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Spray process for in situ synthesizing Ti(C,N)-TiB_2-Al_2O_3 composite ceramic coatings

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Spray process for in situ synthesizing Ti(C,N)-TiB_2 -Al_2O_3 composite ceramic coatings

Jian Zhou [1, a], Hongwei Liu [1, b], Sihao Sun [2, c]

[1]National Key Laboratory of Science and Technology on Remanufacturing, Armored Forces College, Beijing 100072, China
[2]The military representative Bureau of army in Nanjing, Fujian, Fuzhou 350000,China

[a]1025570433@qq.com, [b]hongwlau@126.com, [c]mousehh@126.com

Abstract. Using core wires with Ti-B4C-C as core and Al as strip materials, Ti(C,N)-TiB2-Al2O3 composite ceramic coatings were prepared on 45 steel substrates by the reactive arc spray technology. The influence of spray voltage, current, gas pressure and distance on the coatings was discussed. The spray parameters were optimized with porosity of the coatings as evaluation standard. The results showed that the most important factor which influences the quality of the coatings was spray distance. Then spray gas pressure, current and voltage followed in turn. The optimum process was spray current of 120A, voltage of 36, gas pressure of 0.7MPa and distance of 160mm. The porosity of coatings prepared in this spray process was only 2.11%. The coatings were composed of TiB2, TiC0.3N0.7, TiN, Al2O3 and AlN. Good properties and uniform distribution of these ceramic phases made the coatings have excellent comprehensive performances.

1. Introduction

Ceramics have virtues of high strength, good wear- and corrosion-resistance. That's why they are regarded as favorable structural or coating materials of components working on rigorous service conditions. However, the inherent fragility of ceramics restricts their applications. Toughening ceramics becomes a cosmopolitan difficult problem. Researches indicated that composite ceramics composed of some single-phased ceramics with good physical and chemical compatibility have higher toughness than the single-phased ceramics, and the toughness of ternary ceramics (such as TiB2-TiC-Al2O3, TiB2-TiC- Al2O3-SiC et al) is higher than that of the binary ceramics (such as TiB2-TiC, TiB2- Al2O3, TiC-Al2O3, Al2O3-SiC et al) [1-5]. Among them, TiB2-TiC, TiB2-Ti(C,N) and TiB2-TiC-Al2O3 were widely investigated as coating materials[6,7]. They were widely reported to be prepared by reactive flame spray, argon arc cladding, lazer cladding, electro-thermal explosion spray and reactive plasma spray, whereas seldom reported to be prepared by arc spray technology[2,3,8-11].

As well known, the arc spray technology is mainly used to prepare metal coatings, or ceramic grains strengthening metal-based composite coatings, whose main composition is still metals, but hard to prepare entire ceramic coatings. This paper developed a new ceramic coating preparation method of reactive arc spray (abbr. RAS) by combining self-propagating high-temperature synthesis (abbr. SHS) with arc spray. Ti(C,N)-TiB2 -Al2O3 composite ceramic coatings were prepared on the surface of 45 steel by RAS with core wires with Ti-B4C-C as core and Al as strip materials. The influence of spray voltage, current, gas pressure and distance on the coatings was discussed so as to optimize the spray parameters. The work can provide technological guidance for preparing composite ceramic coatings by RAS.

2. Experimental Procedures

The reactive core wires were prepared with Ti powders (purity of 99.9% and less than 38μm in size), B_4C powders (purity of 98% and less than 5μm in size) as core materials and Al as strip materials. The mole ratio of Ti to B_4C was 3:1. The diameter of reactive core wires was 3mm. CMD-AS-3000 high velocity arc spray system was used to prepare coatings with 45 steel as substrate. The spray parameters depended on the experimental design. Before the spray process, the substrates were sandblasted and deposited with Ni as bottom layer.

The microstructure of coatings was observed with NoVa Nano 650 scanning electron microscope. The composition was analyzed with D/max2200PC X-ray diffraction. Metallographic method was used to measure the porosity of coatings. Ten areas were measured and the average value was chosen to be the porosity of the tested coating. The bonding strength between the coating and substrate was tested in MTS 810 material tensile test machine with loading velocity of 1mm/min according to GB/T8642-2002. The module of the coatings was tested with XP Nano Indenter. Parameters were set as: displacement precision 0.01nm, position precision 400nm, load precision 50nN, maximum indentation depth 500μm, and maximum load 600mN. The hardness of the coatings was tested with Wilson micro-hardness instrument. Parameters were set as: load 200g and time 15s. The wear-resistance of coatings was tested with CETR-3 multi-function abrasion tester. Parameters were set as: load 100N, time 30min and frequency 10Hz.

3. Results and discussion

3.1. Influence of spray process on the porosity of coatings.

Pores will heavily influence the comprehensive performances of sprayed coatings. Therefore porosity of coatings was chosen to be evaluation index of coating quality to discuss the influence of the spray process on the coatings.

