Influence of oxidized ceramics on the tribological properties of Ni60/WC composite coatings

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Abstract

Ni-based composite ceramic coatings with good comprehensive performance are obtained by a supersonic plasma spraying process. A ceramic powder is added to a Ni60/WC powder to make the surface of the sprayed sample more uniform and compact. Pores are present on the surface of the two composite ceramic coatings prepared by NiWT(Ni60/WC + TiO2) and NiWA(Ni60/WC + Al2O3), as well as five phase components. In the microscopic morphology of the two composite ceramic coatings, the surface composition of the NiWT coating is relatively uniform and the surface of NiWA exhibits a cluster structure with more pits than NiWT. The friction coefficient of the NiWT coating at 200 r min−1 is between 0.40 and 0.43 and that of the NiWA coating is between 0.35 and 0.38. Simultaneously, the abrasion width and wear volume of the NiWT and NiWA coatings are small compared with the substrate, while the abrasion width and volume of the NiWT coating are smaller. The composite ceramic coatings prepared by the addition of two kinds of oxidized ceramics, through comparative analysis of the experiment, showed that NiWT had an improved surface micro-morphology and wear resistance than NiWA. The wear morphology of NiWT showed a wear mechanism of abrasive particles and the wear morphology of NiWA showed a fatigue wear mechanism.

1. Introduction

In recent years, with the rapid development of surface engineering technology, the development of thermal spraying coatings with good wear and corrosion resistance has become a major research direction in the field of remanufacturing [1–3]. In addition, nickel-based autolytic alloys, as human spraying materials, are mainly used in mechanical, material and chemical industry surface wear applications. NiCrBSi has become a research hotspot as a result of its excellent mechanical properties and corrosion and wear resistance, and has been widely applied [4–7]. At present, with researchers obtaining better surface coating performance by adding different alloy phases to Ni60 (NiCrBSi), WC has wear resistance and Ni60/WC coatings formed by adding Ni60 powder alloy have good wear and corrosion resistance, which has been applied in many industries [4, 8, 9]. Nanostructured TiB powders were mixed with a Ni60 alloy ball mill for thermal spraying to obtain nanocomposite coatings with good structure, excellent mechanical properties and anti-sliding wear properties [10]. A TiN powder and Ni60 were mixed by thermal spraying to form a composite coating and then re-dissolved to obtain a coating with improved corrosion and wear resistance and stability [11]. By adding Ti to a Ni60/WC powder alloy, a TiC ceramic phase with wear resistance was obtained in the composite coating after thermal spraying, which further improved the wear resistance of the coating [12]. In order to expand the interface between the spraying powder particles reaction, improve the compactness and uniformity of coating surface, and at the same time improve the coating corrosion resistance, wear resistance and service life, this
thesis adopts Co coating WC particles as a ceramic material mixed with Ni60 powder machine, by adding the oxide ceramic particles preparation of Ni base function composite coating materials, and wear properties of epoxy coating were analyzed.

2. Experimental procedure

2.1. Sample material

In this work, the preparation process of a supersonic plasma spraying method, with the use of TiO2 and Al2O3 as Ni60/WC powder add-in phases is studied, in Ni60/WC powder, WC powder is made up of 12%wt.Co and 88%wt.WC (Chengdu nuclear 857 new materials co. Ltd). We use the surface of a 45# steel substrate material to prepare two kinds of Ni60/WC coatings at the same load and speed conditions. The microstructure and wear resistance and mechanisms of the two coatings are also discussed.

