Effect of TiC content on the microstructure and properties of large-area laser-cladded TiC Ni-based composite coatings

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Abstract

The study of effect of TiC content (10%, 20% and 30%) in Ni-matrix on the microstructure and properties of composite cladding prepared by laser cladding was reported in the present. Developed clads were characterized by SEM, EDS, XRD, microhardness tests, friction and wear tests and electrochemical tests. The experimental results show that the TiC/Ni composite coating had good quality and strong metallurgical bonding with the substrate. As the TiC content increases, distribution of TiC densified, the grain size increased, and the average hardness of the coating increased to 667.87 HV0.2, which is approximately three times that of carbon steel. Moreover, as the TiC content increased, the friction coefficient of the coating decreased gradually. However, the friction coefficient of the 10% TiC coating was the most stable, as wear time increased. The electrochemical results showed that the corrosion resistance of the 10% TiC coating was the best. As TiC content increased, the corrosion resistance of the composite coating first decreased and then increased.

1. Introduction

Parts damage is an inevitable problem that occurs during service. To reduce cost, damaged parts are typically repaired rather than replaced. However, the traditional repair method cannot meet the requirements of current complex applications. Problems such as a large active gap and new cracks caused by wear and spalling of the repaired layer easily occur during subsequent use. Therefore, there has not been an effective surface repair method for worn parts. If the quality of the repaired layer is excellent, the part should have high strength, wear resistance and corrosion resistance, thereby ensuring the service life of the repaired part is long. High-energy beam (e.g. laser beam, ion beam,) cladding is a surface modification technology with great potential. It can use special cladding materials to form coatings on substrates with special properties such as wear resistance, high-temperature resistance, corrosion resistance, high thermal conductivity, and high electrical conductivity. Therefore, it has become a popular surface modification research topic. The current cladding technology mainly includes laser cladding and plasma cladding. Laser cladding is a surface modification technique in which a laser beam of a certain power density was directed at the surface of a substrate with certain characteristics and melts and combines it with the microfused substrate. Moreover, the base material becomes slightly molten and condenses to form a low-dilution surface coating. Laser cladding is used in various surface modification technologies because of its excellent technical characteristics, such as a small thermal influence area, low dilution, and additive construction. Because of these characteristics, laser cladding has been widely used in the repair and rapid manufacturing of parts. The high hardness, unique bonding structure and stability of carbide reinforcements give them excellent wear resistance and corrosion resistance. Studies have shown that laser cladding is an effective method to improve the service life of hard particle-reinforced composite coatings reinforced by hard particles on the surface of mechanical parts. It is well known that SiC, Al₂O₃, WC, TiB₂ and
other hard particles are widely used to enhance the wear resistant of alloy coatings. For example, Guo et al. produced WC-reinforced Ni-based composite coatings by laser cladding. They found that the ordinary Ni-based coatings exhibited severe wear during testing, whereas the WC-reinforced composite coatings sustained only slight abrasive wear and adhesive wear under the same conditions. Srinivasan et al. prepared SiC particle-reinforced composite coatings by laser cladding, and the coating had three times the hardness of the rare earth alloy matrix and had higher corrosion resistance. Wang et al. prepared nano-Al2O3 reinforced Ni-based coatings by laser cladding, which eliminated the cracks at the intersection of the coating and the substrate. Moreover, the dispersible nanoceramic particles hindered the spread of elements and inhibited the new phase formation, and the grain refinement effect was obvious. Although the abovementioned hard particles play an important role in increasing the wear resistance of the alloy coating, these hard materials still have some shortcomings. For example, Al2O3 reduces the fracture toughness of coatings due to its high brittleness. Silicon carbide decomposes at 2830 °C, so the mechanical properties of the coating will be diminished when this temperature is exceeded. WC decarburizes and reacts with alloying elements to form brittle phases such as W2C, M6C, and M12C, which increases the brittleness of the coating. Among all ceramic particles, NaCl-type TiC particles with simple cubic structure, low density (4.9 g/cm3), high hardness (3200 HV), high thermal stability and low enthalpy of formation (−184 kJ mol−1) have been widely used as the reinforcing phase of composite coatings.

