Effect of medium entropy alloy powder-core wire on friction wear and corrosion resistance of arc cladding additive layer

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Abstract

Low carbon steel was suitable for industrial fields due to its low price, wide application range and excellent comprehensive performance. However, there were still shortcomings such as poor wear resistance and corrosion resistance in special occasions. In hence, this paper carried out a study on the strengthening process of low-carbon steel parts surface deposition. The TIG welding arc welding method was used to study the strengthening performance of the arc-enhanced medium entropy alloy additive layer. To analyze the elements and microstructure of the medium entropy alloy additive layer by x-ray diffractometer (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and other modern analysis methods. The micro-hardness, friction and wear and electrochemical corrosion detection methods were used to study the friction and wear and corrosion resistance of the medium entropy alloy additive layer. The results show that the microstructure of the medium entropy alloy additive layer is a typical lamellar pearlite, which is wrapped with face-centered cubic solid solution (FCC) and unevenly distributed in the additive layer. The microhardness of the medium entropy alloy additive layer is significantly higher than that of the substrate. As the friction and wear load increases, the friction coefficient of the medium entropy alloy additive layer gradually decreases. The wear rate of the additive layer is much lower than that of the substrate and the wear resistance is doubled compared to the substrate. The form of wear is mainly abrasive wear and fatigue spalling wear. The medium entropy alloy additive layer has excellent corrosion resistance. Its corrosion rate is about one tenth of the substrate. The arc cladding medium entropy alloy powder core wire can meet the surface strengthening requirements of low-carbon steel parts and provide engineering basis for the low-carbon steel large-scale, multi-domain, high-level application.

1. Introduction

Low-carbon steel is widely used in small and medium-sized parts in petrochemical industry, railways, ships, pipelines, automobiles and general machinery manufacturing. And it has the advantages of low cost and easy welding to the same material or different materials. However, when low-carbon steel parts are put into service under wear or corrosion conditions, higher requirements are placed on the performance of the parts. Low-carbon steel is easier to rust and has lower hardness than other types of steel. Corrosion [1–3] and wear [4, 5] will not only shorten the service life of the equipment, but may also bring huge potential safety hazards, so improving the wear resistance and corrosion resistance of materials is crucial. With the development of modern surface strengthening technology, in recent years, domestic and foreign countries have attached great importance to improving the surface properties of workpieces to meet the special requirements of working conditions. P. Cerchier et al [6] have developed PEO coatings containing Cu, which can be used on the surface of materials working in seawater to effectively prevent the erosion of seawater. Shuaishuai Zhu et al [7] Prepared TiN-Al2O3...
ceramic particles by plasma cladding to enhance the HEA coating, which improves the hardness and wear resistance of the coating, eliminates adhesive wear, and fully exerts the work potential of the material, saving a lot of precious metals. At the same time, it also extends the service life of the parts. Therefore, in order to obtain better performance of the steel, other alloy layers are deposited on the surface of the substrate to achieve the surface strengthening of the low-carbon steel.

High entropy alloy [8–13] is an alloy material designed with five or more alloy elements. The alloy world is distinguished by mixed entropy. Traditional alloys belong to the category of low entropy alloys. Medium-entropy alloys are between high entropy alloys and low entropy alloys. It has excellent comprehensive properties similar to high entropy alloys. Traditional arc welding [13–16] (WAAM). The development of welding wire systems has been saturated. On the basis of the principle of the development of the original powder core wire, the author has a different approach. Based on the advantages of medium entropy alloy, medium entropy alloy powder is filled into the metal sheath to make medium entropy alloy powder core wire. The characteristics of this design are the appearance and corrosion resistance of the medium entropy alloy additive layer and the weldability and formability of carbon steel. The medium entropy alloy powder-core wire and low-carbon steel are bonded by arc cladding, in which the medium entropy alloy powder-core wire is an additive layer, and the low-carbon steel is the base material. Such a hybrid structure gives low carbon steel outstanding advantages such as high hardness, excellent wear resistance, corrosion resistance, and satisfactory resource savings. In this paper, the arc welding technology is used to surface strengthen low carbon steel to study the wear behavior of the medium entropy alloy additive layer under different wear loads. The wear resistance and wear mechanism of 20 steel base material and medium entropy alloy additive layer were discussed through friction coefficient, wear volume and wear morphology. At the same time, the corrosion resistance of the medium entropy alloy additive layer on the surface is studied to provide a basis for the surface strengthening application of low-carbon steel arc deposition.

