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Tribological properties of Ni-base alloy composite coating modified by both graphite and TiC particles

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Abstract: In order to reduce the friction coefficient of Ni-base alloy coating and further improve its wear resistance, Ni-base alloy composite coatings modified by both graphite and TiC particles were prepared by plasma spray technology on the surface of 45 carbon steel. The results show that friction coefficient of the composite coating is 47.45% lower than that of the Ni-base alloy coating, and the wear mass loss is reduced by 59.1%. Slip lines and severe adhesive plastic deformation are observed on the worn surface of the Ni-base alloy coating, indicating that the wear mechanisms of the Ni-base alloy coating are multi-plastic deformation wear and adhesive wear. A soft transferred layer abundant in graphite and ferric oxide is developed on the worn surface of the composite coating, which reduces the friction coefficient and wear loss in a great deal. The main wear mechanism of the composite coating is fatigue delamination of the transferred layer.

Key words: Ni-base alloy; plasma spraying; composite coating; graphite; TiC; tribology

1 Introduction

With the rapid development of mechanical equipments, long service life and high reliability of machine parts are urgently requested. engineering technology is an effective method to improve wear resistance of these machine parts and prolong their service lives. Ni-base alloy coatings prepared by thermal spray technology have been successfully applied to machine parts for their excellent properties such as high hardness, high bonding strength, anti-wear and corrosion resistance [1-3]. But under more rigorous friction conditions such as high contact stress, the Ni-base alloy coatings are worn off severely and fail to meet the requests. Many studies have been carried out to improve the wear resistance of the Ni-base alloy coatings by incorporating with ceramic particles, such as WC [4], TiC [5], SiC [6] and Cr_3C_2 [7]. For example, the wear resistance of the WC-Co particles reinforced Ni-base alloy coatings by laser cladding is improved by twice [4]. The wear resistance of TiC/Ni-base alloy coatings is 4 times that of the Ni-base alloy coatings [5].

Presently, it is necessary to economize energy and prolong service lives of machine parts by improving them with excellent tribological performance. However, the above mentioned coatings used as tribological component surface materials usually present high friction coefficients under the friction conditions of high contact stress and no liquid lubrication. One of the feasible methods to reduce friction coefficients of the Ni-base alloy coatings is to add solid lubricant particles such as MoS₂ and graphite to the Ni-base alloy. But these self-lubricated coatings are usually applied to the machine parts operated under low contact stress friction conditions. For example, the Ni60/MoS2 composite coatings are used under the contact stress of 0.03 MPa [8]. The Ni-wrap graphite coatings are prepared on the surface of Ti alloy which is utilized under pressure of 5 MPa [9]. LIN et al [10] prepared Al alloy/graphite composite materials and found that this material presented well anti-friction effect under 0.69 MPa wear condition.

It has been found that composite materials reinforced by both the hard ceramic phase particles and solid lubrication particles exhibit good tribological properties [11]. But there has been not any research report on the composite coatings prepared by thermal spray technology. The composite coatings, which were simply mixed up and directly sprayed on the steel surface, do not present the anticipated properties of wear resistance and anti-friction because of the large difference

of the melting points among different ingredients in the composite materials. For instance, the melting point of TiC particles is nearly 3 000 °C [12], while the graphite may react with the metal matrix at about 500 °C [13].

In this work, the Ni-base alloy composite coating modified by both TiC and graphite particles (abbreviated by the composite coating) was prepared on the surface of 45 carbon steel by plasma spray technology, in which both the TiC and graphite particles were previously wrapped by nickel to obtain high bonding strength and to prevent chemical reaction between graphite and Ni-base alloy matrix. The cooperative modification effects of graphite and TiC on tribological properties of the composite coating were investigated under dry sliding friction conditions under high contact stresses. The wear mechanisms were discussed according to the results of surface analysis.