2. Experimental details

2.1. Sample preparation
In this work, the experimental materials were Q235A steel (100 mm × 50 mm × 10 mm). The powder used in the TiC/Ni composite coating was mainly Ni60A powder (average size: 45~90 μm), and the main ceramic reinforced particles in the composite coating were TiC particles (average size: 45~90 μm). The TiC particles were mixed with Ni60A powder in the mass ratio of 1:9, 1:4 and 3:7, so the amount of titanium carbide added to the mixed powder was 10%, 20% and 30% of the total mass ratio, respectively. As shown in the figure 1(a), a coaxial powder feeding laser cladding equipment was used to prepare the TiC/Ni composite coating (10 mm × 60 mm) on the substrate. The cladding direction and cross-section of the coating are shown in figures 1(b), (c). The whole cladding process occurs in a vessel filled with Ar to avoid oxidation during the cladding process. The specific parameters of the coating are as follows: the copper nozzle was 15 mm away from
the workpiece, the powder feeding gas flow rate was 3 l min$^{-1}$, the power was 1200 W, and the scanning speed is 3 mm s$^{-1}$. Based on the above method and process parameters, we have prepared a composite coating with only a few pores and no visible cracks by laser cladding.

### 2.2. Performance characterization

Scanning electron microscopy (SEM), x-ray diffraction (XRD), and energy-dispersive spectroscopy (EDS) were used to analyze the elemental composition, phase, and morphology of the coatings. The microhardness of the coating was measured with a microhardness tester, where the load was 200 g and the dwell time was 15 s. The microhardness was tested three times from the coating surface to the substrate at 100 $\mu$m intervals, and the average value was recorded. In order to get closer to the actual working conditions, we have carried out experimental tests on frictional wear under high pressure and long loading times. The friction and wear properties of the composite coating were determined with a reciprocating friction tester. The parameters are shown in Table 1. The weight loss was measured with an electronic analytical balance. All surfaces except the coating, including the copper wires brazed on the substrate, were inlaid with epoxy resin or sealed with wax. To ensure its longevity in complex environments, we have tested its corrosion resistance. Electrochemical testing was mainly performed with an electrochemical workstation system in 3.5% NaCl solution. The main test system was composed of reference electrode, a counter electrode, and a working electrode, which were a saturated calomel electrode (SCE), Pt, and the sample, respectively.

### 3. Results and discussion

#### 3.1. Morphologies of the coating interfaces

During the cladding process, the TiC particles dissolved or partially dissolved, then nucleated and grew. As the coating solidified, because the density of TiC (4.09–4.93 g cm$^{-3}$) was lower than that of the base Ni alloy (7.53 g cm$^{-3}$), buoyancy caused the TiC particles in the molten pool to move upwards, as shown in Figure 2, and the magnitude of the buoyancy follows Stokes law: $F = 6\pi \eta \nu R$, where $R$ is the radius of the spherical particle; $\nu$ is the relative velocity of the liquid; $\eta$ is the viscosity coefficient of the liquid; $\nu = 2/9 (r^2 g/\eta) (\rho - \rho_0)$; and the flotation speed is directly proportional to the square of the particle semidiameter [10]. Therefore, larger TiC particles float faster than smaller TiC particles, so TiC particles of different sizes will contact, aggregate and grow in the solidification process. In addition, as the TiC content increases, the probability of aggregation and growth during the floating process will greatly increase and the number of incomplete dissolved particles will increase, which will lead to an increase in the size of the TiC particles.

