Microstructure and Tribological Properties of Ni-Co/WC+G Composite Cladding Layer Postprint

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Abstract

A Ni-Co/WC+G composite cladding layer was prepared on ZG45 steel surface via vacuum cladding technology. The microstructure morphology and phase composition of the composite cladding layer were observed and analyzed, and the influence of graphite content on the tribological properties was investigated through friction and wear testing. The results demonstrate that the addition of graphite creates numerous fine "graphite holes" within the three-dimensional network-textured composite cladding layer. These "graphite holes" can act as reservoirs for lubricating media during friction, thereby enhancing the tribological performance of the composite. With increasing graphite content, the friction coefficient, wear rate of the composite cladding layer, and wear volume of the GCr15 steel counterface disc gradually decrease, attaining minimum values at 6% graphite content. However, at 8% graphite content, the wear volume of the counterface disc abruptly increases by up to 70%.

Full Text

Microstructure and Wear Resistance of Ni-Co/WC+G Composite Coatings

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Abstract

Ni-Co/WC+G composite coatings were fabricated on ZG45 steel substrate by vacuum cladding technology. The microstructure morphology and phase composition of the composite coatings were observed and analyzed, and the effect of graphite content on the friction and wear properties was investigated through tribological tests. The results show that the addition of graphite creates numerous fine "graphite pores" within the three-dimensional network-textured composite coating material, which can serve as reservoirs for lubricating media during friction and enhance the tribological performance. Both the friction coefficient and wear rate of the composite coating gradually decrease with increasing graphite content, reaching minimum values at 6% graphite content. However, when the graphite content reaches 8%, the wear loss of the GCr15 steel counterface suddenly increases by 70%.

Keywords: composite, texture, vacuum cladding, nickel-cobalt alloy, graphite, friction-wear property

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Introduction

Nickel-based alloy composite coatings reinforced with ceramic particles effectively combine the high wear resistance of ceramic particles with the strength and toughness of the alloy matrix. These materials have been successfully applied to critical components in mechanical, mining, metallurgy, aerospace, and military industries, and have been extensively studied [1-4]. However, harsh operating conditions involving high speed, heavy load, and alternating stresses pose severe challenges to the mechanical properties of coating materials. The preparation of coating materials with both excellent tribological properties and superior mechanical performance has become a critical issue in the field of surface engineering.

Previous reports indicate that adding cobalt to nickel-based coatings can improve wear resistance, corrosion resistance, and mechanical properties [5-7]. Therefore, using a Ni-Co alloy as the matrix and adding WC not only enhances the mechanical compatibility between the coating and substrate but also provides good wear resistance. Research on friction materials has shown that adding solid lubricants such as graphite and WS to coating materials under dry friction conditions can reduce friction and further improve wear resistance [8-10]. Yin et al. investigated the effect of graphite particle size on friction coefficient and lubricating effectiveness from room temperature to 500°C, finding that graphite particles of 0.3–0.5 mm were most effective [9]. Our previous research demonstrated that graphite addition reduced the friction coefficient and wear rate to varying degrees [10], while texture treatment of the material structure could further optimize tribological performance [11,12]. Consequently, preparing composite materials with good mechanical properties, lubricating characteristics, and textural features holds significant application value and social benefit for solving industrial friction and wear problems.

In this study, different amounts of graphite were added as a lubricant to Ni-Co/WC composite coatings with three-dimensional network texture morphology. The microstructure and phase composition of the composite coatings were observed and analyzed, and the effect of graphite content on the tribological properties was investigated through friction and wear tests.

1. Experimental Procedures

1.1 Preparation of Cladding Layers

ZG45 steel was selected as the substrate material with dimensions of 50 mm × 50 mm × 10 mm. The cladding material consisted of nickel-based and cobalt-based alloy powders mixed uniformly at a mass ratio of 3:2. The nickel-based alloy powder had a chemical composition (mass fraction, %) of: 0.7 C, 3 B, 4.6 Si, 17 Cr, 3 Fe, balance Ni, with particle size of 50–110 m. The cobalt-based alloy powder composition was: 0.8 C, 1 B, 1.5 Si, 28 Cr, 3 Fe, 5 W, balance Co, with slightly smaller particle size. Irregular block-shaped premium WC powder with particle size of 10–15 m was selected as the reinforcement phase. The mixed Ni-Co alloy powder was then blended with WC powder (30% mass fraction), and 2%, 4%, 6%, and 8% of nickel-coated graphite (abbreviated as G) were added to prepare composite self-lubricating cladding layers. The nickel-coated graphite had a particle size of approximately 60 m.