2. Experimental part

2.1. Wire preparation and WAAM

In this study, Fe, Co, Ni, and Cu powders were mixed in an atomic ratio of 1:1 to make a powder core, and 308 stainless steel tape was used as a substrate to make a medium entropy alloy powder core wire with a diameter of 1.2 mm. The experiment uses a tungsten inert gas shielded welding machine (TIG) and an AC power source. The arc deposition instrument uses an ESBA reverse-flow argon arc welding machine. The wire feeder is a WF-007A multi-function automatic argon arc wire filler. The dimensions of mild steel are 200 mm × 200 mm × 15 mm. The schematic diagram of the WAAM process is shown in figure 1. The WAAM parameters used in this study are listed in table 1. The sample was cut and ground by a wire electric discharge machine. In order to make the constituent phases and grain boundaries clearly visible, the mild steel substrate was etched with a 4% nitric acid alcohol solution (96% ethanol + 4% nitric acid). The medium entropy alloy additive layer was etched with nitrohydrochloric acid solution (HNO₃ : HCl) for 15 s. X-ray diffractometer (HD-XpretPRO) was used to analyze the phase of the medium entropy alloy additive layer. Observing the structure through an optical...
Table 1. WAAM parameters.

| Test parameters          | Value |
|--------------------------|-------|
| Welding current (A)      | 180   |
| Wire feed speed (cm min⁻¹)| 190   |
| Welding speed (mm min⁻¹) | 140   |
| Wire feeding Angle (°)   | 50    |
| Tungsten electrode diameter (mm) | 3.2 |
| Gas flow of Protective gas (l min⁻¹) | 15 |

metallurgical microscope (Nikon-MR5000) and observe the element distribution and content of the medium entropy alloy additive layer with an energy dispersive spectrometer (EDS).

2.2. Microhardness test
The hardness of the medium entropy alloy additive layer and the substrate is tested by a Vickers hardness testing machine in accordance with ASTM E10-14. During the test, a digital display turret microhardness tester (HVS-1000B) was used to apply a load of 200 gf to the sample for about 5 s to test 10 points.

2.3. Friction and wear, surface topography scanning
The friction and wear sample size is 20 mm × 10 mm × 5 mm. The surface of the sample block is polished and polished. The friction and wear condition is dry friction. The friction couples are made of hard ceramic balls with a diameter of 6 mm. The sample was clamped on the sample platform of a micro friction and wear tester (Nanovea Tribometer). The experiment was conducted at room temperature. Put the friction couple (hard ceramic ball) into the indenter and tighten the indenter screw, so that the hard ceramic ball makes a linear reciprocating sliding movement of 5 mm on the sample surface. The friction rate is 100 mm min⁻¹. The load range is 2 N, 4 N, 6 N, 8 N. The experiment took 5 min. The surface profile was scanned by 3D optical profiler (Nanovea PS50) to observe the wear scar width, depth and wear volume. The scanning area is 2 mm × 2 mm. The step size is 10 μm. The scanning speed is 3.33 mm s⁻¹. After the test, the friction and wear samples were placed in acetone for ultrasonic cleaning. Scanning electron microscope (SIGMA 500) was used to observe the wear morphology of the sample pieces to judge their wear behavior.

2.4. Electrochemical corrosion experiment
The anti-corrosion performance of the sample is tested by the electrochemical workstation (PGSTAT 302N) simulating the marine environment. The sample size is 20 mm × 10 mm × 2 mm. Using non-conductive epoxy resin to seal the sample area below the insulating glue. The surface to be etched exposed 10 mm × 10 mm is exposed to the solution. The experiment tested the potential polarization of the medium entropy alloy additive layer. The data obtained was compared with the corrosion performance of the substrate. All samples were tested 3 times in 3.5% NaCl solution to obtain accurate dynamic potential polarization curves.

3. Results and discussion
3.1. Physical and structural analysis
It can be seen from figure 2 that XRD inspection shows that there are two simple phases on the surface of the medium entropy alloy additive layer and no other obvious metal compounds are precipitated. It is in line with the definition that the medium entropy alloy is composed of four principal components with similar content and the increase in mixing entropy inhibits the formation of other metal compounds. There are FCC phase and austenite γ phase of medium entropy alloy powder core in the additive layer. The intensity difference between the two phases is small. According to the analysis and calculation of jade software, the following results are obtained: the γ phase is 26.6 nm, and the FCC phase is 24.8 nm. It can be seen that the intensity of the γ phase and the FCC phase are basically the same and the grain size is uniform.

