Preparation and research of metal-base cold spray seawater-corrosion-resistant coatings

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Abstract. Four composite coatings of aluminum, zinc, aluminum zinc and high aluminum bronze were prepared by low-pressure cold spraying technology on 45 steel substrate. Study on microstructure and corrosion resistance of coating by scanning electron microscopy, electrochemical workstation and static immersion. The results showed that compared with the other three coatings. The high aluminum bronze coating was the lowest porosity(0.41%), the highest self-corrosion potential (-1.38v), and the lowest corrosion rate (0.044mm/a), The coating shows good corrosion resistance and can provide long-term and effective protection for the substrate.

Introduction

In the traditional thermal spraying process, due to the use of high temperature heat sources, such as high temperature plasma, arc, combustion flame, usually powder particles or wire are heated to melting state[1].This kind of high temperature inevitably causes a certain degree of oxidation, decomposition, evaporation and grain growth of metal or metal ceramic materials in the process of spraying, which influences the performance of the coating[2-3].

Cold spray, also known as cold air-powered spray, the process is through the pressurized preheated air flow, gradually scaling nozzle and pressurized powder feeder, resulting in fine highly focused spray flow [4] .Compared with thermal spraying, cold spraying has the advantages of low spraying temperature [5], high deposition rate [6], less susceptibility to oxidation, without decarburization and phase transformation during powder spraying [7-10].

In this experiment, four kinds of metal-based composite coatings of aluminum, zinc, aluminum-zinc and high-aluminum bronze were prepared by low pressure cold spray technique. The coatings were subjected to static immersion and potentiodynamic polarization curve test. Study the four kinds of coatings before and after corrosion of the micro-morphology.

Test materials and methods

Experimental powder

The experiment uses the aluminum powder and high aluminum bronze powder prepared by the atomization method, the zinc powder prepared by electrolysis as the matrix phase, and the irregular aluminum oxide powder as the reinforcing phase, powder ratio and spray parameters are optimized process. The ratio of spray powder is Al-15%Al_2O_3, Zn-10%Al_2O_3, (Al-15% Zn)-10%Al_2O_3, (Cu-14Al-X) -30% Al_2O_3. The matrix is 45 steel. Before spraying the substrate sandblasted.

Test method

Coatings were made using the GDU-3-15 spray coating machine from Belarus, before spraying the high aluminum bronze powder modification used muffle furnace, the treatment temperature is 300 ˚C, insulation for two hours. Spraying process parameters are as follows: The carrier gas is compressed air, the pressure is 0.6Mpa, the spraying distance is 20mm, the spraying gas temperature of the aluminum powder is 300 ˚C, the zinc powder is 200 ˚C, the aluminum zinc powder is 300 ˚C, the high aluminum bronze powder is 500 ˚C. The epoxy resin and ethylenediamine are mixed according to a certain proportion, and the uncoated surface of the sample is encapsulated. After being solidified for 48 hours at room temperature, the coated surface is polished to a bright surface with 400-1000 grit paper, and after being cleaned by ultrasonic wave, after 24 hours in the desiccator, measure the area and mass of the sample.

Using JSM6700F scanning electron microscope before and after corrosion on the sample surface and cross-sectional morphology were observed.

Electrochemical experiments were performed using a electrochemical workstation to measure the potentiodynamic polarization curve. The auxiliary electrode was a platinum plate. The test area was 10 mm × 10 mm and the corrosion medium was 3.5% NaCl solution. The scanning speed For 1mV / s.

