The Influence of CEO₂ Content on the Microstructure and Hardness of Ni-WC Coating Formed by Vacuum Fusion Sintering

Lu Miao, Nan Jiang, Yanhui Jiang, Zheng Zhang, Shiyi Cui, Hui Xu

Institute of Applied Technology, University of Science and Technology Liaoning, Anshan, Liaoning, 114044, China;

Abstract. Made Ni-WC-CEO₂ composite coatings of different CEO₂ content on 45 steel matrixes by vacuum fusion sintering. The coatings microstructure and the morphology of WC were observed by SEM, the elements diffusion between WC and Ni-base alloy by EDS; The Rockwell hardness of coatings' surface and micro-hardness of coatings' longitudinal section were measured by Rockwell hardometer and microhardness instrument. The results showed that: The defects in the coatings become less, WC in the coating is further refined, and its distribution changes uniform with adding content CEO₂. When the content of CEO₂ is 0.5%, the surface's hardness and section's microhardness are the highest, In this paper, the optimum content is 0.5%. **Keywords:** Ni-WC-CEO₂ composite coatings, Microstructure, Hardness.

1. Introduction

Nickel based self fluxing alloy is a commonly used alloy coating material in the field of metal corrosion prevention and wear resistance[1~3]. Generally, thermal spraying, laser cladding, induction cladding, vacuum melting, and other methods are used to coat the coating powder preset on the substrate surface on the substrate surface, and form a metallurgical bond with the substrate[4-5]. During practical application, it is found that different component ratios and processing methods affect the microstructure, properties, and corrosion resistance of alloy coatings Abrasion resistance has an important impact. Coatings with good performance can significantly extend the service life of equipment, while reducing maintenance costs and improving work efficiency[6].

2. Test Conditions and Methods

2.1 Specimen Preparation

Experimental base material: rolled 45 steel, size 25mm $\times 10$ mm $\times 10$ mm $_{\odot}$

Experimental coating: The chemical composition and properties of Ni45B, nickel coated WC powder KF-56, and CEO₂ composite powder with different additions are shown in Table 1 and Table 2 in turn.

	1 au	CCrFeSiNiMelting point/°CParticle size/mesh0.715 ≤ 12 3.5Bal1100~1150 $-140~+320$					
В	C	Cr	Fe	Si	Ni	Melting point/°C	Particle size/mesh
3.0	0.7	15	<12	3.5	Bal.	1100~1150	-140~+320
Table 2 Composition and properties of WC+Ni powder							

Table 1 Composition and properties of Ni45B self-fluxing alloy powder

Tungsten carbide	nickel	Particle size/mesh	mechanical behavior
70~90	10~30	-140~+320	High hardness and wear resistance

Advances in Engineering Technology Research	ICACTIC 2023
ISSN:2790-1688	Volume-6-(2023)

2.2 Test Method

Using SEM to observe the microstructure of the sample; EDS was used to analyze the diffusion of elements between the coating and WC; The Rockwell hardness and cross section microhardness of the coating surface were measured using a Rockwell hardness tester and a microhardness tester, respectively. The effect of CEO2 addition on the microstructure and hardness of the coating was studied through the above experiments.

3. Experimental Results

3.1 Microstructure of the Coatings

SEM was used to observe the microstructure and morphology of coatings with different CEO₂ additions, and the results are shown in Figure 1.



Fig.1 SEM pictures of coatings' longitudinal section with different CEO₂ content (a)0%CEO₂ (b) 0.25%CEO₂ (c)0.5%CEO₂ (d)0.75%CEO₂ (e)1.0%CEO₂

From Figure 1, it can be seen that there are a large number of complex shaped hard phases distributed on the coating substrate inside the coating, and there is a transition zone between the coating and the base metal that firmly combines with the base metal. The morphology of WC in the coating with rare earth CEO₂ added is finer and more dispersed than that of the coating without adding rare earth CEO₂, and the morphology of WC in the coating gradually becomes finer from 0% to 0.5%. After the addition of rare earth CEO₂ exceeds 0.5%, the morphology of WC gradually coarsens. At the same time, it can be seen from Figure 1 that both the coating layer (a) without adding rare earth CEO₂ and the coating layer (d) and (e) with excessive addition of rare earth CEO₂ have porosity defects in the coating, while the coating layer (b) with 0.25% and 0.5% addition has porosity defects in the coating layer (b) (c) The internal structure is dense, free of porosity defects, and the WC structure is not concentrated at the junction between the substrate and the coating, moving relatively towards the top of the coating. These phenomena all indicate that the addition of appropriate amounts of rare earth CEO₂ can significantly refine the morphology of WC, improve the fluidity of the coating, and facilitate the removal of gases and impurities from the coating,

