Comparison of Performance and Microstructure of Two Kinds of Cold Spray Anticorrosion Composite Coatings on High-strength Steel

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Abstract. Objective to study the performance of Zn/Ni composite coatings and Al/Zn composite coatings, which were deposited by Cold Gas Dynamic Spray. Methods: Those coatings was sprayed by Zn and Ni mixture powder and Al and Zn mixture powder on 300M high-strength steel surface, the SEM images and micro hardness tester analyzed the two kinds coatings' morphology and microstructure. The corrosion resistance of Zn/Ni coatings can be compare with Al/Zn coatings, which was investigated by neutral salt-spray test and coating furcated test. Results The results indicate that Zn/Ni coatings porosity is 0.8%, it is same as Al/Zn coatings. The micro hardness of Zn/Ni coatings is 70.8HV, which is higher than Al/Zn coatings 61.2HV. However, the salt spray result of Al/Zn coatings can reach 1000h and it can reach 770h even the coatings fails; which is better than Zn/Ni coatings, their salt spray resistance can reach 770h and it can reach 350h when the coatings fails. Conclusion those coatings could both be efficient corrosion resistance coatings on 300M high strength steel surfaces.

1. Introduction
High strength steel members have the characteristics of high strength, good transverse plasticity, high fracture toughness, excellent fatigue performance, and good resistance to stress corrosion [1]. Therefore, it is widely used in automobile, aircraft, ship and other large machinery manufacturing industries. Cadmium coating is widely used in corrosion protection of high strength steel [2]. However, since cadmium coating is toxic and unfavorable for environmental protection, and cannot be applied at a temperature higher than 230℃ [3], otherwise it will cause cadmium embrittlement and lead to fracture failure. Therefore, it is urgent to develop green and environment-friendly cadmium protection technology for high strength steel.

As a corrosion resistant coating [4], aluminum-zinc composite coating not only has the function of isolating corrosive media, but also is an anodic material for steel and other matrix materials, whose corrosion resistant performance is better than that of pure aluminum and pure zinc coating, so it is widely used as corrosion resistant for steel components [5]. Similarly, the corrosion resistance of zinc-nickel composite coatings in industrial and marine atmospheres is comparable to that of cadmium plating [6], which is 3–6 times higher than that of plating pure aluminum [7]. Moreover, zinc-nickel alloy has excellent machining performance, which is especially suitable for surface protection of high-strength...
steel parts [8]. A large number of studies have been carried out at home and abroad on the application of these two corrosion resistant coatings as alternative cadmium coatings, including the use of cold spraying technology to prepare these two composite coatings for the protection of high-strength steel [9].

Cold spraying, also known as low temperature pneumatic spraying technology, is a new spraying technology invented by Russian scientists in the 1990s [10-12]. The technology uses high-speed gas (air, nitrogen or argon) after preheating and pressing to accelerate the powder particles, and the powder particles reach the sound velocity after passing through the Laval nozzle. Under the condition of complete solid state, the coating is deposited by impinging on the substrate and forming plastic deformation. Compared with the traditional thermal spraying, the cold spraying has little thermal effect on the matrix, and the powder particles do not undergo oxidation and phase transition during the spraying process, which can completely maintain the microscopic characteristics and physicochemical properties of the powder in the initial state [13-17].

2. Experimental Equipment and Methods

2.1. Laboratory equipment and materials

The 300M steel used in the matrix material is a kind of low alloy and high strength steel successfully developed by International Nickel Company in the 1950s. Before the test, acetone is used to clean the surface oil, then blow dry and blow sand. The aluminum powder, zinc powder and nickel powder used in spraying are all provided by Beijing Mining and Metallurgical Institute. The atomization method is prepared to get the purity of above 99.99%, and the surface morphology is shown in Figure 1. The particle size range of pure aluminum powder is 38μm - 74μm, the average particle size of pure zinc powder is about 44μm, the average particle size of pure nickel powder is about 47, and the powder particles are mainly circular, which is beneficial to the deposition of cold spray coating.

![Figure 1. Al, Zn and Ni power particle SEM images](image)
(a) Al powder; (b) Zn powder; (c) Ni powder.

The cold spraying equipment used in the experiment was introduced from the Institute of Theoretical Mechanics and Application of Siberian Branch of the Russian Academy of Sciences in 2007. The working parameters for preparing the two kinds of composite coatings are shown in Table 1.

| Table 1. Cold spray parameters. |
|---------------------------------|
| Mass proportion | Working gas | Temperature | Gas pressure | Moving Speed |
|------------------|-------------|-------------|-------------|--------------|
| Zn: Ni = 85:15   | Compressed  | 300-400 °C  | 2.0-2.5     | 30-50        |
| Al: Zn = 80:20   | air         | MPa         | mm/s        |              |
2.2. Experimental methods

2.2.1. Microstructure. SEM is used to analyze the surface and cross section of cold sprayed Zn-Ni composite coating, to observe the powder particle deposition structure, and to calculate the porosity of the coating.

