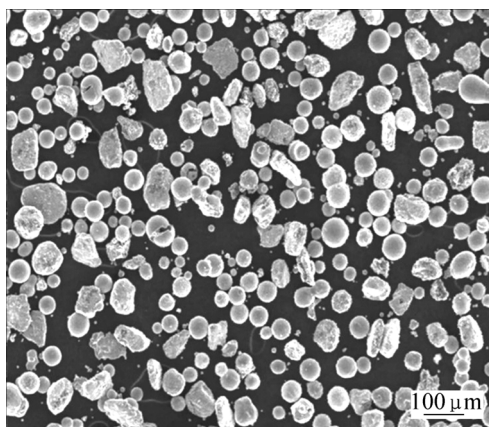


Fig.4 SEM morphology of particles water-quenched at flight distance of 220 mm

Before the presence of liquid titanium melted from solid powders, the reaction is controlled by solid diffusion between the individual powders in one agglomerated particle. After titanium is partially melted the procedure is determined by dissolution-precipitation mechanism. Atoms C and B dissolve and spread into the liquid Ti chemically combining with Ti atoms. Subsequently, the eutectic crystal resultant of TiC-TiB₂ precipitates from the liquid.

However, not as ideal as described by chemical equation, nitrification and oxidation of the reactants during spraying are inevitable for the reason of exposure to the air. In-situ TiC and TiN trend to mix into Ti(C, N) solid solution. It can be deduced, that from Fig.2(b) that the matrix with different brightness is corresponding to the different solubility of both atoms C and N. Furthermore, the surrounding oxygen leads to oxidation of titanium and over-burning of B₄C. Thermodynamic calculation of enthalpy and Gibbs free energy for all possible reactions indicates that B₄C is easy to oxidize, which can further lead to the decrease of TiB₂ content compared with as expected.

4 Conclusions

1) Using Ti-B₄C-C as combustion system TiC_xN_y-TiB₂ multi-phase ceramic coatings were prepared by SHS reactive flame spraying on steel substrate. By orthogonal experiment three key parameters were optimized. Spraying distance of 220 mm, delivery gas

pressure of 0.3 MPa and preheat temperature to particles at 240 °C. And the highest performance with 2.5% porosity and HV1 595 are achieved in the coating.

2) The coating is composed of Ti(C, N) solid solution (mainly TiC_{0.3}N_{0.7}) matrix with different solubilities of atoms C and N, in which irregular TiB₂ particles disperse homogeneously and evenly.

3) In-situ SHS reaction between Ti and B₄C powders merely occurs in an agglomerated particle. The exothermic reaction with accessory flame energy can melt the particles into liquid droplet, which can be proved by water quenching method. Self-propagating and thermal explosion are the two modes existing in the ignition of reactive agglomerated system. Solid diffusion and dissolution-precipitation are the two mechanisms which control the synthesis reaction.

References

- [1] ROBERTA L, ROBERTO O, GIACOMO C. Self-propagating combustion synthesis and plasma spraying deposition of TiC-Fe powders[J]. *Ceramics International*, 2003, 29: 519–526.
- [2] KUNG H, LU Y C, BARTLETT A H, CASTRO R G. Structural characterization of combustion synthesized MoSi₂-Si₃N₄ composite powders and plasma sprayed MoSi₂-Si₃N₄ composites[J]. *J Mater Res*, 1998, 13(6): 1522–1529.
- [3] DU Xin-kang, WANG Jian-jiang. Al₂O₃-Al₂Cu₃ coating produced by SHS reactive spraying[J]. *Materials Science Forum*, 2003, 423/425: 547–550.
- [4] TEE K L, LU L, LAI M O. Improvement in mechanical properties of in-situ Al-TiB₂ composite by incorporation of carbon[J]. *Mater Sci Eng A*, 2003, 349: 227–231.
- [5] WANG H Y, JIANG Q C, ZHAO Y Q. Fabrication of TiB₂ and TiB₂-TiC particulates reinforced magnesium matrix composites[J]. *Mater Sci Eng A*, 2004, 372: 109–114.
- [6] LEVASHOV E A, LARIKHIN D V. Self propagating high temperature synthesis of functionally graded PVD targets with a ceramic working layer of TiB₂-TiN or Ti₅Si₃-TiN[J]. *Journal of Materials Synthesis and Processing*, 2002, 10(6): 319–330.
- [7] KUSTAS F, MISHRA B, ZHOU J. Fabrication and characterization of TiB₂/TiC and tungsten co-sputtered wear coatings[J]. *Surface and Coatings Technology*, 2002, 153: 25–30.
- [8] KITTY W L, CHEN Y H, CHUNG Y W. Hardness, internal stress and thermal stability of TiB₂/TiC multilayer coatings synthesized by magnetron sputtering with and without substrate rotation[J]. *Surface and Coatings Technology*, 2004, 177/178: 591–596.
- [9] KLINGER L, GOTMAN I, HORVITZ D. In situ processing of TiB₂-TiC ceramic composites by thermal explosion under pressure: Experimental study and modeling[J]. *Mater Sci Eng A*, 2001, 302: 92–99.
- [10] ROGACHEV A S, MUKAS A S, MERZHANOV A G. Structural transitions in the gasless combustion of titanium-carbon and titanium-boron systems[J]. *Dokl Phys Chem*, 1987, 297: 1240–1243.

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