This is because after adding CEO_2 to a Ni45 self fluxing alloy, due to the strong interaction between CEO_2 and sulfur in the nickel based alloy, and the impact of sulfur on the surface tension of the nickel based alloy is thousands of times greater than that of ordinary alloy elements, the addition of CEO_2 can effectively reduce the surface tension of the molten coating, resulting in significantly improved fluidity of the molten cladding layer, good diffusion and extension, and good metallurgical bonding between the coating and the substrate, It is also conducive to the formation of

Volume-6-(2023)

gas leakage during internal melting of the coating, which is not easy to form pores or air gaps, and the surface quality is good. However, as the amount of CEO_2 added gradually increases, the coating quality gradually deteriorates. This is because the CEO_2 melting point is as high as 2600 °C, which is far higher than the Ni45B melting point of 1050~1150 °C. However, the energy obtained by the coating material during vacuum melting and sintering is the same. Due to the large amount of energy required to be absorbed during the melting and diffusion processes, materials with high melting points absorb more energy, Therefore, when the CEO_2 content is too high, the coating quality will gradually deteriorate, that is, there is an optimal value for the CEO_2 content.

In order to more clearly analyze the refining effect of CEO₂ on the hard phase WC, EDS was used to conduct energy spectrum analysis of three different morphologies of hard phase WC in the coating with the best 0.5% addition of coating quality. The results are shown in Figure 2.



Elment	W/wt%	Ni/wt%	Fe/wt%	Cr/wt%
1	94.51	5.49	-	-
2	80.68	13.74	2.60	2.98
3	68.64	23.42	5.98	1.96

Fig2 Spot-scanning energy spectrum picture of hard-phase with different shape in the coatings (1)lumps (2) strips (3)particles

From Figure 2, it can be seen that the constituent elements of WC hard phases with different morphologies are different. The bulk phase consists of Ni and W, indicating that it is KF-56 in the original coating powder; In addition to Ni and W, elements Fe and Cr were added to the strip and particle phases. Compared to the bulk phase, the content of Ni, Cr, and Fe in the particles increased, while the content of W decreased, indicating that element diffusion occurred between the hard phase and the nickel based alloy matrix, refining the hard phase from the original bulk to the strip and particle phases. The addition of CEO₂ promoted the mutual diffusion of atoms among the elements.

3.2 Hardness of the Coatings

The coatings with different CEO_2 additions were smoothed with 400 # coarse abrasive paper and polished with metallographic abrasive paper. The Rockwell hardness of the coating surface was measured using a Rockwell hardness tester. The experimental results are shown in Table 3.

Tables Rockwein hardness of coatings					
Content of CEO ₂ /wt%	0%	0.25%	0.5%	0.75%	1%
HRC	46.3	52.3	55.6	54.5	51.7

From Table 3, it can be seen that the surface hardness of the coating increases with the addition of CEO₂. The Rockwell hardness of the coating surface first increases and then decreases with the increase of the amount of CEO₂ added. When the amount of CEO₂ added is 0.5%, the maximum surface hardness of the coating is HRC55.6, which indicates that the addition of CEO₂ can improve the surface hardness of the coating, but the more CEO₂ added, the better, but there is an optimal value. This is because the addition of CEO₂ promotes the refinement of the hard phase WC and its mutual diffusion with the surrounding Ni base. WC has a high elastic modulus and extremely high hardness, which is used as a dispersion strengthening phase in the coating. The finer and more dispersed WC is, the higher the hardness of the coating. As can be seen from Figure 2, the finer WC is in each coating layer, so the hardness is improved. When the addition of CEO₂ reaches 0.5%, WC is the most refined and dispersed, so the coating surface hardness is the highest.