The Ni60(NiCrBSi) powder used in the test, the particle size of the powder was 45–105 μm, The density of the powder was 4.19 g cm⁻³. Its main chemical components are shown in table 1.

| Table 1. Chemical composition of NiCrBSi (wt%). |
| Cr | B | Si | Fe | C | Ni |
|---|---|---|---|---|---|
| 15–17 | 3.0–4.0 | 3.5–5.0 | ≤5 | 0.6–1.2 | Bal. |

The test adopts #45 steel as the matrix material, the sample size is 20 × 20 mm, and the density is 7.85 g cm⁻³. Its main chemical components are shown in table 2.

| Table 2. Chemical composition of steel 45# (wt%). |
| Fe | C | Si | Mn | P |
|---|---|---|---|---|
| Main | 0.42–0.50 | 0.17–0.37 | 0.50–0.80 | ≤0.03 |
| S | Cr | Ni | Cu |
| ≤0.035 | ≤0.25 | ≤0.25 | ≤0.25 |

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2.2. Sample preparation

In order to improve the bonding strength of the coating and matrix, the surface of the matrix material was cleaned before spraying. The surface of the matrix material was smoothed by a grinding wheel and all dirt on the surface was cleaned by acetone and alcohol. A sandblasting machine could be used to sandblast the coating, after which the roughness of the matrix surface could be increased, so as to improve the bonding strength of the two materials [13]. In contrast, sandblasting can change the distribution of the residual stress, thus effectively avoiding the stress concentration of the coating. Firstly, the matrix parts were preheated in the heat preservation furnace to remove the moisture on the surface of the parts. Simultaneously, the contact temperature of the two materials could be increased, the thermal expansion coefficient of the two materials could be reduced and crack generation of the coating could be avoided [14]. A proper heat treatment could also improve the service life of the coating.

2.3. Spraying equipment and process parameters

The model of the coating preparation instrument adopted supersonic plasma spraying equipment (DH-2080, Shanghai dahao spraying co. Ltd), which is mainly composed of a spray gun, a feeding device, a dusting device and a cooling water pump. The process parameters of spraying equipment are shown in table 3.

NiWT and NiWA ceramic composite coatings were prepared by supersonic plasma spraying. During the spraying process, the powder feeder sent the spraying powder into the plasma jet. After rapid heating, the powder presented a molten or semi-molten state, and rapidly collided with the matrix.
2.4. Wear test
The coating wear is tested by friction and wear testing machine (HT-1000, Lanzhou zhongke kaihua technology development co. Ltd). The experimental equipment is shown in figure 1. The geometric size of the matrix material was 10 × 20 mm. A load of 50 N, a rotation speed of 200 r min⁻¹ and a rotation radius of 5 mm were adopted. The technical indexes of the friction and wear testing machine are shown in table 4.

The friction pair for the wear experiment adopted a GCr15 ball with a diameter of 5 mm. A dry friction experiment was carried out on the friction and wear testing machine. GCr15 had high hardness, uniform organization, good wear resistance and high contact fatigue performance. The contents of GCr15 chemical components are shown in table 5.

3. Result and analysis
3.1. Coating surface morphology
The coating surface scans are shown in figures 2(a) and (b) for NiWT and NiWA, respectively. Two kinds of the porosity of the coating surface are more. The causes of the formation of porosity may be as follows. On the one hand, the collision matrix powder surface underwent splash and powder particle mutual accumulation. On the other hand, they may fail to fully mix, leading to the appearance of pores. Simultaneously, most of the particles in
figure 2(a) were molten particles, while the presence of molten particles could also be observed in figure 2(b), there were also non-molten particles.

3.2. Coating phase structure
As can be seen from figure 3(a), the Ni coating was mainly made up of the gamma phase, followed by the WC alloy, with small amounts of FeNi3, Cr2Ni3 and alpha Al2O3. Two new alloy compound phases, FeNi3 and Cr2Ni3, also appeared. The reasons for their formation were that the chemical properties of Fe at high temperatures were energetic and the nickel reaction generated new metal compounds. In figure 3(b), there were also γ-Ni, WC, FeNi3 and Cr2Ni3 in the phase analysis, with no TiO2 found, but Fe3Ni12 present. The reason for not finding TiO2 was that the amount of addition was too small and not within the detection range of the energy spectrometer. The reason for the detection of Fe3Ni12 was caused by the chemical reaction of Ni-Fe.