Put the sample into 3.5mol/L NaCl solution, soak 168h at room temperature and then remove the sample, corrosion products are removed according to the Metal Corrosion Handbook: Aluminum and aluminum-zinc coating with 70% HNO_3 to remove corrosion products, zinc coating with saturated ammonium acetate to remove corrosion products, high-aluminum bronze coating volume ratio of 1: 1 HCl and H_2O mixed solution to remove corrosion products (the regular shape of the epoxy resin were placed in NaCl solution, calculate the mass loss per unit area, to amend the sample loss data). The corrosion rate of the coating is calculated as follows:

$$V = \frac{W_0 - W_1}{st}. \quad (1)$$

In the formula: V—Corrosion rate during weightlessness ($g \cdot m^{-2} \cdot h^{-1}$)

W_0—The initial weight of the metal specimen（g）

W_1—The weight of the metal after the corrosion product has been removed（g）

S—Metal sample area（m^2）

t—Corrosion time（h）

$$D = 8.76\frac{V}{r}. \quad (2)$$

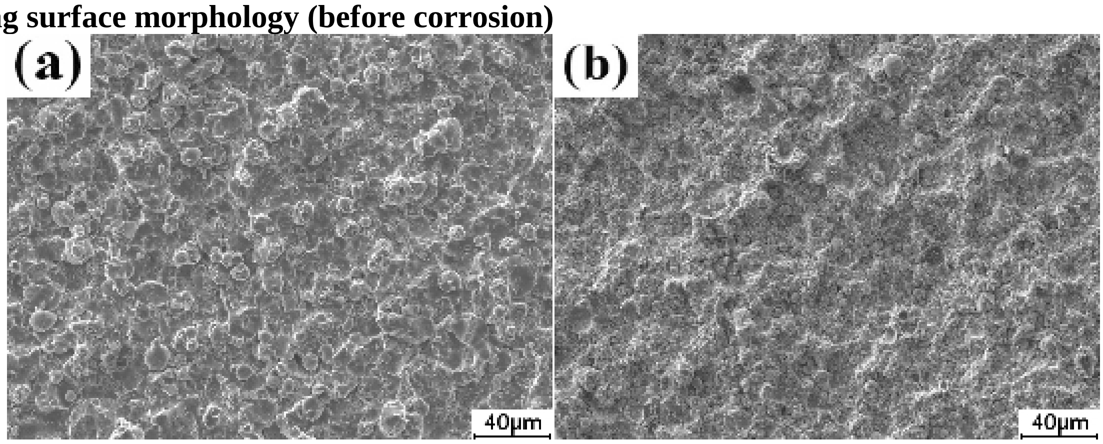
In the formula: V—Corrosion rate during weightlessness ($g \cdot m^{-2} \cdot h^{-1}$)

D—Corrosion depth ($mm \cdot a^{-1}$)

ρ—Metal density ($g \cdot cm^{-3}$)

Results and analysis

Coating surface morphology (before corrosion)



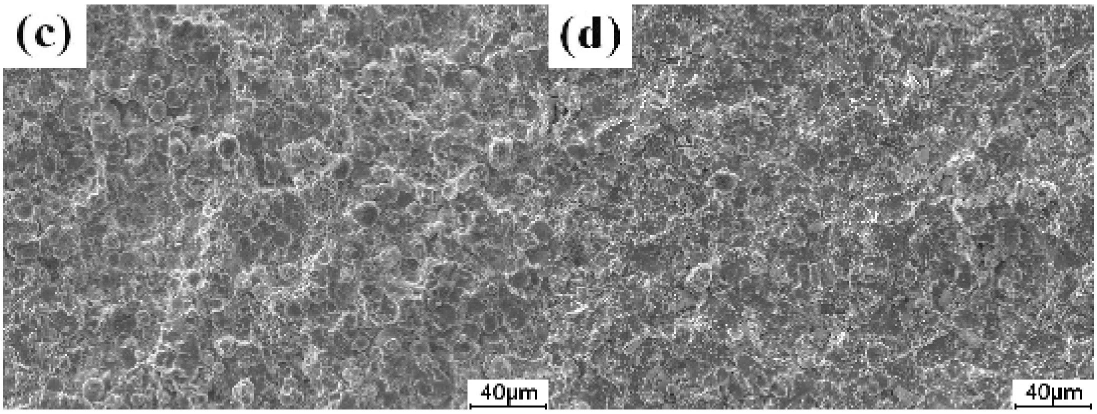


Fig.1 Microstructure of coating: (a) Aluminum; (b) Zinc; (c) Aluminum-zinc and (d) High-aluminum bronze

As shown in Fig.1 for the four coating morphology, we can see that the four coating surface are relatively flat, no significant depression; Using the image software to measure the porosity of the four coatings, the results of the four coatings were 0.47%, 0.56%, 0.58%, 0.41%. It can be seen that the porosity of the four coatings is very small, but in contrast, the performance of high aluminum bronze coating is the best.