Figure 3 shows a cross section of the coating with different TiC contents. As can be seen in Figure 3, the coating cross-section is divided into three zones: the substrate, the diffusion zone, and the coating zone. Black TiC particles were distributed in the coating, which can be verified by the EDS results. The distribution of TiC was mainly concentrated near FeNi dendrites and in interdendritic regions. The main reasons for this distribution were the convection in the molten pool, the interactions between the TiC particles and the interactions between the TiC phase and the liquid-solid interface. The fine TiC particles were mainly distributed near the dendrites, as indicated in Figure 4. The grain size of the TiC was mainly concentrated in the 0.8–1.6 $\mu$m range, and the particles tended to aggregate and grow as the TiC content increased. TiC aggregates can be

![Figure 2. Schematic diagram of distribution process of TiC.](image-url)

| Grinding ball | The diameter of grinding ball (mm) | Wear distance (mm) | Load (N) | Round trip frequency (Hz) | Test time (min) |
|--------------|----------------------------------|--------------------|----------|--------------------------|----------------|
| SiN          | 4                                | 10                 | 150      | 5                        | 30             |

Table 1. Friction and wear test parameters.
observed in figure 4(b). TiC particle with a diameter greater than 2 μm can be found in figure 3(c). Large TiC particles are present between the dendrites; these particles are mainly TiC precipitated from the solid-liquid interface and undissolved TiC, as shown in figure 4, wherein the grain diameter can reach 100 μm. When the coating solidified, fine TiC grains were readily absorbed by the solid-liquid interface and bound to the FeNi branched crystals. In contrast, larger TiC grains were repelled by the mobile liquid-solid interface and formed the final solidification region between the FeNi branched crystals. As shown in figure 3, a fusion line formed between the coating and the substrate, and its width gradually widened from 0.92 μm to 4.27 μm to 5.19 μm as the TiC content increased. This occurred because the temperature gradient was higher at the root of the melt pool, and the subcooling of the components and solidification rate were lower [11]. Special solidification conditions caused the melt near the bottom of the molten pool to solidify and form a fusion line, which is essentially a narrow planar zone with ultra-fine crystalline particles [12]. The presence of fusion lines indicated...
that elemental diffusion was occurred between the layer and the matrix, and formed high quality metallurgical bonds to the matrix [12–14]. The SEM images in figures 3 and 4 show that the composite coating consisted mainly of black particles, a grey microstructure and white dendrites.

XRD patterns of the composite coatings with different TiC contents are shown in figure 5. The patterns show that the main phases of the composite coating are Fe3C, Cr23C6, TiC and FeNi. The results also show that the intensity of the TiC peak increased with the increasing TiC content, whereas some carbide peaks decreased or even disappeared. Based on the surface scan data in figure 6, the point scanning data in table 2, and the XRD results, it can be concluded that the black particles were TiC particles and that the main composition of the dendrites was FeNi with a small amount of carbides, such as Fe3C and Cr23C6. According to the point scanning data, the grey phase was mainly FeNi with elevated M3C and M23C6 contents.

3.2. Microhardness

Figure 7 shows the micro-hardness distribution of the composite coating from the surface to the substrate at different TiC contents, and the average microhardness values of the 10%, 20% and 30% TiC coatings were 441.97 HV0.2, 437.05 HV0.2 and 630.01 HV0.2, respectively. The hardness of the composite coating gradually decreased from the surface to the substrate, and the maximum hardness of 10%, 20% and 30% TiC coatings was 470 HV0.2, 480.13 HV0.2, 667.87 HV0.2, respectively. The average hardness of the substrate was 211.43 HV0.2. Therefore, the hardness of the coating was obviously higher than that of the matrix. For the 10%, 20% and 30% TiC coatings, the hardness of the coating was 1.05, 1.03 and 1.98 times greater than that of the matrix, respectively. As shown in the figure 7, the microhardness of the 10% and 20% TiC coatings decreased gradually from the surface to a depth of 500 μm, while the hardness exhibited little change from this depth to the heat-affected zone. Moreover, the results showed that the microhardness of the 30% TiC coating was significantly higher than that of the 10% and 20% TiC coatings. This was primarily due to the high hardness of TiC, and the strengthening effect became more pronounced as the TiC content increased.

3.3. Friction and wear testing

Figure 8 displays the wear mass loss for the three coatings, and the results show that the mass loss of 10% TiC coating was significantly lower than that of the 20% TiC and 30% TiC coatings. This indicates that the coating with 10% TiC has the higher wear resistance in the 30-min friction test. Although this composite coating had high hardness, it also effectively resisted the friction of the wear ball and hindered plastic deformation, thereby increasing the wear resistance of the coating [15–17]. The TiC that was peeled off during the wear process formed new abrasives, which accelerated wear during subsequent frictional processes. The wear resistance of the
20% and 30% TiC coatings was higher than that of the base material. However, the coating thickness decreased as TiC content increased, so it was easier to wear to the substrate over the long wear process; hence, the wear loss was higher in the 20% and 30% TiC coatings than in the 10% TiC coating.