2 Experimental

2.1 Specimen preparation

The composition of the composite coating materials of Ni-base alloy modified by both graphite and TiC particles is listed in Table 1. The coating consisted of three kinds of powders, i.e. Ni-base alloy powders, TiC wrapped by nickel powders and graphite wrapped by nickel powders. The chemical composition of the Ni-base alloy powders with particle size ranging from 55 to 128 μm was 15.5% Cr, 3% B, 4% Si, 14% Fe, 0.75% C and residue of Ni (mass fraction). The TiC wrapped by nickel powders with particle size ranging from 22 to 36 μm contained 35.45% (mass fraction) nickel and the graphite wrapped by nickel powders with particle size ranging from 75 to 128 μm contained 75% (mass fraction) nickel.

The 45 carbon steel was chosen as the substrate, which was previous treated by degrease and rust cleaning. The coating materials were sprayed on the surface of 45 carbon steel by plasma spray equipment of DH1080. The spray technological parameters were current of 600 A, voltage of 40 V and spray distance of 80 mm. The specimens were discs with diameter of 60 mm and thickness of 7 mm. The thickness of the composite coating was 500 μ m and its surface roughness was 0.3 μ m after being ground by diamond wheel.

Table 1 Composition of spray composite coating materials (mass fraction, %)

Graphite wrapped by nickel	TiC wrapped by nickel	Ni-base alloy
20	40	Residue

2.2 Tribological tests

The tribological tests were carried out in an

HT-500 ball-on-disc tribometer at room temperature. The upper specimen was a GCr15 steel ball with a diameter of 4 mm, the surface roughness of 0.05 μm and the micro-hardness of HV 739. The down specimen was the plasma spray coating. The GCr15 steel ball slid against the coating under dry sliding friction condition at speed of 0.1 m/s and normal load of 10 N. At the beginning of the test, it was point contact between the ball and the coating, therefore, contact stress exceeded yield strength of the ball and materials worn out, then the spherical surface of the ball became plane. The wear loss of the specimen was measured by the balance of TG328A with an accuracy of 0.1 mg.

2.3 Surface analysis

The metallographs of the Ni-base alloy coating and the composite coating were carried out by a DMM-330C optical microscope. The microstructure and worn surfaces of the coatings were observed by a QUANTA200 scanning electronic microscope. The element composition of the worn surfaces and wear debris was respectively tested by energy-dispersive X-ray analysis attached to the SEM.

3 Results and discussion

3.1 Effects of graphite and TiC particles on microstructure of composite coating

The OM images of the Ni-base alloy coating and the composite coating are shown in Fig. 1. As shown in Fig. 1(a), the matrix in white color of the Ni-base alloy coating is γ-Ni austenite, the block grains are Ni₃B and the rhombus grains are CrB [14]. The size of these grains is in the range of 10-100 µm. It is found that the grain size of the composite coating dramatically decreases to less than 10 µm, indicating that the Ni-base alloy matrix grains are refined because of the incorporating effect of graphite and TiC particles. The graphite and TiC particles are uniformly dispersed in the Ni-base alloy matrix and the particles may impede the grains of Ni-base alloy matrix from further growing, so the grains of the matrix are refined. Besides, the thermal conductivity of the Ni-base alloy is about 30 W/(m·°C) at high temperature [15], which is much lower than that of graphite of 400 W/(m·°C) [16]. So graphite in the composite coating might accelerate the cooling speed and lead to the refining of the grains of Ni-base alloy matrix. The refined grains elevate the strength of the composite coating and improve the anti-plastic deformation and anti-microcutting ability.