3.3. Coating microstructure
The NiWT and NiWA coatings were prepared on a 45# steel matrix. The samples were polished using different sandpapers, with the coating section scan shown in figure 4. Figure 4(a) shows the section diagram of the NiWT coating. It can be seen that the coating was divided into three regions, namely, the matrix, the binding and the coating regions. Into the layered coating area and the associativity of coating and base is good, but for the coating area it can be found that there were some part of the pore because: (1) the process of spraying and the powder materials sputtering in shock when the substrate surface, so the powder was not entirely without vacant land filling on the surface of substrate material; (2) the spraying powder material itself was porous, so the impact on the surface there were pores [15–18]. Figure 4(b) gives the section diagram of the NiWA coating, which is also composed of the same three regions. The coating was well combined with the matrix, but there were obvious pits in the matrix, which may be caused by coarsening. Meanwhile, the coating area was also layered and orderly spread, but there were also some pores in the coating area.

The two coating materials, NiWT and NiWA, were polished using different mesh sandpapers by means of a metallographic sample polishing machine. The surface was then cleaned with anhydrous ethanol and dried with a hair dryer. The surface microstructure of the coating was shown in figure 5.

Figure 5(a) shows the NiWT coating scanning diagram and figure 5(b) presents the NiWA coating surface scanning diagram. It can be seen that the surface composition of figure 5(a) is relatively uniform with some pits.

3.4. Friction and wear test
At room temperature, a 50 N load was applied and the running time was set at 30 min. The variation law of the friction coefficient of the two coatings was obtained, as shown in figure 6. Figure 6(a) shows the changing trend of the
NiWT coating friction coefficient and figure 6(b) shows the changing trend of the NiWA coating friction coefficient. It can be seen from the figure that the friction coefficient can be roughly divided into three stages, an initial stage for ‘running-in’ of ~3 min, which quickly increased to a maximum friction coefficient. The reason for GCr15 was just the contact friction pair and the coating surface, the friction surface was relatively rough, friction pair and bumps on the coating first contact, so there was a rapid increase in the friction coefficient. The second stage was the ‘transition stage’. After the friction coefficient reaches the peak value in the run-in stage, it gradually decreased. The reason was that the convex peak of the contact surface was cut off and flattened, and the coating surface becomes relatively smooth. The third stage was the ‘stable running-in stage,’ which can be seen after 10 min gradually producing a stable friction coefficient [19]. The NiWT coating friction coefficient was 0.40–0.43 and the NiWA coating friction coefficient was 0.35–0.38 range because the uneven surface tends to smooth. Simultaneously, the GCr15 friction pair after wear and tear, by the point contact surface contact, friction contact area increase, the wear rate decreases. However, the friction coefficient in a certain area was larger or smaller, the reason was that a tiny chip may wear into the furrows, causing the contact surface to be rough, so the coefficient of friction may increase, at the same time in the process of continuous wear, abrasive dust into the pit, likely also leading to contact by uneven becoming relatively smooth, with a smaller friction coefficient.

