The corrosion behavior of cold spray coating on 2219 aluminium alloy joints prepared by friction stir welding

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Abstract: A compact coating was deposited on the surface of a friction stir welded 2219-T6 aluminum alloy joint via cold spraying for corrosion protection. The results showed that a relatively dense coating could be formed in the FSW joint surface. Corrosion resistance of the coating is pretty good with the average discharge potential of -0.638 V (vs. SCE) and corrosion current density is 7.034 μA·cm⁻². Immersion tests in the exfoliation solution confirmed that the presence of coating significantly decreased the corrosion attack. The corrosion of coating begins with pitting, which is mainly at the coating porosity. It gradually developed into the intergranular corrosion and exfoliation corrosion ultimately.

Key words: Friction stir welding; 2219 aluminum alloy; Cold spraying; Corrosion behavior.

1. Introduction
Friction stir welding (FSW) is an innovative solid state process invented by The Welding Institute (TWI) at 1991, which is seen as another revolutionary technology after laser welding. Now it has been widely used in many industries, like aerospace, vehicle orbit and shipbuilding [1]. In the past decades, the studies of friction stir welded aluminum alloy have focused on joint organization analysis and mechanical properties [2, 3]. However, in some aggressive service environments, the corrosion performance of joints should have to be considered.

At present, there are some researches on the corrosion behavior and stress corrosion cracking resistance of welds. Due to the thermomechanical processing conditions during FSW, the joints present a different grain structure, which as a result changes the corrosion susceptibility of joints [4]. Numerous studies [5-7] showed that the joint corrosion resistance is worse than the base metal. There...
are some methods to improve corrosion resistance of joints: post-weld heat treatment [8], micro-arc oxidation [9] and laser cladding [10]. However, when using the above methods the structure is limited, the element is enriched and so on. Cold spraying (CS) technology has been developing rapidly since 1990 as a new type of anticorrosion coating preparation. It is widely used in all kinds of metal surface protection [11]. To date, only W.Y. Li [12] showed the protection of FSW joint by Al₂O₃ and pure Al coatings. The results indicate that CS is a promising method to protect FSW joints against corrosion. In this work, Al coating was cold sprayed on the surface of FSW 2219 joints to investigate its effect on the properties of joints, including the corrosion behavior of the coating.

2. Experimental procedures

A 6-mm thick 2219 aluminum alloy plate in T6 temper condition was used in this paper. Two plates were butt-welded by FSW at a rotation speed of 400 rpm and a welding speed of 150mm/min. The tilt angle of FSW tool was 3° with respect to the vertical direction. Al coating was deposited by the cold spray system developed in Xi’an Jiaotong University, China. The feedstock of the coating was a gas-atomized 2219 Al alloy powder with spherical morphology (-325 mesh). Ultimately, a 0.5-mm thick coating was deposited on the surface of a FSW 2219 aluminum alloy joint. Corrosion studies have been carried out using potentiodynamic polarization tests. A flat cell was used for all the experiments and a 10 mm wide specimen is used as working electrode, a platinum mesh is used as auxiliary electrode and saturated calomel electrode as reference electrode. 3.5% NaCl was used as the electrolyte. Potentiodynamic polarization tests were carried out a scan rate of 1 mV/s with an initial potential of 0.2 mV.

All solutions in this study were prepared according to the ASTM G34-01 standard. The exfoliation corrosion (EXCO) solution was prepared as follows as: 4 mol/L NaCl + 0.5 mol/L KNO₃ + 0.1 mol/L HNO₃ at pH 0.4 in 25°C. The surface morphology was observed using scanning electron microscope (SEM) methods.

3. Results and discussion

3.1. Characteristics of CS coating and FSW joint

Figure 1 shows the cross-section of friction stir welded joint. It can be seen that the joint is divided into four characteristic zones, base material (BM), heat-affected zone (HAZ), thermos-mechanically affected zone (TMAZ) and weld nugget zone (WNZ). BM zone is consisted of coarse grains elongated along the rolling direction. The obvious coarsening phenomenon occurred in the grain of HAZ. Grains in TMAZ are slightly elongated and bent along the rotating direction. The grain structure within the WN is consisted of fine equiaxied recrystallized grains, due to the intensive thermo-mechanical effects during the welding process.

A 0.5mm thick CS coating was obtained on the surface of the FSW joint. The microstructure cross-section of CS coating is shown in Figure 2 (high magnification of the region marked by red rectangle in Figure 1). It is clearly seen from Figure 2a that the interface between the coating and the joint is obvious but no crack and pore, which is shown that the connection between the coating and the joint is mainly mechanical bite with only a few metallurgical bonds. In the inner region of the coating (Figure 2b), due to the huge impact of cold spraying and the pressure of the surface coating particles
on the internal particles, the coating particles are severely deformed and the cross-section presents a flattened morphology. There is no evidence of pores in the inner coating.

![Cross-section of the FSW joint.](image1)

**Figure 1.** Cross-section of the FSW joint.

![Microstructure cross-section of CS coating.](image2)

**Figure 2.** The microstructure cross-section of CS coating: (a) coating and FSW joint interface, (b) the inner coating.