Figure 2(a) shows the micro-structure of the composite coating, in which there are three typical areas, i.e., the grey area (marked A), the grayish area (marked B)

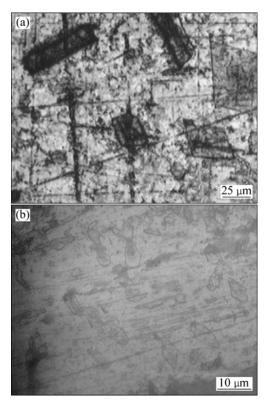


Fig. 1 OM images of Ni-base alloy coating (a) and composite coating (b)

and the black area (marked C). As shown in Fig. 2(b), the EDX spectrum of region A indicates that it is mainly composed of TiC and a little Ni, Cr and Fe, which are from the Ni-base alloy matrix. The dispersion of TiC particles in the matrix of Ni-base alloy may greatly improve the wear resistance of the composite coating. Region B is the matrix of Ni-base alloy according to the EDX spectrum as shown in Fig. 2(c). The EDX spectrum of region C shows that the element in this area is C, which suggests that the black structure is graphite (Fig. 2(d)). The graphite does not react with other elements of the Ni-base alloy in the spray process because it is previously wrapped by nickel. So, it can exhibit lubrication effect and reduce friction coefficients in friction process.

3.2 Tribological results and discussion

Figure 3 shows the friction coefficients of the two coatings as a function of time. The average friction coefficient of the Ni-base alloy coating is 0.47, while that of the composite coating is 0.247. Compared with the former, the latter is decreased by 47.45%. Friction coefficient of the composite coating also fluctuates less than that of the Ni-base alloy coating, which indicates a more steady state of the composite coating in friction

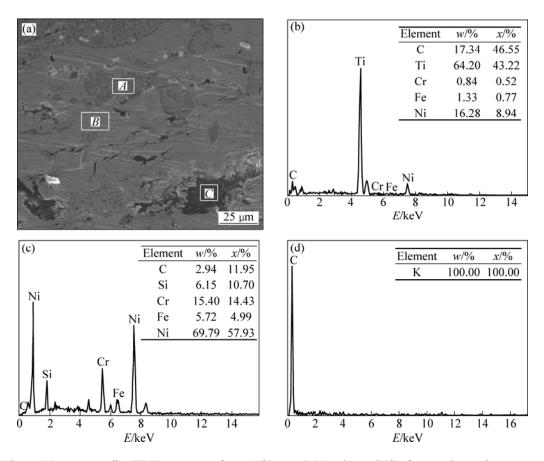


Fig. 2 SEM image (a), corresponding EDX spectrums of area A (b), area B (c) and area C (d) of composite coating

process. In Fig. 4, the wear loss of the composite coating is 0.9 mg, which is 59.1% lower than that of the Ni-base alloy coating. It can be concluded that the friction coefficient and wear loss of the composite coating are decreased due to the cooperative effects of graphite and TiC particles.

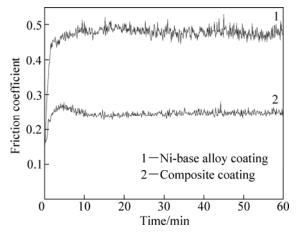


Fig. 3 Friction coefficient vs time for coating

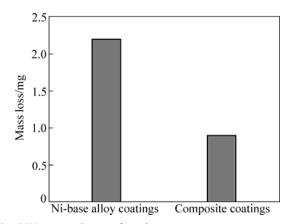


Fig. 4 Wear mass losses of coatings

3.2.1 Friction and wear mechanisms of Ni-base alloy coating

The SEM image of the worn surface and EDX spectrum of the Ni-base alloy coating are shown in Fig. 5. Figure 5(a) shows the morphology of the worn surface, in which the arrow shows the sliding direction. It can be found that there are a series of parallel slip lines vertical to the sliding direction in some areas (marked *A*), suggesting that sheared plastic deformation took place on the worn surface in the friction and wear process. The EDX spectrum Fig. 5(b) of the typical area *A* shows that the worn surface of the Ni-base alloy coating is mainly composed of 1.21% C, 8.44% O, 3.98% Si, 16.85% Cr, 11.41% Fe and 57.34% Ni (mass fraction). The proportions of C, Si, Cr, Fe and Ni on the worn surface are consistent with those in the Ni-base alloy, which indicates that there is no transferred phenomenon of Fe

from the friction counterpart of GCr15 steel to the worn surface of Ni-base alloy coating. Adhesive action between the GCr15 steel and the Ni-base alloy coating which leads to large shear force and high friction coefficient of 0.47 in sliding friction process is supposed to be the main friction mode of the Ni-base alloy coatings.