Figure 9 shows the coefficient of friction curves of the three coatings with respect to the wear time. As shown in Figure 9, the friction coefficient of the 10% TiC coating was relatively stable (i.e., the fluctuations were small) at approximately 0.44. However, the coefficient of friction of the 20% TiC coating fluctuated substantially: it was approximately 0.52 for a short time, then it decreased to 0.45 at approximately 100 s, stabilized at approximately

![Figure 6. The EDS mapping images of TiC composite coatings with different TiC content: a–c with 10%, 20%, 30% of TiC content in order.](image)
0.4 at 600 s, then increased gradually and finally stabilized at approximately 0.47. The coefficient of friction of the 30% TiC coating slowly increased from 0.37 to 0.47. Analyze argued that at the beginning of the wear phase, the sample had a high hardness due to the high TiC content on the surface. As the wear time increased, the hardness of the coating decreased and new abrasive particles were added in the process, the combination of which led to an increase in the coefficient of friction. When the grinding ball was pressed into the coating, the TiC particles in the coating, which were exposed by wear, generated a torque in the opposite direction of the movement of the grinding ball. The magnitude of the torque was $F \cdot R \cdot \sin \alpha$, which effectively hindered the wear process of the coating, as illustrated in figure 10. However, the coefficient of friction gradually decreased between 100 s and 700 s as the TiC content increased, which is consistent with the observed change in hardness as the TiC content increased. Moreover, because the hardness of the 10% TiC coating was relatively uniform, the friction coefficient fluctuated little. The 30% TiC coating, which had the highest hardness, had a relatively small coefficient of friction. However, owing to the large grain size and high content of TiC, there was more residual TiC in the wear debris, which had a greater wear effect on the remaining coating. Hence, the friction coefficient was unstable and increased over time.

The wear surface topography of the coating is shown in figure 11. There were ploughing grooves, adhesive craters, transfer layers formed by plastic deformation and dislodged abrasive debris, which verified that adhesive and abrasive wear occurred. Because the medium was air and a large amount of heat was generated during the long, high-speed friction process, Fe oxide transfer layers were generated, which fractured and formed wear debris under the action of subsequent contact stress and friction and the increasing number of friction thermal cycles [4]. The formation of a transfer layer on the wear surface of the composite coating can protect the surface and reduce the adhesion wear of the coating to a certain extent. Furthermore, because the hardness of Ni is much lower than that of TiC, the TiC microprotrusions will be pressed into the Ni over the long-term wear process and will eventually fall off and influence the subsequent wear process. Of course, a certain amount of TiC-reinforced phase was equally dispersed in the Ni substrate, which can prevent Ni substrate from being ploughed, so that only some shallow grooves can be observed [18-20]. In addition, the solid solution strengthening and dislocation stapling effect of the TiC precipitates gave the coating high strength. Therefore, the wear surface of the coating did not sustain significant plastic deformation. Based on the above analysis, we conclude that the wear mechanism of the TiC-reinforced Ni-based composite coating in this experiment was micr-o ploughing and adhesive wear.

![Figure 7. Microhardness distribution of the TiC/Ni coatings with different TiC content.](image)

| Table 2. Chemical composition analysis for the 3 point element in figures 2(a)-(c). |
|-----------------------------------|
| Composition (at%) |  |
| Point | Fe | Ni | Cr | Ti | C | Si | Phase |
| 1 | 18.12 | 17.23 | 5.36 | 47.62 | 11.67 | / | TiC |
| 2 | 54.52 | 26.23 | 4.19 | 1.43 | 12.32 | 1.31 | FeNi,Fe3C,Cr23C6 |
| 3 | 55.22 | 22.26 | 10.12 | 0.84 | 8.91 | 2.65 | FeNi,Fe3C,Cr23C6 |
Figure 8. Wear weight loss of coatings with different TiC content.