The EDS element analysis of the surface of the medium entropy alloy additive layer is shown in figure 3. It can be seen from the figure that the metal alloy elements are basically uniformly distributed on the surface of the weld bead, and there is no component segregation. The content of Fe is maintained at a relatively high level, and the content of other metal elements such as Co, Ni, Cu, etc is average. It can form solid solution in the welding layer stably. The EDS line scan inspection of the whole sample is shown in figure 4. At the interface between the base material and the medium entropy alloy additive layer, the elements show dramatic fluctuations. The Fe element in the substrate accounts for the vast majority, and the content of other elements is small. The content of
Fe in the medium entropy alloy additive layer dropped sharply, while the elements of Cr, Co, Ni, and Cu showed a significant upward trend, which verified the feasibility of WAAM medium entropy alloy powder core wire.

The optical metallographic examination is shown in figure 5(a). The formed sample has no obvious defects such as cracks and pores. After the samples are formed, all are completely fused and the welding quality is good. When welding 20 steel and medium entropy alloy powder core wire, carbon migration will occur, forming a carbon-enhanced layer and a decarburized layer. The relatively high content of Cr in the medium entropy alloy powder-core wire has C-friendly properties, causing C to diffuse and migrate to the side of the medium entropy alloy additive layer through the welding line. A decarburized layer is formed on the side of 20 steel, while a carbonized layer is formed on the side of the medium entropy alloy additive layer. Carbide gathers near the fusion line to form a carbonized zone. It can be seen from figure 5(b) that the medium entropy alloy additive layer is mainly pearlite. The pearlite grains are obviously coarser, which is related to the pearlite coarsening

Figure 2. XRD pattern of medium entropy alloy additive layer.

Figure 3. Medium entropy alloy additive layer surface element distribution map.
caused by phase transformation. Pearlite shows a typical lamellar structure, in which the face-centered cubic solid solution phase (FCC) is wrapped and unevenly distributed in the additive layer. Figure 5(c) shows the microstructure of the substrate. The gray-white mass polyhedron structure is ferrite, and the black irregular structure is pearlite. Ferrite and pearlite are relatively uniformly mixed and distributed in a band shape and have a certain deformation direction orientation.

Figure 6 shows the microhardness of the medium entropy alloy additive layer and substrate. As shown in figure 6, the hardness of the medium entropy alloy additive layer is significantly higher than that of the substrate. In WAAM, two kinds of hard Co and Ni elements are added to the medium entropy alloy powder core wire, both
of which have the effect of increasing the hardness of the substrate. A large amount of lamellar pearlite formed in the medium entropy alloy additive layer is much larger than the base material. The structural density of the flake pearlite is also much higher than that of the base material, so that the hardness of the additive layer is distributed uniformly as a whole. Furthermore, the formed FCC has a certain strengthening effect on the relative surface, making the medium entropy alloy additive layer harder than the substrate itself. Based on the close relationship between hardness and wear resistance, when studying the friction properties of surface-reinforced parts, it is generally believed that the higher the hardness of the material under the same conditions during wear, the better the wear resistance. The increased hardness provides the basic conditions for improving the wear resistance of the material. In sliding wear, it will provide a certain degree of resistance to plowing.

3.2. Friction and wear performance analysis
Table 2 shows the friction coefficient of the substrate and the medium entropy alloy additive layer under different loads. As show in table 2, Under different loads, the friction coefficient of the medium entropy alloy additive layer is lower than that of the substrate. At the same time, the coefficient of friction decreases with increasing load. Figure 7 shows the friction coefficient diagram of the medium entropy alloy additive layer under dry friction conditions with a friction rate of 100 r min⁻¹, a test time of 5 min, a reciprocating stroke of 5 mm and different loads. It can be seen from the figure that under the same friction rate, the same friction time and different loads, the friction coefficient increases with time and shows the same trend. When the load is 2 N, the friction coefficient is about 0.622 on average. When the load is 8 N, the friction coefficient is about 0.427 on average. As the load increases, the friction coefficient gradually decreases, but the magnitude of the decrease becomes smaller. Especially when the load is 6 N and 8 N, the friction coefficient changes little. I think the reason may be that when the load increases, the real contact area between the hard ceramic ball and the sample increases and the increase speed is significantly higher than the load speed. In the course of the experiment, the heat energy generated by friction cannot be dissipated in time, resulting in the formation of an oxide film on the sample surface and affecting the friction coefficient [17].