After 30 min of friction and wear experiments between the substrate and the coating, the wear morphology diagram was obtained, as shown in figure 7. Figure 7(a) presents the wear morphology of 45# steel as the matrix diagram. Figure 7(a1) shows the 45# steel wear surface topography to enlarge. The friction marks of the
substrate are very clear and there is obvious furrow and part of the chip. Simultaneously, there was a smaller flake pit and the steel mainly experiences abrasive wear because its material strength is weak, friction pair GCr15 ball in turns, will pressure into the base material, so produce furrows, rotating chip produced during grinding at the same time. Figure 7(b) shows the NiWT coating wear, where a narrow grinding crack can be seen. Figure 7(b1) shows the grinding crack and local topography, the NiWT coating surface furrow lighter, less wear debris, but produced a large peeling pit, so the NiWT coating mainly experiences abrasive wear and tear, accompanied by fatigue wear. This was because after adding the coating, in which high hardness of the hard phase and increased the wear resistance of the material, furrow becomes shallow, peeling pit was due to the coating surface micro raised hard phase and in the process of friction and wear experiments, continuously through the impact of the shear stress of GCr15, microcracks occur. As the experiment goes on, the spalling pit was formed. Figure 7(c) shows the NiWA coating wear, narrow also appeared on the surface of grinding crack, figure 7(c1) for grinding crack local topography, NiWA can be seen from the figure in the furrows of the coating surface is not visible, but you can see more peeling pit, so the NiWA coating occurred mainly fatigue wear and spalling pit is also due to the friction and wear experiments shear stress, constantly shedding of hard phase, and NiWT and NiWA coating friction marks is not obvious, it can be seen that two kinds of coatings are effective in improving the wearability of the matrix.

When the rotational speed was 200 r min$^{-1}$, compared with the wear morphology of the matrix material, the NiWT and NiWA coatings significantly improved the wear resistance of the matrix, making furrow marks shallower and grinding debris less. Compared with the NiWA coating, the NiWT coating wear morphology was
coarser. This was also verified by at 200 r min$^{-1}$, where the NiWT coating of the friction coefficient fluctuation was more apparent, but the NiWA coating microcracks and pits were more apparent. These cracks were usually the first residual stress concentration occurring in the coating, such as porosity, friction and wear experiments. The shearing stress of the ball constantly promoted the propagation of the crack reaching a certain extent, appeared layer organization fall off or peeling off pit, peeling also demonstrated that the coating’s block structure combining ability was weak. The NiWT and NiWA coatings significantly increased the wear resistance of the matrix and the performance of the NiWT coating was better.

3.5. Wear volume analysis

The wear volume is a weight index to measure the wear resistance of the coating, that is, the smaller the wear volume, the better the wear resistance of the coating [20].

$$\Delta V = \frac{1}{2} \left( r^2 \arcsin \left( \frac{d}{2r} \right) - \frac{d}{2} \sqrt{r^2 - \left( \frac{d}{2} \right)^2} \right) = \frac{Ld^3}{12r}$$

(1)

The table 6 shows that for the rotating speed of 200 r min$^{-1}$, the grinding crack width of the matrix and the wear volume are large. This also illustrated that the GCr15 friction ball from the beginning of point contact to the

Figure 7. Wear morphology of the coating surface, (a) 45#, (b) NiWT, (c) NiWA.
surface contact, thereby the grinding crack width wider, wear volume was larger, the NiWT and NiWA coatings grinding crack width and wear volume compared with the matrix has greatly reduced. This showed that the two kinds of coating effectively increased the wear resistance of matrix, and the at the same time compared with the NiWA coating, the NiWT coating grinding crack width was narrower, the wear volume was smaller, which also suggested that the wearability of the NiWT coating was better than the NiWA coating.

3.6. Coating surface elemental analysis

Electronic Data Systems (EDS) can be used to analyze the types and contents of materials. The characteristic energy released by each element in the process of energy level transition is different and the characteristic wavelength of the x-ray can be determined by different energies. EDS works by using different energies for component analysis. The EDS energy spectrum of the NiWT coating wear surface is shown in figure 8. As can be seen from the spectrum, the NiWT coating surface elements were mainly O, Cr, Fe and Mn, followed by Ni, Ti, C

| Sample   | Grinding width (mm) | Wear volume (mm³) |
|----------|---------------------|-------------------|
| substrate| 0.7708              | 0.4796            |
| TiO₂     | 0.1458              | 0.0032            |
| Al₂O₃    | 0.1563              | 0.0040            |

Figure 8. EDS of NiWT coating wear surface.