(1) Spray voltage. The porosity of the coatings prepared with spray current of 120A, gas pressure of 0.7MPa, distance of 160mm and voltage of 28V, 32V, 36V and 40V respectively was shown as Fig.1. It was indicated that when the spray voltage was low as 28V, the porosity was relatively high, and when the voltage increased as 32V, the porosity decreased evidently. Whereas the decreasing trend was unconspicuous after the voltage was higher than 32V.

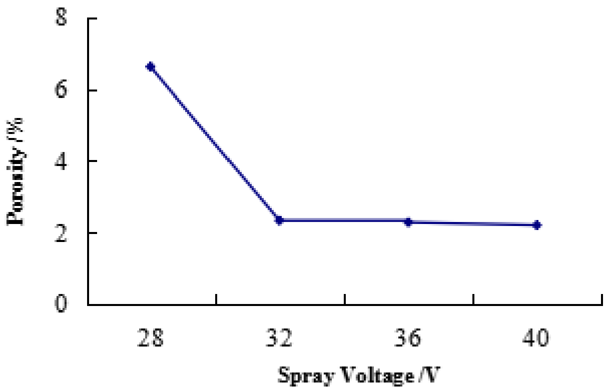

Figure.1 Porosity of coatings prepared with different spray voltage

During the spray process, the voltage mainly influences the output energy, further influences the arc temperature. When other spray parameters keep invariable, larger the voltage is, higher the arc temperature is. In this work, after the spray materials entered the arc field, its self-propagating high-temperature synthesis (SHS) reaction was ignited by the arc. The velocity of the spray particles was quick, whereas the length of the arc was short. When the spray voltage was low, the arc temperature was not high enough to ignite all of the spray particles. The SHS reaction of them couldn't be completed fully, which led to high coating porosity. When the spray voltage was higher than 32V, the arc could ignite the SHS reaction of spray particles fully. So the coating porosity was much lower.

(2) Spray current. The porosity of the coatings prepared with spray voltage of 36V, gas pressure of 0.7MPa, distance of 160mm and current of 100A, 105A, 115A and 120A respectively was shown as Fig.2. It was shown that the coating porosity took on the character of increasing first, and then decreasing with the increase of spray current. The spray current mainly controlled the supplying velocity of spray wires. When spray current increased, the supplying velocity of wires became quicker, and the heated time of the spray particles in the arc became shorter relatively. So the SHS reaction of spray particles was negatively influenced. That's why the porosity of coatings became bigger with the increase of spray current. However, it should be noticed that the spray current also influenced the medium-term flight process and the latter bumping process with the substrate except for the early heating process. The particle deposition on the substrate was a discrete process during the reactive arc spray process. The distance between particles in the flight and the interval between particles depositing were all controlled by the supplying velocity of spray wires, furthermore controlled by spray current. Properly increasing the spray current wouldn't enhance the heated process, and could enhance the heat effect between spray particles, which would defer the cooling of particles and prolong the high temperature phase of them. That was why the coating porosity decreased with the increase of spray current. However, the changing range of porosity was relatively small in the tested area, which indicated that the spray current had slight influence on the porosity. That had been proved by the latter orthogonal experiments.

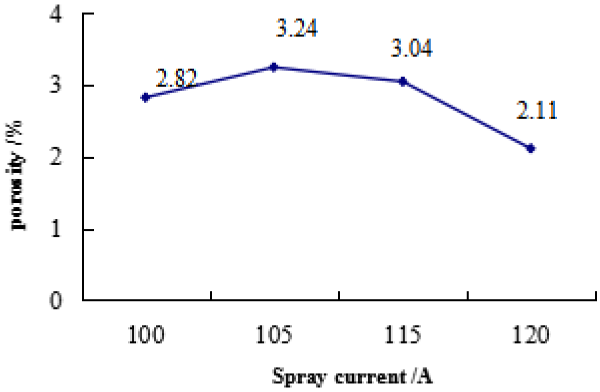

Figure.2 Porosity of coatings prepared with different spray current

Gas pressure. The porosity of the coatings prepared with spray voltage of 36V, current of 120A, distance of 160mm and gas pressure of 0.4MPa, 0.5MPa, 0.6MPa and 0.7MPa respectively was shown as Fig.3. It was shown that the coating porosity decreased with the increase of gas pressure evidently, which was same as the rule of common thermal spray. The reason was evident too. The velocity of spray particles was controlled by the spray gas pressure. When the spray distances kept invariable, the velocity of spray particles depositing on the substrate was mainly decided by the gas pressure. With the increase of gas pressure, the deforming and spreading ability of molten particles on the substrate enhanced too, which would be helpful to remove the gas in the coatings. So the coating porosity decreased evidently.