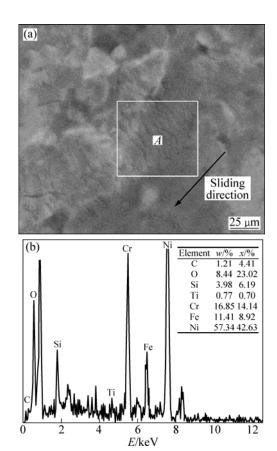
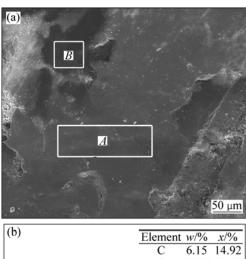


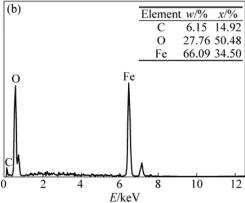
Fig. 5 SEM image (a) and EDX spectrum of area A (b) on worn surface of Ni-base alloy coating

After repeating scratching actions of the counterpart GCr15 steel ball, the coating materials suffer from multi-plastic deformation, and the micro-cracks are generated along the slip line and then extend into the inferior surface, which results in desquamation of the coating materials. So, the main wear mechanisms of the Ni-base alloy coating are adhesive wear and multi-plastic deformation wear.

3.2.2 Friction and wear mechanisms of composite coating

The worn surface morphology of the composite coating is shown in Fig. 6(a). It is found that the worn surface is covered by a flat and smooth transferred layer, and the EDX spectrum is shown in Fig. 6(b). The transferred layer is mainly composed of 6.15% C, 27.76% O and 66.09% Fe (mass fraction). The content of element C is much higher than that in the matrix of





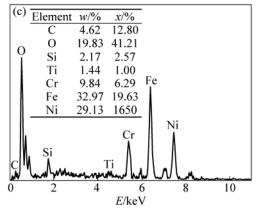


Fig. 6 SEM image (a), EDX spectrum of area A (b), EDX spectrum of area B (c) of worn surface of composite coating

Ni-base alloy, which means that a large amount of graphite might be squeezed out of the interior of the coating and accumulated on the friction surface. The high content of element Fe indicates that the element Fe transferred from the GCr15 surface and/or the wear debris of GCr15 was adhered to the coating surface in friction process. The content of element O existing in the transferred layer may also illustrate that Fe is oxygenated because of the friction heat and produces ferric oxide such as Fe_2O_3 .

There are still some black areas on the worn surface marked by B in Fig. 6(a). The EDX spectrum of this area

is shown in Fig. 6(c). The coating elements such as Ni, Si and C are detected in area B. The contents of Fe and O are 32.97% and 19.83%, respectively, which are comparatively higher than those in the matrix of the Ni-base alloy, but smaller than those in area A. This phenomenon means that the black area B is a developing transferred layer and it does not completely cover the composite coating surface.

When the composite coating wears against GCr15 steel ball, the transferred layer which is mainly composed of ferric oxide and graphite is gradually developed on the composite coating surface with the proceeding of friction and wear. Then, the friction and wear between the composite coating and GCr15 steel gradually change into those between the transferred layer and GCr15 steel. In addition, the microhardness of the transferred layer is HV37.93, which is measured by DHV-1000 microhardness tester, so the layer is soft and with low shearing strength. Therefore, the friction coefficient of the tribo-couple can be greatly reduced because of the low shearing strength and the solid lubrication effect of graphite and ferric oxide in the transferred layer.