Table 6. Abrasion width and volume of the three samples.
and Si. Moreover, from the distribution diagram of the elements below, it can be found that Ni and Mn elements were evenly distributed and dense, and Si, B and Mn elements were also evenly distributed, indicating that the coating was evenly distributed during the preparation and evenly worn when in contact with the friction ball. The NiWT coating wear surface element mass percentage and atomic percentage are shown in table 7. The content of Fe was particularly high, which also verified that the NiWT coating had adhesive wear with GCr15 pellets, and a large amount of Fe in GCr15 pellets appeared on the surface of the coating. As for the friction and wear experiment, the friction pair between the heat generated by the increased slowly, make the GCr15 contact oxidation, gradually forming oxide, thus fell off, under the action of a shear stress of the oxide in constantly

| B  | C  | O  | Si | Ti | Cr | Mn | Fe  | Ni  |
|----|----|----|----|----|----|----|-----|-----|
| 1.97 | 8.03 | 10.03 | 0.43 | 0.16 | 15.55 | 1.51 | 53.00 | 9.32 |

Figure 9. EDS spectra of NiWA coating wear surface.
rotating flat out on the coating surface, forming a local oxide layer, thus promoting the sliding friction between the friction pair.

As can be seen from figure 9, the main elements of the NiWA coating surface were Ni, O, Cr, W and Mn, followed by Co, B, C and Al. It can be seen from the element distribution diagram above that Ni and Mn elements were evenly distributed and densely distributed, and Al and W elements were also evenly distributed, indicating that when the coating was prepared, all kinds of powders were evenly filled and evenly distributed, and the coating was evenly worn when frictional wear occurs with GCr15 pellets.

The NiWA coating wear surface element mass percentage and atomic percentage are shown in table 8. It can be seen that there were more O, Cr, Ni and W elements, while Fe elements on NiWA coating surface were less than those on NiWT coating surface. This also proved that when NiWA coating is rubbing with GCr15, adhesive wear was less.

| B  | C  | O   | Al | Si | Cr  | Fe | Co | Ni  | W  |
|----|----|-----|----|----|-----|----|----|-----|----|
| 2.03 | 3.55 | 17.88 | 0.30 | 1.81 | 10.78 | 2.96 | 1.35 | 41.91 | 17.43 |

Table 8. NiWA coating surface element percentage (wt%).

3.7. Experimental mechanism of friction and wear

The friction and wear experimental mechanism diagram was established with the coating as the object of action, as shown in figure 10. The powder sprayed was mainly mechanical combination. For the NiWT and NiWA coatings, the friction ball acted on the coating surface and the coating was subjected to the vertical compressive stress and horizontal shear stress generated by the GCr15 ball during continuous rotation. Under the action of compressive stress, grinding debris and friction balls will press into the coating surface, resulting in furrows and cracks. Under the action of shear stress, the pores on the surface of the material and the hard protruding will meet to be cut, while the evenly distributed hard meeting in the coating hindered the generation of cracks, furrows and other phenomena.

4. Conclusion

The following conclusions were obtained through the experiment of two coating materials, NiWT and NiWA, prepared on the 45# steel matrix and friction ball of GCr15:

(1) The friction coefficient of coating can be divided into three stages: ‘run-in stage,’ ‘transition stage’ and ‘stable run-in stage.’ When the speed was 200 r min\(^{-1}\), the friction coefficient of the NiWT coating was 0.40–0.43 and 0.35–0.38 during the stable run-in phase.
(2) When the rotating speed was 200 r min$^{-1}$, the wear morphology of the NiWT and NiWA coatings was significantly weaker than that of the matrix. The NiWT coating mainly suffered from abrasive wear and the fatigue wear was mainly caused by the NiWA coating.

(3) When the rotational speed was 200 r min$^{-1}$, the wear width and wear volume of the NiWT and NiWA coatings were small compared with the matrix, and the wear width and volume of the NiWT coating were smaller.

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