2.2.2. Coating hardness. The micro hardness of the coating is measured by micro hardness meter, and the point is taken from the surface to the inside.

2.2.3. Corrosion resistance. The neutral solution of industrial sodium chloride with purity ≥95.5% is used as corrosion acceleration solution, and its pH is 6.5~7.2. It can be pressed to form a fine mist evenly distributed on the surface of the sample. At the same time, 300M steel substrate and two kinds of composite coatings are added to observe the corrosion of salt spray regularly, and the corrosion resistance of cold sprayed Al-Zn composite coating and Zn-Ni composite coating is compared [18].

3. Results and discussion

3.1. Microstructure

![Figure 2. Cold spray Al/Zn and Zn/Ni coating SEM images (a) Al/Zn coating surface; (b) Al/Zn coating cross-section; (c) Zn/Ni coating surface; (d) Zn/Ni coating cross-section.](image)

Figure 2. Cold spray Al/Zn and Zn/Ni coating SEM images (a) Al/Zn coating surface; (b) Al/Zn coating cross-section; (c) Zn/Ni coating surface; (d) Zn/Ni coating cross-section.

Figure 2 (a) and (b) is the surface microstructure and cross section morphology of cold sprayed Al-Zn composite coating. It can be clearly seen from the Figure that the Al-Zn particles are deposited in different deformation conditions. The Al particles are larger in size and have sufficient deformations, and the mechanical occlusion phenomenon is more obvious; while Zn particles are small in size, most of which are embedded in the deformed aluminum particles, and the two kinds of Al and Zn particles can be clearly distinguished from the Figure. Figure 2 (c) and (d) is the surface microstructure and cross section morphology of cold sprayed Zn-Ni composite coating. As can be seen from the Figure, the
binding between the coating itself is very dense and the microcracks are very small. The two kinds of particles have different volumes and are clearly distinguishable. The pores and cracks in the coating can hardly be seen, and the joint with the 300M matrix is very compact. The Figure shows that the particles are completely deformed during the spraying process, forming a very compact coating.

It can be seen from the Figure 2 that two kinds of composite coating is very even and dense, and the average porosity of the two kinds of composite coatings is also about 0.6% by SEM analysis, while porosity of ordinary flame spraying is 10%~20%, of electric arc spraying is generally around 10%, and of plasma spraying is 2%~5% [19-21]. Compared with traditional thermal spraying, cold spraying significantly improves the porosity of coating. Furthermore, the internal compressive stress of both composite coatings is favourable for the preparation of thick coatings. It can be seen from Figure 2 (b) and (d) that the composite coating forms a mechanical bite at the convex and concave surface of the sand blowing surface of the matrix, and there is an obvious interface between the coating and the matrix without transition layer. The defects and holes can hardly be seen under electron microscope, which indicates that the bonding strength and mechanical properties of the Zn-Ni composite coating are very good.

3.2. Coating hardness
Coating hardness is one of the important indexes of reactive coating properties, which can characterize the wear resistance of the coating to a certain extent. The micro hardness of the two cold-sprayed composite coatings is measured by taking 10 points from the surface to the inside, and the distance between the two points is about 40μm, the average micro hardness of the cold-sprayed Zn-Ni composite coating is 70.8HV0.49, the average micro hardness of cold-sprayed aluminum-zinc composite coating is HV 61.20.49 (Table 2).

Table 2. Results of micro hardness of samples

| Sample | Micro hardness (HV0.49) | Mean |
|--------|-------------------------|------|
| Zn/Ni  | 74.7  66.6  71.0  70.8  70.8  67.8  70.9  74.8  73.8  66.8 | 70.8 |
| Al/Zn  | 63.7  64.0  49.8  65.3  52.4  63.8  59.8  69.8  60.4  62.8 | 61.2 |

The results show that the hardness distribution of the two cold spray coatings is basically uniform from the surface to the inside of the coating. This is because in the process of cold spraying, the first deposited particles are impacted by the subsequent particles to form micro-forging structure, which makes the bonding with the substrate or the deposited coating more firm and the coating more compact. In addition, the hardness of the composite coating is evenly distributed instead of stepping [22]. Moreover, the hardness of cold sprayed Zn-Ni composite coating is higher than that of cold sprayed Al-Zn composite coating because nickel particles act as strengthening phase in the middle of the coating and improve the hardness of the whole coating [23]. This makes the Zn-Ni composite coating have good wear-resisting ability, and can play the double protective effect of corrosion resistance and wear resistance.