Coating surface morphology (after corrosion)

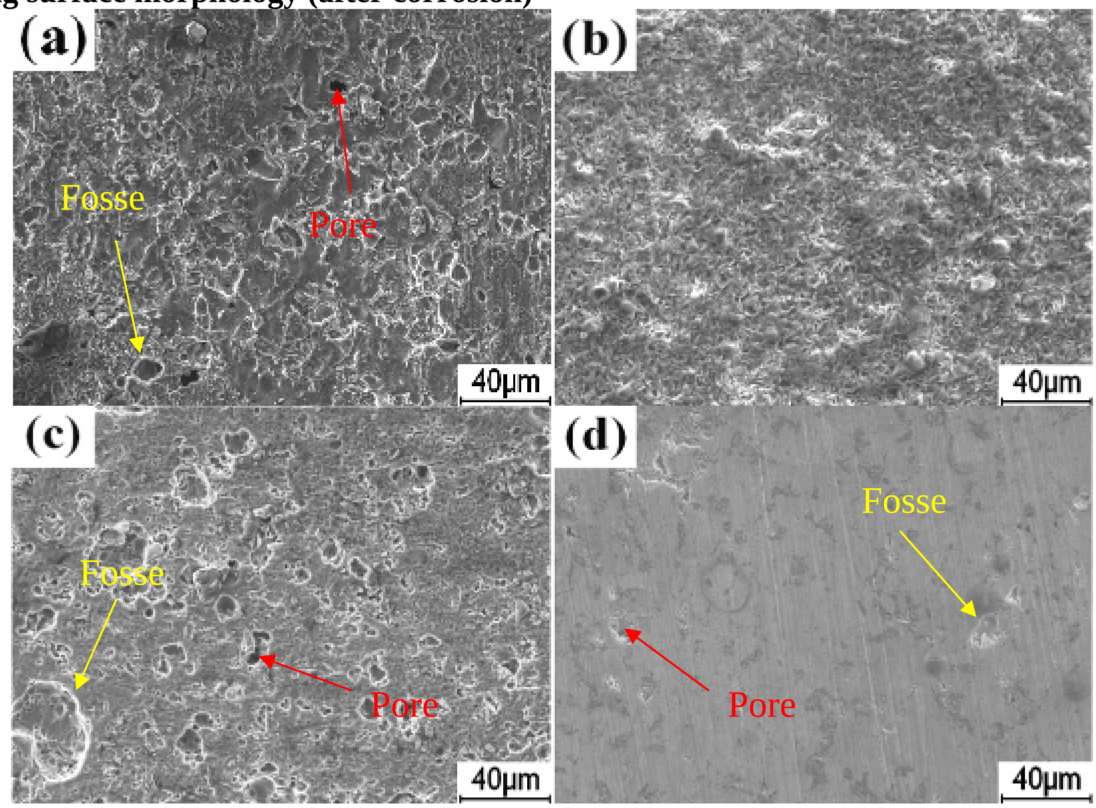


Fig. 2 Microstructure of coating: (a) Aluminum; (b) Zinc; (c) Aluminum-zinc and (d) High-aluminum bronze

As shown in Fig. 2, after the four coatings were etched, different degrees of corrosion holes (red arrows) and corrosion pits (yellow arrows) appeared on the coating surface. The corrosion pits and corrosion holes are the most on the surface of aluminum-zinc coating, and the corrosion pits and corrosion holes are relatively large, the coating corrosion resistance is poor; the surface of zinc coating is acicular structure, there are many evenly distributed small pores; in contrast, high aluminum bronze coating surface is relatively flat, without pit corrosion, EDS spectrometry, the dark gray area of high alumiunm bronze coating are aluminum particles, from 1.1 we can see that the high aluminum bronze coating corresponding to the original alumina powder content is the largest, so the coating also contains more alumina particles, indicating that the alumina coating porosity play a very good filling effect, inhibits the intrusion of corrosive media.