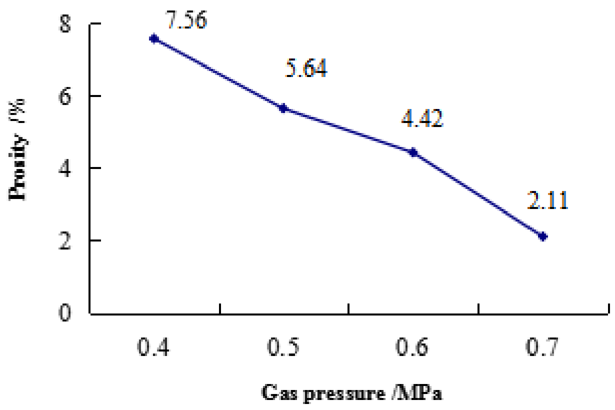

Figure.3 Porosity of coatings prepared with different spray gas pressure

(4) Spray distance. The porosity of the coatings prepared with spray voltage of 36V, current of 120A, gas pressure of 0.7MPa, and distance of 140 mm, 160 mm, 180 mm and 200mm respectively was shown as Fig.4. It was shown that the spray distance greatly influenced the coatings porosity. With the increase of spray distance, the coatings porosity decreased at first, and then increased greatly. The spray distance influenced the coating porosity in two different aspects during the reactive arc spray process. On one hand, the spray distance influenced the depositing velocity of particles on the substrate, so as to influence the coating porosity. When the spray distance was short, the spray particles were in the being accelerated period. That was why the porosity of coatings was high. When the spray distance was as long as 160mm, the particles reached near their fastest velocity, so the porosity of coatings was low. On the other hand, the physical state of spray particles during the depositing process was also the important factor influencing the quality of coatings. The spray particles experienced a series of thermal processes of being heated, reacting and rapidly solidifying. When the spray distance was optimal, the spray particles were in good state of being molten, that was good for the densification for the coatings.

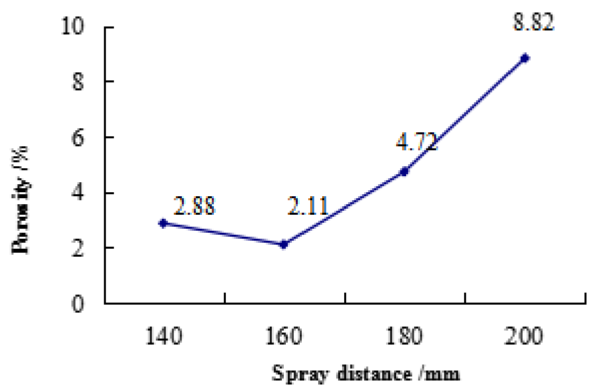

Figure.4 Porosity of coatings prepared with different spray distance

3.2. Orthogonal optimization of spray parameters

Different levels of parameters in orthogonal experiment were shown as Tabe.1. The orthogonal experiment design and tested results were shown as Tabe.2. The results showed that the optimal spray parameters were spray current of 120A, voltage of 36V, gas pressure of 0.7MPa and distance of

160mm. To validate the conclusion, coatings were prepared by this spray process. It was found the average porosity of them were as low as 2.11%, which is lower than any tested results in Table.2.

Table 1 Factors and levels of reactive arc spray technology parameters

Levels	Gas pressure/MPa	Voltage/V	Current/A	distance/mm
1	0.5	32	100	140
2	0.6	36	110	160
3	0.7	40	120	180

By the analysis of variance, it can be found that the most influential factor was spray distance. Then gas pressure, current and voltage followed in turn. That was consistent with what was analyzed before.

Table 2 Orthogonal experiment design and results analysis

Test number	Pressure/MPa	Voltage/V	Current/A	Distance/mm	Porosity（%）
1	0.5	32	100	140	6.33
2	0.5	36	110	160	2.33
3	0.5	40	120	180	4.44
4	0.6	32	110	180	5.78
5	0.6	36	120	140	4.67
6	0.6	40	100	160	3.89
7	0.7	32	120	160	2.33
8	0.7	36	100	180	3.00
9	0.7	40	110	140	3.78
k_1	4.37	4.81	4.41	4.93	
k_2	4.78	3.33	3.96	2.85	
k_3	3.04	4.04	3.81	4.41	
R	1.74	1.48	1.60	2.06	

3.3. Microstructure

The XRD analysis result was shown as Fig.5. It was found that the coatings were composed of several ceramic phases of TiB_2, $TiC_{0.3}N_{0.7}$, Al_2O_3, TiN, AlN. These ceramic phases had favorable physical and chemical compatibility, which made them be able to form multi-phased ceramics with excellent performances. There were no diffraction peaks of Ti, B_4C and Al in Fig.5, which meant the SHS reaction of the spray system had finished during the spray process. It was the remarkable virtue of reactive arc spray different from the common arc spray technology that multi-phased ceramic coatings can be in situ synthesized by the SHS reaction of spray system. Besides Ti, B_4C, Al and C (decomposed from precursor sucrose), O_2 and N_2 would take part in the reaction of the spray system during the spray process due to the atmosphere spray condition. The multi-system became composite coatings composed of TiB2, TiC0.3N0.7, Al2O3, TiN, AlN through a complicated chemical reaction process [13].