Figure 9. The coefficient of friction curves of the three coatings with respect to the wear time.

Figure 10. Schematic diagram of TiC strengthening.
3.4. Corrosion analysis

The potential dynamic polarization curves for the coatings in 3.5% NaCl solution are shown in figure 12, wherein the corrosion potential was between 0.2 and 0.5 V. The curves show that the 30% TiC coating had a significant passivation effect when the corrosion potential was between $-0.34$ and $-0.13$ V. As the potential increased to $-0.13$ V, the passivated film on the coating surface was destroyed and the corrosion current increased rapidly. The corrosion potential of the coating was approximately $-0.4$ V. The current density increased significantly when the polarization potential exceeded $-0.4$ V. This is due to damage to the oxide film produced by the anodic polarization of the coating surface, resulting in a significantly higher corrosion rate. The correlation data derived from the Tafel diagram was shown in table 3. $E_{corr}$, $I_{corr}$, BA, BC, and RP are the

![Figure 11. The coating wear morphology: a–c with 10%, 20%, 30% of TiC content in order.](image)

![Figure 12. The potential dynamic polarization curve for a coating in 3.5% NaCl solution.](image)

|        | $E_{corr}$ (V) | $I_{corr}$ (A cm$^{-2}$) | BA (mv) | BC (mv) | BP (Ω cm$^2$) |
|--------|----------------|--------------------------|---------|---------|--------------|
| 10%TiC | $-0.267$       | $4.378 \times 10^{-8}$   | 81.261  | 66.943  | 364518       |
| 20%TiC | $-0.395$       | $3.049 \times 10^{-5}$   | 87.788  | 326.158 | 9866         |
| 30%TiC | $-0.378$       | $6.144 \times 10^{-6}$   | 58.051  | 346.500 | 7342         |
corrosion potential, corrosion current density, anodic Tafel constant, cathodic Tafel constant, and polarization resistance, respectively, and polarization resistance, which were extracted directly from the dynamic polarization potential curves using the Tafel fitting method. The following conclusions can be drawn from the results in table 2. Corrosion voltage: \( E_{\text{corr}} \) (10% TiC) \( > E_{\text{corr}} \) (30% TiC) \( > E_{\text{corr}} \) (20% TiC). Corrosion current: \( i_{\text{corr}} \) (10% TiC) \( < i_{\text{corr}} \) (30% TiC) \( < i_{\text{corr}} \) (20% TiC). Polarization resistance: \( R_{\text{P}} \) (10% TiC) \( > R_{\text{P}} \) (20% TiC) \( > R_{\text{P}} \) (30% TiC). From the perspective of the corrosion rate, the higher the corrosion voltage was, the more difficult it was to corrode. From the perspective of corrosion kinetics, the smaller the corrosion current was, the lower the corrosion rate [21]. Therefore, the corrosion resistance of the coating decreased as the TiC content increased.

4. Conclusion

1. The presence of fusion lines between the coating and the substrate with widths of 0.92 \( \mu \text{m} \), 4.27 \( \mu \text{m} \) and 5.19 \( \mu \text{m} \) respectively. The existence of the fusion line indicates that elemental diffusion had occurred between the coating and the substrate, and that a high quality metallurgical bond had been formed.

2. The average micro-hardness of the coatings was 441.97 HV0.2, 437.05 HV0.2 and 630.01 HV0.2 for 10%, 20% and 30% TiC content respectively, which was 1.05, 1.03 and 1.98 times higher than that of the substrate.

3. The wear mechanism of the composite coating was micro-ploughing wear and adhesive wear. For a very short time (10 min), the friction coefficient decreases with increasing TiC content. However, from the results of the long-term wear test, the friction coefficient of the composite coating containing 10% TiC was more stable and maintained at about 0.44.

4. The results showed that with the increases of TiC content, the corrosion resistance of the composite coating first decreases and then increases. The composite coating containing 10% TiC had a high self-corrosion voltage and the smallest corrosion current, indicating that the coating was more difficult to corrode, and its corrosion rate was low after the start of corrosion.

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