Due to the existence of different degrees of corrosion pits and corrosion holes on the surface

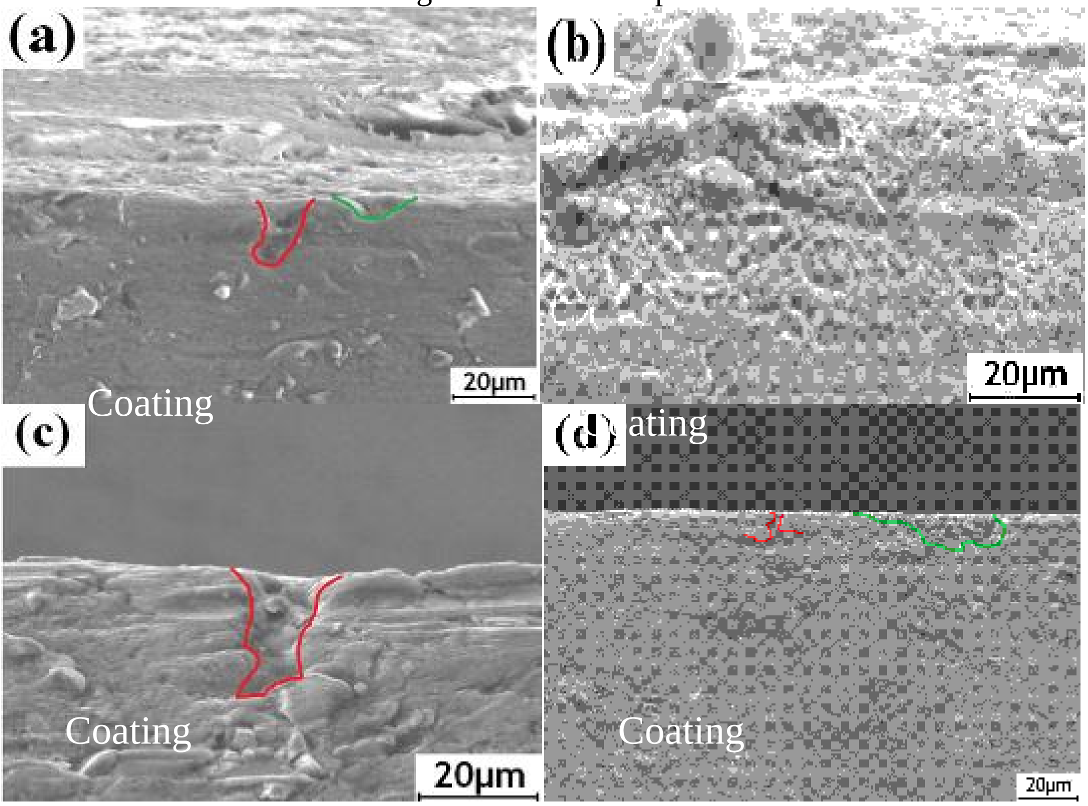


Fig. 3 Microstructure of coating cross-section: (a) Aluminum; (b) Zinc; (c) Aluminum-zinc and (d)

of the four coatings, in order to prevent the phenomenon of "*perforation*", the micro-morphology of the coating cross-section was characterized. As shown in Figure 3, the red marking area in the coating is a corrosion hole and the green marking area is a corrosion pit. The inner corrosion area of the zinc coating is a through hole and the holes are evenly distributed. Since the depth of the etching holes in the four coatings is relatively shallow, only a thin layer of corrosion is formed on the surface of the coating without "*punching*", the coating can still provide good protection for the substrate.