During the composite bonding process, a homemade binder NJB was first used to bond a 1 mm thick layer of the mixed Ni-Co alloy powder onto the ZG45 surface as a transition layer to enhance bonding strength between the cladding layer and substrate. Then, the Ni-Co alloy and ceramic composite powder with added graphite was bonded to a thickness of approximately 2 mm to form a preform block, which was finally dried in a muffle furnace (200°C × 2 h). The preform samples were sintered in a ZT-18-22 vacuum carbon tube furnace at a vacuum level of 6.67 × 10 Pa (1080°C × 20 min) with a heating rate of 40°C/min, followed by furnace cooling to below 150°C.

1.2 Microstructural Observation and Analysis

The metallographic structure of the cladding layers was observed using an MEF-3 optical microscope. Phase composition was analyzed using a D/max-2400 X-ray diffractometer (XRD) with Cu target. Microstructural morphology and phase distribution were examined using a Quanta450-FEG scanning electron microscope (SEM), and energy dispersive spectroscopy (EDS) was employed to analyze elemental distribution variations in different micro-regions of the cladding layers.

1.3 Friction and Wear Testing

As shown in [Figure 1: see original paper], friction and wear tests were conducted using an EMM-1 tribometer in a pin-on-disc configuration. The disc was made of quenched and tempered GCr15 steel (composition: 0.8 C, 0.11 Si, 0.2 Mn, 1.2 Cr, balance Fe) with surface hardness of 60–63 HRC, diameter of 50 mm, thickness of 5 mm, and surface roughness Ra 0.2 m. The pin specimens were Ni-Co/WC+G composite cladding layers with different graphite contents, cut along the cladding thickness direction into cylinders of 5 mm diameter and 12 mm length, with the cladding side ground into a spherical shape with radius of 2.5 mm and surface roughness Ra of 0.28–0.50 m.

Tests were performed at room temperature in air atmosphere under a load of 15 N, with the tribometer motor frequency at 30 Hz, sliding speed of 3.36 m/s, and test duration of 1 h. The friction coefficient was automatically recorded by computer. The wear rate of the cladding layer was calculated from the spherical cap volume, while the wear loss of the disc was determined by weight measurement using an electronic balance (0.1 mg precision). Both friction coefficient and wear values represent averages from three repeated tests.

2. Results and Discussion

2.1 Microstructure

[Figure 2: see original paper] shows the XRD pattern of the Ni-Co/WC+G composite cladding layer. The main phases present are Cr C , Cr C , Ni Si, CrB, WC, C, and -Ni(Co) solid solution. The WC phase originates from the added WC particles. During melting and solidification of the alloy powder, Cr reacts with C and B to form large amounts of chromium carbides Cr C and Cr C , as well as the hard phase CrB. The low-melting-point eutectic element Si diffuses rapidly at high temperature, readily forming Ni Si that disperses within the eutectic structure and distributes in the solid solution formed by Ni, Co, and other alloying elements.

[Figure 3a: see original paper] presents the overall cross-sectional morphology of the Ni-Co/WC+G composite coating sample, which consists primarily of the substrate zone, Ni-Co alloy fusion transition zone, and composite zone with added WC and graphite. [Figure 3b: see original paper] shows an enlarged view of the fusion transition zone at the bonding interface marked by the square in [Figure 3a: see original paper]. The fusion interface is uneven, and the entire transition region includes a diffusion zone, metallurgical fusion band, and transition layer zone. The diffusion zone, identified on the left side of the image, comprises a 25–30 m Fe-based solid solution structure formed by diffusion of alloying elements. Adjacent to this is a 10–15 m wide fusion zone containing a "WC band," as shown in the figure. [Figure 3c: see original paper] displays the magnified morphology of the "WC band," clearly revealing fine WC particles and Fe-based solid solution. Elemental analysis of the lamellar pearlite structure at location B and the Fe-based solid solution at location C shows that location C contains 3–5% higher Fe content than location B, along with small amounts of Ni, Co, and other alloying elements, resulting in a smoother surface after etching. [Figure 3d: see original paper] shows the line scanning elemental distribution along the line segment in [Figure 3c: see original paper], demonstrating that the Fe content in the diffusion solid solution zone is significantly higher than in the substrate zone, with Fe content gradually decreasing thereafter, indicating mutual diffusion of the main elements Ni and Fe from the substrate to the fusion zone.