### 3.2. Local electrochemical measurements

The local electrochemical open circuit potentials (OCP) of the CS (red rectangle in Fig.1), BM(black rectangle in Fig.1), TMAZ/HAZ(blue rectangle in Fig.1), and WNZ(pink rectangle in Fig.1) regions in 3.5% NaCl solution at 25°C are measured. The OCP measurement was recorded for 600 s. The potential of the parent alloy reached -0.74 V vs. SCE, while those of the HAZ/TMAZ and weld nugget regions are -0.79 V vs. SCE and -0.59 V vs. SCE. Relatively, the potentials of the cold spray coating is similar to that of the parent alloy, which is due to the fact that they are made of 2219 aluminum alloy and without a thermomechanical processing.

Figure 3 shows the potentiodynamic polarization curves for the CS coating and FSW joints in 3.5% NaCl solution. The self-corrosion potentials and self-corrosion current density are shown in Table 1. The $E_{\text{corr}}$ values of CS coating is much higher than that of HAZ/TMAZ, and slightly higher than that of BM. Relatively, the $E_{\text{corr}}$ value of WNZ is the highest. High $E_{\text{corr}}$ values indicate better corrosion resistance. There are similar trends in self-corrosion current density. The $i_{\text{corr}}$ of HAZ/TMAZ is the highest, which is mean that it has a faster corrosion rate when the corrosion occurred. The $i_{\text{corr}}$ of WNZ is the lowest, which is because the welding nugget area undergoes the significant plastic deformation and recrystallization in the process of FSW, resulting in the fine grain and the microstructural homogenization. For CS coating zone, the $i_{\text{corr}}$ reaches 7.034μA•cm$^{-2}$, which is better than BM (9.900μA•cm$^{-2}$) and HAZ/TMAZ (15.00μA•cm$^{-2}$). So, the HAZ/TMAZ are corrosive sensitive areas, the CS coating has a good protective effect on the HAZ/TMAZ. The CS coating can reduce the
corrosion sensitivity of the joint, and improves the holistic corrosion resistance of the FSW joint.

![Polarization curve of CS coating and FSW joint in the 3.5%NaCl solution.](image)

**Figure 3.** The polarization curve of CS coating and FSW joint in the 3.5%NaCl solution.

| Selected zone | Corrosion potential E/(V, SCE) | Corrosion current density i/(μA·cm$^{-2}$) |
|---------------|-------------------------------|------------------------------------------|
| BM            | -0.700                        | 9.900                                    |
| WNZ           | -0.480                        | 6.026                                    |
| HAZ           | -0.825                        | 15.00                                   |
| CS            | -0.638                        | 7.034                                   |

**Table 1.** Self-corrosion potential and self-corrosion current density of CS coating and FSW joint.

3.3. Corrosion behavior of CS coating

Figure 4 shows the microscopic morphology under different corrosion time. It is seen from Figure 4a that the corrosion was started from the pitting. With the time go on, the corrosion degree deepened constantly, the pitting expanded, and the surface corrosion was more uniform. When the corrosion time reaches 6h (Figure 4b), the local area of the surface began to be darken. It was shown that a lot of corrosion products were produced. The pitting began to connect with each other, and the size of the pitting increased greatly. When the corrosion occurred 12h (Figure 4c), the coating surface was completely black, and the corrosion products on the surface began to fall off. The size of the pitting reached about 200μm. Lamellar morphology can be seen from the local area of the surface. When the corrosion occurred 24h (Figure 4d), the corrosion products have been basically fallen off. The surface became uneven and wavy. The color of the coating surface was shallower, the inner coating particles were exposed and the surface of the particles was obvious.
The corrosion started from the interfaces between the deposited particles (Figure 5a). A larger electrode potential difference is produced between the solution and Al coating, becoming a microscopic corrosion cell. The shape of pitting is prolate and crescent with the size between 10 and 50μm. The corrosion spreads along the surface and depth with erosion time extending (Figure 5b). Because of the strong penetration, Cl can spread to the grain interior quickly, causing intergranular corrosion on the surface of grains (Figure 5c). The grains are coated by corrosion products with a vermicular shape, lose the original smoothness. It is clearly seen from Figure 5d, at the end of the corrosion, the volume of Al coating is expanding, due to a "wedge effect" [13].

**Figure 5.** Corrosion micro morphologies of the coating corroded for (a) 2h, (b) 6h, (c) 12h, (d) 24h.
4. Conclusions
(1) A relatively dense coating could be formed on the weld surface without pores or cracks, and well bonded to the weld by the use of CS with appropriate spray parameters.
(2) Electrochemical tests found that the worst corrosion resistance of FSW joints is heat affected zone. The best corrosion-resistant area is the nugget area. The electrochemical sensitivity of the coating area is similar to the base metal, between the nugget area and the heat affected zone.
(3) In the EXCO corrosive environment, the local pitting preferentially occurs in the coating area, and the pits are mostly located at the junction of coating particles. In the late stage of corrosion, the coating particles have the typical intergranular corrosion and appear vermicular morphology. A large area of crack and obscission are appearing on the surface of the coating eventually.

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