3.3 Microhardness of the Coatings

Grind and profile the cross section of the coating, use a microhardness tester to test the hardness load of 50g, and maintain the pressure for 12s. Measure from the upper surface of the coating on the cross section through the junction to the substrate in steps of 0.1mm, and measure three points in a transverse parallel position at each point, and then take the average value to represent the microhardness of the section. The experimental results are shown in Figure 4.



Fig.4 Microhardness curve of coatings with different CEO₂ content

As can be seen from Figure 4, the microhardness curves of the cross sections of the coatings with five different CEO₂ additions have corresponding peaks in the range of 0.2 to 0.3 mm and 0.5 to 0.6 mm from the junction, while the hardness decreases when it reaches the coating surface. High hardness values in the 0.5~0.6mm region are very beneficial to the wear resistance of the coating. However, within the range of - 0.2 to+0.2 mm from the junction, the values of the five curves are not significantly different, and the curve changes smoothly. There is no obvious step jump at the junction. This gradient distribution feature of microhardness is precisely the result of mutual diffusion of alloy elements at the interface, indicating that the adhesion between the vacuum melted coating and the substrate at the junction is very strong. In addition, it can be seen from the figure that the CEO₂ addition amount of 0.5% is located at the top, with the maximum microhardness peak.

From Figure 2, it can be seen that the morphology of WC in the coating varies greatly. WC without CEO₂ coating is relatively coarse and blocky, while WC with 0.5% CEO₂ added becomes fine and needle like or granular. This is mainly because CEO₂ is extremely prone to segregate at the grain boundaries, reducing the driving force for grain growth, refining the grains, and improving the microhardness of the coating. When excessive addition occurs, the defects in the coating increase and the coating quality deteriorates, resulting in a decrease in hardness. In addition, CEO₂ also has a certain impact on the distribution of WC in the coating, but the impact is not significant. The overall trend is that there is relatively little WC near the junction, which is mainly due to the low melting point eutectic in Ni-based alloys, which is easy to infiltrate at the melting temperature, and the unfused WC particles float upward; Then, WC is relatively small and dense, becoming sparse and bulky at the middle part, then becoming small and aggregated, and finally, there is almost no WC on the coating surface. This distribution of the hard phase WC causes the microhardness of the sample to vary according to the rule shown in Figure 4, which also affects the wear resistance of the coating.

4. Conclusions

1.An appropriate amount of CEO_2 can effectively improve the fluidity of the molten pool during the cladding process, reducing defects such as pores and inclusions in the coating.

2.An appropriate amount of CEO_2 addition refines the grain size of the hard phase WC in the coating, making its distribution more uniform. In this experiment, when the CEO_2 addition amount is 0.5%, the hard phase WC in the coating is the smallest and the most dispersed.

3.Appropriate CEO_2 addition improves the hardness of the coating. When the CEO_2 addition amount is 0.5%, the surface hardness and longitudinal section microhardness of the coating are the highest.

References

- Yuan L, Wang H M. Corrosion behaviors of a γ-toughened Cr13Ni5Si2/Cr3Ni5Si2 multi-phase ternary metal silicide alloy in NaCl solution [J]. Electrochimica Acta, 2009, 54(2): 421-429.
- [2] Xu W, Chen M, Lu X, etal. Effects of Mo content oncorrosion and tribocorrosion behaviours of Ti-Mo orthopaedic alloys fabricated by powder metallurgy [J]. Corrosion Science, 2020, 168: 108-557
- [3] Yazdi R, Ghasemi H M, Wang C, etal. Bio-corrosion behaviour of oxygen diffusion layer on Ti-6Al-4V during tribocorrosion[J]. Corrosion Science, 2017, 128: 23-32.
- [4] Qu Z P, Zhang B B, Zhao Y F, Analysis on Microstructure and Electrochemical Corrosion of Nickel-based Alloy Coating Prepared by Thermal Spraying-Induction Fusion Welding[J]. Hot Working Technology 2023, 52:92~96
- [5] Bankiewicz D, Vainio E, Yrjas P, etal .Application of bipolar electrochemistry to accelerate dew point corrosion for screening of steel materials for power boilers [J]. Fuel, 2020, 265:16-26.
- [6] Lu Y, Chen Z, Wang C, etal. Protection of 304 stainless steel by nano-modified silicone coating in cyclically alternate corrosion environment[J]. Corrosion Science, 2021, 190:10-12.