3.3. Corrosion resistance
Neutral salt spray test is used to evaluate the corrosion resistance of cold spray composite coating by artificial accelerated corrosion simulation. Neutral salt spray test is carried out on cold sprayed Al-Zn composite coating and Zn-Ni composite coating samples at the same time to observe the surface condition and compare the experimental results. In addition, in order to investigate the protective ability of the coating to the substrate after being damaged, the coating surface is crossed to make the coating damaged to the substrate before the experiment, and then the salt spray experiment is carried out.

After 350h of neutral salt spray experiment, red corrosion appears on the surface of the fork specimen of Zn-Ni composite coating, which is the corrosion product of the matrix steel. The broken area of the
fork specimen of Al-Zn composite coating is completely covered by white corrosion products, but no red rust is produced; after 770h, red corrosion appears on the surface of the forked sample of Al-Zn composite coating, the complete samples of the two kinds of coating show corrosion, with white surface and obvious granular sensation; after 1000h, matrix red rust and obvious corrosion pits and corrosion cracks appear on the surface of the Zn-Ni composite coating, but no corrosion occurs on the Al-Zn composite coating, and the surface morphology is uniform and dense. This indicates that the cold spray Al-Zn composite coating has better corrosion resistance than the Zn-Ni composite coating. Red rust appears in the Zn-Ni composite coating after 350h salt spray test, indicating that even if the coating is damaged, the substrate could still be protected within 350h. Similarly, the aluminum zinc composite coating can protect the matrix within 770h under the state of damage.

The salt spray test of cold sprayed pure zinc coating is 360h, while the salt spray test result of Zn-Ni composite coating is 770h, and the salt spray test result of Al-Zn composite coating is 1000h, which is better than that of pure zinc coating. The corrosion condition of the two composite coatings is basically the same as that of the pure zinc coating, and Zn$^{2+}$ is formed by the zinc oxidation reaction within the coating, and then combined with the OH$^-$ generated by oxygen absorption reaction to form Zn(OH)$_2$. Due to the presence of a large amount of Cl$^-$ in the salt spray experiment, the Zn(OH)$_2$ in the late corrosion stage will further generate ZnCl$_2$·4Zn(OH)$_2$·H$_2$O and a small amount of Zn$_4$CO$_3$(OH)$_6$·H$_2$O. Unlike pure zinc coatings, ZnO is not found in the corrosion products of cold-sprayed Zn-Ni composite coating. The main reason is that the nickel in the coating can effectively stabilize Zn(OH)$_2$, making it difficult to transform into ZnO. In addition, different from the corrosion resistance principle of electroplate Zn-Ni alloy, there is no stablelyphase Zn-Ni alloy in the composite coating, but due to the effect of nickel, the corrosion product of the composite coating ZnCl$_2$·4Zn(OH)$_2$·H$_2$O can cover the coating uniformly and compactly, which is not easy to conduct electricity, so that the cold spraying Zn-Ni composite coating has good corrosion resistance. The Al-Zn composite coating forms oxide film on the surface at the initial stage of corrosion. In addition to delaying the corrosion of the coating surface, it can also plug up the pores and further prevent the penetration of corrosive media. The two kinds of composite coatings are sacrificial anode coatings relative to the matrix of high strength steel. Therefore, when the coating is damaged, the coating will corrode first to protect the matrix material.

![Figure 3. Test images of cold Spray composite coating salt spray. (a) Zn/Ni furcates coating 350h; (b) Al/Zn furcates coating 350h; (c) Zn/Ni coating 770h; (d) Al/Zn furcated coating 770h; (e) Zn/Ni coating 1000h; (f) Al/Zn coating 1000h](image)

4. Summary
First, the Zn-Ni composite coating and Al-Zn composite coating with cold spraying are all compact and free of pores and cracks, with an average porosity of 0.8%. The particle deformation is quite sufficient, and the mechanical occlusion phenomenon is obvious.
Second, the micro hardness of Zn-Ni composite coating with cold spraying is 70.9HV_{0.49}, and that of Zn-Ni composite coating with cold spraying is 61.2HV_{0.49}. The strengthening effect of nickel particles in Zn-Ni composite coating improves the hardness of coating and makes it higher than that of Al-Zn composite coating.

Third, Zn-Ni composite coating and Al-Zn composite coating have very good corrosion resistance. The salt spray test of Zn-Ni composite coating is more than 770h, even if the coating is damaged, it can reach 350h. The salt spray test of Al-Zn composite coating exceeds 1000h, even if the coating is damaged, it can reach 770h.

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