The friction and wear results under 6 N load were scanned by the profiler on the friction samples of the substrate and the medium entropy alloy additive layer. Use them to analyze the wear resistance of the substrate.

![Figure 6. Microhardness of substrate and medium entropy alloy additive layer.](image-url)
and the medium entropy alloy additive layer. Figure 8 shows the three-dimensional morphology of the wear scar of the substrate and the medium entropy alloy additive layer under a load of 6 N. The wear results of the additive layer and the substrate are shown in Table 3. As shown in figure 8, the base material has a larger wear scar width than the medium entropy alloy additive layer. The maximum wear scar depth of the substrate ($2.86 \times 10^{-2}$ mm) is deeper than the medium entropy alloy additive layer ($1.81 \times 10^{-2}$ mm). The wear resistance of the medium entropy alloy additive layer is greater than that of the substrate. The wear rate of the sample is calculated from the obtained profile data. The wear rate of the substrate is $1.15 \times 10^{-3}$ mm$^3$/(N·mm), while the wear rate of the medium entropy alloy additive layer is only $5.44 \times 10^{-4}$ mm$^3$/(N·mm). The wear rate of the additive layer is much lower than the substrate itself. The wear volume of the substrate is large. The wear resistance of the additive layer is doubled compared to the substrate. In summary, the wear resistance of the medium entropy alloy additive layer is better than the substrate itself. According to Akkad’s law, materials with high hardness always show a lower wear rate and good wear resistance [18, 19].

Figure 9 shows the SEM image of the wear morphology of the medium entropy alloy additive layer under the conditions of dry friction, different loads, and the same rate. It can be seen that with the increase of the load, the
damage appearance of the wear scar becomes more and more serious. The increased load leads to an increase in normal stress and shear stress during material wear. When the surface stress of the material increases, the probability of failure and plastic deformation is greater. The increase of shear stress increases the cutting effect of hard ceramic balls on the sample. The combination of the two causes the material to wear more seriously. As shown in figure 9(a), when the load is 2 N, the surface of the material is peeled off by the hard ceramic balls. A small amount of abrasive particles are scattered on the surface of the material and the rest are smooth areas. The wear mechanism is typical abrasive wear. As the load increases, the abrasive particles will adhere to the surface of the material under the stress of the hard ceramic balls. The formation of regional accumulation is shown in figure 9(b). As the friction progresses, the accumulation thickens. The surface of the sample showed a typical slight bite or continuous wear mechanism and there were grooves formed by slight plows. When the load is increased to 6 N, the wear scars change from shallow and fine furrows to fatigue cracks. The abrasive particles on the surface of the material adhere to the surface of the material under the action of compressive stress. And as the load increases, when the hard ceramic ball is subjected to sliding friction, due to the periodic load, a large alternating stress is generated in the friction area of the sample, causing plastic deformation of the friction surface. Cracks were caused in the weak surface layer, and many peeling pits appeared on the surface of the material. The main wear mechanism is fatigue peeling wear, but its scratches are shallower than under 8 N load. As shown in figure 9(d), the hard ceramic ball with large load causes obvious strip-shaped fatigue cracks, layered spalling and brittle pits during the wear process [20], which causes serious wear.

### 3.3. Corrosion performance analysis

The sample surface of the substrate and the medium entropy alloy additive layer need to be smoothed with sandpaper. Wrap the test part of the sample with non-conductive epoxy resin and only expose the surface to be tested. By measuring the polarization curves of the samples of the substrate and the medium entropy alloy

| Sample                        | Maximum depth/mm | Crosssectional area of wear marks/mm² | Wear volume/mm³ | Wear rate mm³/(N·mm) |
|-------------------------------|------------------|---------------------------------------|-----------------|----------------------|
| Substrate                     | 2.86 × 10⁻²      | 6.88 × 10⁻³                           | 3.44 × 10⁻²     | 1.15 × 10⁻³          |
| Medium entropy alloy additive layer | 1.81 × 10⁻²  | 3.26 × 10⁻³                           | 1.65 × 10⁻²     | 5.44 × 10⁻⁴          |