[Figure 3e: see original paper] illustrates the transition zone morphology between the fusion zone and composite zone. As indicated by markers D and E, this region uniformly distributes gray-black and white regular-shaped phases. The phase at location D exhibits hexagonal, quadrilateral, or pencil-shaped cross-sections. According to relevant studies, chromium carbides primarily exhibit quadrilateral or hexagonal morphologies [13], and EDS elemental analysis confirms that the main constituent elements are Cr and C, identifying this phase as chromium carbide. The phase at location E, as shown by EDS analysis, consists mainly of W and C, confirming it as WC originating primarily from the Co-based alloy powder. The light gray area at location F in [Figure 3e: see original paper] contains mainly Ni and Co along with small amounts of Fe and Ni Si. Based on the structural characteristics of the cladding layer, a metallurgical fusion process occurs in the transition layer, during which eutectic phases form. Therefore, the transition layer region consists mainly of Ni- and Co-based solid solutions, chromium carbides, and eutectic phases containing Ni Si and Ni-Co solid solutions. [Figure 3f: see original paper] shows the magnified morphology of the composite zone at square A in [Figure 3a: see original paper], clearly revealing that white WC particles form a three-dimensional network structure in the Ni-Co alloy matrix, with WC particles connected by Ni-Co alloy. The structure within the approximately circular or elliptical mesh grids is similar to that in the transition zone, comprising black rod-shaped chromium carbide hard phases distributed in the Ni-Co solid solution matrix, with fine "graphite pores" also present in the matrix.

2.2 Formation Mechanism Analysis

During heating of the cladding preform, the particle surfaces melt first. Since unmelted preforms contain uniformly distributed pores, molten droplets above the substrate move toward the substrate under gravity and vacuum, forming a neat "WC band" near the interface under the interfacial tension between droplets.

Under high-temperature holding conditions, the nickel-based and cobalt-based alloy powder particles melt. Under the combined effects of vacuum, gravity, and capillary suction in the preform pores, short-range creep flow occurs. The thin nickel layer on the surface of nickel-coated graphite particles melts under the multiple effects of high temperature, liquid creep flow, and its own buoyancy. After the nickel layer melts, the graphite splits into finer particles due to its light weight, porous nature, and layered structure. These fine graphite particles disperse uniformly in the molten metal, forming numerous very fine graphite "pores." The three-dimensional network structure characteristic of the composite zone forms from the uniform mixing of initial fine WC particles with relatively large nickel-based and cobalt-based alloy powder particles during heating and holding. The heating and holding temperature is equivalent to their melting point, meaning fine WC particles fill the spaces between large spherical Ni-Co alloy particles. The molten liquid metal has low fluidity and undergoes only creep flow near individual particles under vacuum, gravity, and capillary suction. During this process, wetting of WC particles is completed, their positions are adjusted, and a certain amount of liquid metal fills the spaces between WC particles. During solidification, the WC particles essentially maintain their original positions without large-scale agglomeration, forming a three-dimensional network structure. As shown in the figures, with 30% WC content, the thickness and continuity of the three-dimensional network "veins" are not uniform [14]; when WC content increases further, the network becomes more uniform.

2.3 Friction and Wear Properties

[Figure 4: see original paper] compares the friction coefficient and wear rate of Ni-Co/WC+G composite coatings with different graphite contents, showing consistent trends for both parameters. As graphite content in the coating increases, the friction coefficient and wear rate gradually decrease. The wear rate shows minimal variation after 4% graphite content and reaches its minimum at 4% graphite, with the wear rate at 6% graphite being only 9.7% higher than at 4%. The wear rates at 8% and 6% graphite contents are similar, while the friction coefficient reaches its minimum at 6% graphite, increasing slightly at 8% graphite. Comparing the friction and wear performance of Ni-Co/WC+6%G coating with our previous research results on Ni/20%WC+6%G coating [15] reveals that the friction coefficient and wear rate decrease by 8.5% and 70.5%, respectively. This demonstrates that adding an appropriate amount of Co and increasing WC to 30% not only enhances the ductility and toughness of the coating but also forms a denser network structure, effectively reducing the friction coefficient and wear rate.

[Figure 5: see original paper] shows the variation in wear loss of the GCr15 counterface disc during friction against composite coatings with different graphite contents. The wear loss of the disc increases slightly when a small amount of graphite is added to the Ni-Co/WC composite coating, but subsequently decreases and then increases again with increasing graphite content. The wear loss of the disc reaches a minimum at 6% graphite content, while at 8% graphite content, the disc wear loss increases dramatically by 70%. This phenomenon occurs primarily because when a small amount of graphite is added to the Ni-Co/WC composite coating, the graphite cannot fully spread to form an anti-friction film on the friction surface during wear. After reducing the coating density, abrasive wear and oxidative wear intensify, and the resulting wear debris causes a slight increase in counterface wear. As graphite content in the Ni-Co/WC+G composite coating increases, the graphite gradually spreads to form an anti-friction film during friction and wear, resulting in continuously decreasing friction coefficient, wear rate, and counterface wear loss. However, when graphite content reaches 8%, the coating density decreases, potentially causing WC particle detachment during friction and intensifying abrasive wear. Additionally, the metal matrix with slightly reduced density is more easily worn away, allowing protruding WC to grind against the disc, both contributing to increased disc wear. Considering the friction coefficient, wear rate, and counterface wear loss of composite coatings with different graphite contents, the Ni-Co/WC+6%G composite coating exhibits excellent friction and wear performance.