The developed transferred layer on the composite coating surface can effectively protect the composite coating material from scratching by the counterpart of GCr15 and the wear resistance is increased by 2.44 times. But the transferred layer may be also damaged by the multi-repeat squeezing action of the counterpart. Fatigue crack that generated in the transferred layer is shown in Fig. 7(a), and it would cause delamination of the transferred layer, as shown in Fig. 7(b). The composition of the exposed area of the composite coating after delamination (marked area A) was analyzed by EDX (Fig. 7(c)). It is found that the exposed area is mainly composed of the elements in Ni-base alloy, namely, this area is the matrix of the composite coating. The fatigue delamination of the transferred layer is the main wear mechanism of the composite coating when it wears against GCr15 under sliding friction condition.

Therefore, on the one hand, the transferred layer can effectively protect the composite coating to decrease the friction coefficient and improve wear resistance; on the other hand, its fatigue delamination may also result in the wear mass loss of the composite coating material to a certain extent. After the delamination of the transferred layer, it may also gradually develop into new transferred layer area by continuous accumulating debris and/or Fe element diffusion from GCr15 to the composite coating surface in the black area *B* marked in Fig. 6(a) with proceeding of friction and wear between GCr15 and the composite coating.

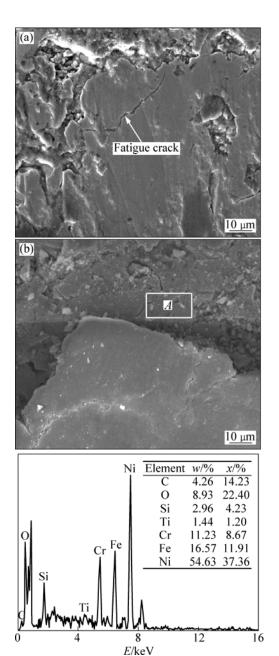


Fig. 7 SEM images of fatigue crack (a) and delamination area (b) and EDX spectrum of *A* on delamination area (c)

4 Conclusions

- 1) The graphite/TiC/Ni-base alloy composite coating is in a dense micro-structure, in which the grains of the Ni-base alloy matrix are refined because of the incorporating modification of graphite and TiC particles. The friction coefficient of the composite coatings is decreased by 47.45% compared with that of the Ni-base alloy coatings, and the wear mass loss is reduced by 59.1%.
- 2) The main wear mechanisms of the Ni-base alloy coating are adhesive wear and multi-plastic deformation

wear because severe sheared plastic deformation takes place on the worn surface when wears against GCr15 steel

3) A transferred layer that contains ferrous oxides and graphite is gradually developed on the worn surface of the composite coating, which acts as solid lubrication to decrease the friction coefficient and improve the wear resistance of the composite coating. The main wear mechanism of the composite coating is fatigue delamination of the transferred layer.

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石墨/TiC 改性镍基合金复合涂层的摩擦学性能

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摘 要: 为降低纯镍基合金涂层在高接触应力下的摩擦因数并进一步提高其耐磨性能,运用等离子喷涂技术在 45[#] 钢表面制备石墨/TiC 协同改性镍基合金复合涂层。结果表明: 复合涂层的摩擦因数较纯镍基合金涂层降低 47.45%,磨损质量降低 59.1%。纯镍基合金涂层与 GCr15 钢对摩时,表面产生明显的滑移和粘着变形,从而使纯镍基合金涂层表现出多次塑变磨损和粘着磨损。在复合涂层的磨损表面形成较软的、富含石墨和铁氧化物的转移层,使得其摩擦因数显著降低,质量磨损大为减少。复合涂层的磨损机理主要为转移层的疲劳剥落。

关键词: 镍基合金; 等离子喷涂; 复合涂层; 石墨; 碳化钛; 摩擦磨损

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