Electrochemical test results

It can be seen that there is no difference between the cathodic polarization curves of the four kinds of coatings, all of which occur in the reduction reaction $O_2 + H_2O + 4e \rightarrow 4OH^-$. However, the anodic polarization curve is quite different. the high-aluminum bronze coating, zinc coating and aluminum-zinc coating enter the passivation stage after transient dissolution. As the potential increases, the passivation film breaks down, the coating continues to corrode. However, there is no obvious passivation zone in the aluminum coating because as the current enters the etching solution, the aluminum on the coating surface begins to electrolyze, forming Al^- into the etching solution and

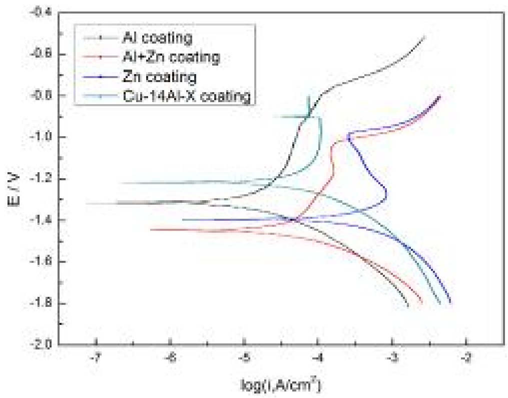


Fig. 4 aluminum, zinc, aluminum zinc, aluminum bronze coating polarization curve subsequently with OH^- to form $Al(OH)_3$ oxide film, covering the coating surface, but the oxide film is thin, have not had time passivation, it has been dissolved in the etching solution. A comparison of the self-corrosion potentials of the four coatings shows that the highest corrosion potential of the high-aluminum bronze coating (-1.217V) indicates that the high aluminum bronze coating is more resistant to corrosion.

Static soaking results

As shown in Fig. 5, the abscissa 1-4 respectively represents aluminum, zinc, aluminum zinc, high aluminum bronze coating, it can be seen that the corrosion rate of high-aluminum bronze coating is the smallest (0.044mm/a) and the corrosion rate of aluminum-zinc coating is the highest (0.1293mm/a) according to the depth of corrosion, which agrees well with the results of polarization curve. Four kinds of coating corrosion rates are very low, according to the depth of corrosion level four standard division, high aluminum bronze coating is corrosion level (very corrosion resistance), the other three coatings belong to corrosion two (corrosion resistance), the four coatings are corrosion-resistant materials, can provide long-term effective matrix protection.

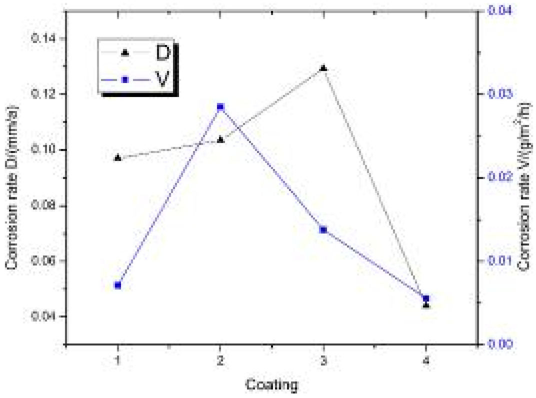


Fig.5 Four kinds of coating corrosion rate

Conclusion

（1） Aluminum, zinc, aluminum zinc and high aluminum bronze coatings prepared by low-pressure cold spraying have excellent densification.

（2） The corrosion rate of the high-aluminum bronze coating is the least after 168 hours of static soaking of the four kinds of coatings, and the phenomenon of "perforation" of the four kinds of coatings does not appear, which can provide effective protection for the substrate.

（3） Compared with the other three, high aluminum bronze coating has the highest self-corrosion potential and the coating has the best corrosion resistance.

Acknowledgments

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