Figure 9. Wear profile of Additive layer under different loads.
additive layer to compare the corrosion resistance of the two. Figure 10 shows the potential polarization curves of the base material and the medium entropy alloy additive layer exposed to 3.5% NaCl solution. It can be seen from the figure that the polarization curve of the medium entropy alloy additive layer fluctuates slightly, which is caused by the roughness of the surface of the additive layer. Because of no sign of transition in the polarization curve, it indicates that the additive layer exhibits excellent self-passivation properties in solution and formed a protective film of corrosion potential on its surface. Furthermore, the medium entropy alloy additive layer shows a certain degree of bluntness. The additive layer is rich in Cr element. Cr dissolution will form a chromium oxide protective oxide film. Chromium oxide makes the additive layer more resistant to corrosion, which further hinders dissolution [21, 22]. The results of E_{SCE}, |J_{corr}| and the average corrosion rate obtained from the potentiodynamic polarization curve are shown in table 4. As shown in table 4, the self-corrosion potential of the medium entropy alloy additive layer is about −0.300 V_{SCE}, and the self-corrosion potential of the substrate is about −0.597 V_{SCE}. The medium entropy alloy additive layer has a higher self-corrosion potential than the substrate. This indicates that the corrosion tendency of the material is weak. In addition, the corrosion current density of the medium entropy alloy additive layer (1.710 × 10^{-6} A cm^{-2}) is much smaller than that of the base material (1.422 × 10^{-5} A cm^{-2}). The corrosion rate of the medium entropy alloy additive layer (0.0367 mm·year^{-1}) is nearly one tenth of that of the substrate. It shows that the medium entropy alloy additive layer has strong corrosion resistance. The test results of the polarization curve show that the corrosion resistance of the medium entropy alloy additive layer is significantly higher than that of the substrate. Therefore, medium entropy alloy powder-core wire arc welding of low-carbon steel can effectively improve the corrosion resistance. This is due to the improvement of the intergranular corrosion resistance of the medium entropy alloy additive layer after the grain refinement. The pits are small and scattered when pitting occurs. The finely dispersed pits reduce the area of the cathode when corrosion occurs and can also reduce the anode current density, further improving the pitting corrosion resistance of the medium entropy alloy additive layer. In theory, according to the mixing effect, the medium entropy alloy powder core wire contains many elements of Ni and Co, which have excellent corrosion resistance in 3.5% NaCl solution. This allows them to form a passivation film on the surface of the medium entropy alloy additive layer to prevent further corrosion of the surface. Therefore, the medium entropy alloy additive layer has better corrosion resistance than the substrate.

Table 4. Specific parameters of electrochemical corrosion performance.

| Sample                              | E_{SCE}/V     | |J_{corr}|/(A·cm^{-2}) | Corrosion rate/(mm·year^{-1}) |
|-------------------------------------|---------------|-----------------|-----------------|-----------------|
| Substrate                           | −0.597        | 1.422 × 10^{-5} | 0.3255          |
| Medium entropy alloy additive layer | −0.300        | 1.710 × 10^{-6} | 0.0367          |

Figure 10. Polarization curve of electrochemical corrosion.
4. Conclusions

This study successfully carried out arc welding of medium entropy alloy powder core wire to strengthen the surface of low carbon steel. The microstructure, wear mechanism and corrosion resistance of the medium entropy alloy additive layer were explored. The main conclusions are as follows:

1. The medium entropy alloy additive layer is significantly improved compared to the substrate microhardness. The microstructure is a lamellar structure of pearlite, which is wrapped with a face-centered cubic solid solution phase (FCC) unevenly distributed in the additive layer.

2. Under dry friction conditions, the friction coefficient of the medium entropy alloy additive layer decreases with increasing load. The wear mechanism is mainly represented by abrasive wear and fatigue spalling wear. The wear rate of the additive layer is much lower than that of the substrate. The wear resistance is doubled compared to the substrate.

3. In the 3.5% NaCl corrosion solution, the medium entropy alloy additive layer has excellent corrosion resistance. The corrosion rate of the additive layer is almost one tenth of the substrate.

4. Arc cladding medium entropy alloy powder core wire can meet the surface strengthening requirements of low-carbon steel parts. It can provide a basis for the application of low-carbon steel in a wide range, multiple fields and high levels. Research has proved that it can be applied to surface strengthening work.

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