[Figure 6: see original paper] shows the worn surface morphologies of Ni-Co/WC+G composite coatings with different graphite contents. [Figure 6a: see original paper] presents the worn surface morphology at 2% graphite content, clearly showing WC particles with slight plowing grooves. Elemental analysis at location L (Table 1) reveals mainly O and Fe, indicating oxidation occurred in this region. The smooth, flat area H contains a large amount of Fe (Table 1), far exceeding the Fe content in the coating itself, which results from Fe transfer from the counterface disc, along with some C from the added graphite. [Figure 6b: see original paper] shows the worn surface morphology at 4% graphite content, where graphite spreads relatively uniformly on the wear surface. Some areas experienced oxidation, and the oxidized wear debris intensified abrasive wear, creating slight plowing grooves. However, the circled area clearly shows WC and Ni-Co alloy matrix at the same wear surface level without protrusion, indicating that graphite provided effective lubrication during wear. The varying image contrast, combined with the higher friction coefficient of this composition, suggests that partial oxidation occurred in the coating during friction due to heating.

[Figure 6c: see original paper] shows the worn surface morphology at 6% graphite content, revealing a clear, smooth surface without obvious plowing grooves. The worn surface still clearly shows the outlines of chromium carbide hard phases and WC particles. [Figure 6d: see original paper] presents the worn surface morphology at 8% graphite content, where fine pits are faintly visible. Elemental analysis at location M on the worn surface shows high C content (Table 1) along with certain amounts of Fe and O, indicating the presence of oxidized areas and spalling pits on the worn surface, both resulting from slightly reduced coating density when graphite content increases beyond a certain level.

[Figure 6e: see original paper] shows the carbon element distribution map of the worn surface in [Figure 6c: see original paper]. Compared with [Figure 7: see original paper] showing the carbon distribution on the unworn surface of the 6%G composite coating, the carbon distribution on the worn surface is more uniform than before wear. This occurs because graphite particles slide and spread uniformly under shear stress during friction to form an anti-friction film, reducing damage to the overall composite coating material during friction and decreasing the friction coefficient. [Figure 6f: see original paper] shows a further magnified SEM morphology of the worn surface of the 8% graphite composite coating, revealing sporadically distributed black pits, microcracks, and fractured WC particles from the friction and wear process. These pits likely form from spalled WC particles and fine pores left after graphite lubricant is consumed. Under high-speed friction, the interaction of normal stress, shear stress, and micro-vibration in localized wear regions makes these fine pores crack initiation sites, generating microcracks. Additionally, increased graphite content slightly reduces coating density and consequently decreases mechanical properties such as plasticity and toughness, causing fatigue cracks in the coating during friction. Therefore, analysis of worn surface morphology also indicates that the Ni-Co/WC+6%G composite coating has superior friction and wear performance. Appropriate graphite addition improves tribological performance, as graphite forms an anti-friction film on the counterface under the combined action of frictional shear stress and normal stress, thereby reducing friction coefficient and wear rate. However, excessive graphite content also slightly reduces coating density, and too many graphite pores can degrade overall tribological performance.

[Figure 8: see original paper] shows the macro-hardness distribution of composite coatings with different graphite contents. Hardness increases slightly at 2% graphite content but decreases slightly with further graphite addition due to the reduced coating density caused by graphite addition. At 8% graphite content, hardness decreases by 8.9% compared with the graphite-free coating, while the 6%G composite coating hardness is slightly higher than that of the 4%G coating and only 2.4% lower than the graphite-free coating. As previously mentioned, the friction coefficient and wear rate decrease by 8.5% and 70.5%, respectively, making the hardness reduction negligible compared with the improvement in friction and wear performance. The relatively high hardness of the 6%G composite coating also confirms its good wear resistance.

Conclusions

(1) The Ni-Co/WC+G composite coating exhibits a three-dimensional network structure that effectively improves friction and wear performance. Graphite addition creates many fine "graphite pores" uniformly distributed within the coating material that can store lubricating media. During friction, graphite acts as a lubricant that spreads on the friction surface to

form an anti-friction film, reducing the friction coefficient and improving wear resistance.

(2) Adding graphite to Ni-Co/WC coatings reduces the friction coefficient, wear rate, and wear loss of the GCr15 steel counterface disc. The coating with 6% graphite content shows the minimum friction coefficient and wear rate.

(3) When graphite content reaches 8%, the density and ductility-toughness of the coating material decrease slightly, leading to microcrack formation and WC particle fracture during friction and wear, which creates abrasive wear and intensifies the wear degree.

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Note: Figure translations are in progress. See original paper for figures.