The microstructure of the coatings was shown as Fig.6. The coatings had the typical sprayed layered structure. It was density and the distribution of different phases was uniform. The coatings were mainly composed of light grey continuous base phase A, dark grain phase B, grey discontinuous phase C and a little of porosities D. It can be judged by EDS that A, B, C were TiB_2, $TiC_{0.3}N_{0.7}$ and Al_2O_3 respectively. TiN and AlN hadn't been observed by SEM because of a small amount of them. There was some pore phase in the coatings besides the above phases. The pores came from the undischarged gases during the transforming and spreading processes of spray particles on the substrates. The strengthening and fracture toughness of coatings can be improved by dispersion reinforcement mechanism because of the microstructure of continuous phase uniformly distributed with other discontinuous hard phases. That was of significance to gain the coatings with favorable comprehensive performances.

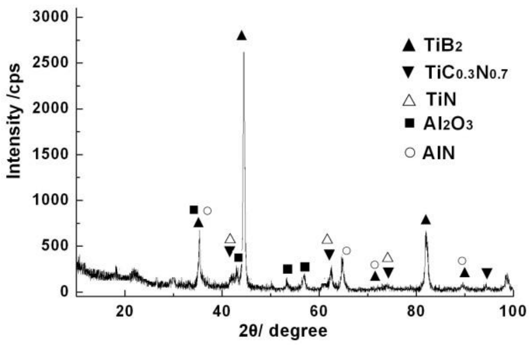

Figure.5 XRD result of composite coatings

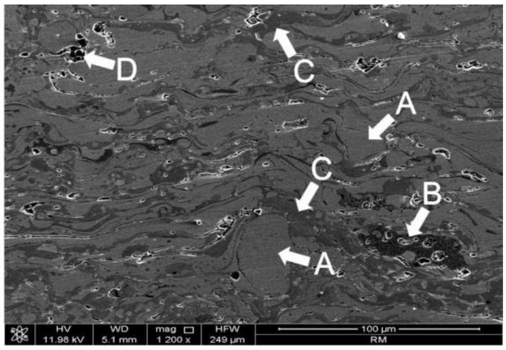

Figure.6 SEM photo of composite coating

3.4. Mechanical properties

The tested properties of the coatings were shown as Table.3. The binding strength between coatings and substrates was 20.4±3.2MPa. The average micro-hardness and elastic module of coatings were 1024±309$HV_{0.2}$ and 462±17GPa, which were 3.8 times and 2.1 times to that of 45 steels respectively. The coatings were composed of hard ceramic materials, whose hardness was much higher than that of substrate. That's why the micro-hardness and elastic module of coatings were much higher. The value of tested micro-hardness fluctuated in a relatively large range because the coatings contained several phases with different hardness as well as some pores. The friction coefficient of coatings was 0.52±0.3, which was 25% lower than that of 45 steel. And the abrasion resistance of coatings was 3 times higher than that of substrates. As a whole, the composite coatings had excellent comprehensive performances due to the good performances and uniform distribution of its component ceramic phases.

Table 3. Main mechanical properties of coatings

binding strength /MPa	micro-hardness /$Hv_{0.2}$	elastic module / GPa	friction coefficient	abrasion loss (coatings)/mm^3	abrasion loss (45 steel) /mm^3
20.4±3.2	1024±309	462+17	0.52±0.3	7.2±0.8	32.8±0.5

4. Conclusion

Due to the in situ synthesizing of coating materials during the reactive arc spray process, the most influential factor to the coatings quality is spray distance, then spraying gas pressure, current and voltage follow in turn. The optimal reactive arc spray parameters are distance of 160mm, spraying gas pressure of 0.7MPa, current of 120A and voltage of 36V. The porosity of composite coatings prepared in this optimal process was only 2.11%. The in situ synthesized composite coatings were composed of TiB_2, TiB, $TiC_{0.3}N_{0.7}$, TiN, Al_2O_3 and AlN. The average bonding strength between the coatings and substrate was 20.4MPa, the average micro-hardness and elastic module were 1024$Hv_{0.2}$ and 462GPa, and the friction coefficient of the composite coatings was 0.52. The Ti(C,N)-TiB_2-Al_2O_3 composite ceramic coatings had excellent comprehensive performances.

Acknowledgments
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