Electrochemical corrosion behavior of arc sprayed Al−Zn−Si−RE coatings on mild steel in 3.5% NaCl solution

Qiong JIANG, Qiang MIAO, Fei TONG, Yi XU, Bei-lei REN, Zhi-mei LIU, Zheng-jun YAO

College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics,
Nanjing 211100, China

Abstract: Al−Zn−Si−RE coating with high Al content was deposited on mild steel by arc spraying. The electrochemical behavior of Al−Zn−Si−RE coating in 3.5 % NaCl solution was systematically studied by potentiodynamic polarization, corrosion potential (φ_{corr}) and electrochemical impedance spectroscopy techniques (EIS). The impedance data were fitted to appropriate equivalent circuits to explain the different electrochemical processes occurring at the electrode-electrolyte interface. The results indicate that Al−Zn−Si−RE coating reveals the similar polarization behavior as Zn−15Al coating. The coating has no passive region in the anodic polarization, but far lower corrosion current and much higher corrosion potential. Al−Zn−Si−RE coating provides effective sacrificial protection for steel substrate and the sacrificial anodic protection plays dominant role during the immersion process. In addition, the φ_{corr} evolution and EIS plots indicate that the corrosion process can be divided into five stages: pitting−dissolution−redeposition, activation corrosion, cathodic protection, physical barriers and the coating failure.

Key words: Al−Zn−Si−RE coating; corrosion potential; corrosion behavior; polarization plots; electrochemical impedance spectroscopy

1 Introduction

Zn−Al sacrificial coatings by flame and wire-arc spray have been widely used for the long-term corrosion protection of steel by combining the great galvanic protection of Zn with the satisfactory erosion resistance of Al [1−4]. In these coatings, the presence of micro porosity and/or oxide content is no longer be a problem, since the coating acts as sacrificial anode with respect to the substrate and protects the latter at its own expense by itself corroding or dissolving preferentially. ORLANDO et al [2,5] found that the thermally sprayed Zn−Al coating exhibited excellent corrosion resistance, even without the use of sealant, providing excellent galvanic protection to the substrate. Therefore, there has been recently growing interest in exploring the corrosion behavior of Zn−Al coating, which offers valuable insights into the improvement of corrosion resistance.

Several studies showed that the addition of micro alloying elements such as Si, Mg, Mn and rare earth (RE) elements into Zn−Al alloy can produce substantial improvements in corrosion resistance and abrasion resistance [6−9]. RE elements, primarily La and Ce, can also improve the wettability and fluidity of molten melts, purify melts and refine the cast microstructure of metals which will not appreciably affect their resistance to corrosion [9−11]. In addition, precious researchers [12−15] found that the corrosion resistance of Zn−Al alloy coating could be dramatically improved by increasing the Al content. Therefore, the research on multicomponent Zn−Al-based alloy wires with high Al content has evoked great interest during the last few years. FENG et al [16] developed series of Al−Zn−Si−RE alloy solid wires. However, there was no systematic studies on the corrosion behavior and mechanism of Al−Zn−Si−RE coating.

The corrosion behavior of thermally sprayed Zn and Zn-based coatings has been studied and reported [12,17], however, little research has been conducted on the

corrosion mechanism of the Al−Zn-based coatings with high Al content up to 50%. Electrochemical evaluation techniques, such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), have been shown in corrosion research to be efficient and convincing tools for analyzing the corrosion behavior of metals [18,19]. In this study, potentiodynamic polarization, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) techniques were carried out to study the corrosion behavior of the Al−Zn−Si−RE coating with high Al content systematically in quiescent 3.5% NaCl solution.

2 Experimental

2.1 Coating material

Zn−15Al and Al−Zn−Si−RE alloy wires (2 mm in diameter), were used as wire materials, and their compositions are listed in Table 1. Cold-rolled Q235 steel plate with dimensions of 5 cm × 7 cm × 0.3 cm was used as substrate. The substrates were degreased ultrasonically in acetone and grit blasted with corundum at the pressure of about 550 Pa just prior to spraying, to remove any contamination from the surface and generate roughened surface that promotes coating adhesion. Compressed air was used to remove any residue from the grit blasting. The coatings were deposited with HAS-02 high velocity arc spraying gun and system CDM AS3000 at normal temperature. Spray conditions are summarized as follows: spraying voltage of 30−32 V, spraying current of 120−140 A, air pressure of 0.65 MPa and spraying distance of 60−120 mm. The samples were cut into small sections (2 cm × 2 cm) in order to allow corrosion tests whose cut edges were sealed by epoxy.

Table 1 Elements content of alloy wires (mass fraction, %)

Alloy	Al	Si	RE	Zn
Al−Zn−Si−RE	50−55	0.2−3	0.02−2	Bal.
Zn−15Al	10−15	−	−	85−90

At least two rare-earth elements selected from the group consisting of La, Ce, Pr and Nd

2.2 Corrosion tests

In order to have better understanding of the corrosion behavior of the coatings, the corrosion potential (φ_{corr}) evolution curves, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were carried out using CHI660d electrochemical working station. All tests were conducted in naturally aerated 3.5% NaCl (mass fraction) solution at room temperature. These experiments were carried out several times and were reproducible. Traditional three-electrode cell was used, with 4 cm^2 platinum sheet as counter electrode, saturated calomel electrode (SCE) immersed in saturated KCl solution as the reference electrode and test specimen with exposed area of 1.0 cm^2 as the working electrode. The coating thickness was around 60 μm.
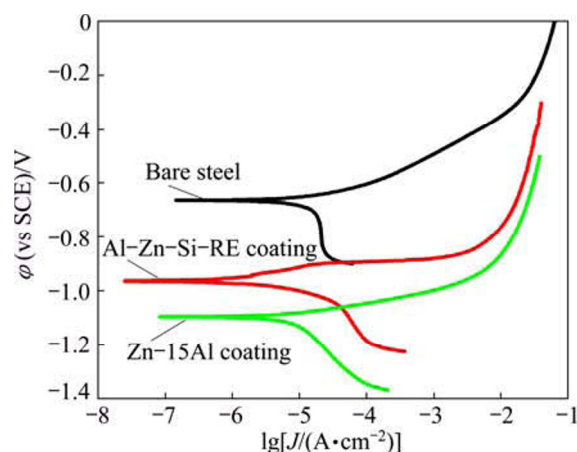
All potentials in this study were reported with respect to saturated calomel reference electrode (SCE). Potentiodynamic polarization studies were carried out in the potential range from −0.30 V to 0.60 V versus corrosion potential at sweep rate of 2 mV/s. All potentiodynamic polarization experiments were conducted after stabilization of free corrosion potentials. The EIS measurements were measured at φ_{corr} over a frequency range from 10 mHz to 100 kHz. The EIS data were analyzed and fitted to appropriate equivalent circuits using the ZSimpWin software. The quality of fitting to equivalent circuit was judged firstly by the Chi-square value (χ^2, i.e., the sum of the square of the differences between theoretical and experimental points) and secondly by limiting the relative error in the value of each element in the equivalent circuit to 5% [20,21]. The equivalent circuits were chosen based on the number of time constants and the quality of fits [22,23].

3 Results

3.1 Potentiodynamic polarization

Figure 1 shows the potentiodynamic polarization curves of Al−Zn−Si−RE coating, Zn−15Al coating and bare steel in 3.5% NaCl solution during initial stage of immersion. The electrochemical parameters such as corrosion potential (φ_{corr}), corrosion current density (J_{corr}), polarization resistance (R_p), anodic Tafel slope (β_a) and cathodic Tafel (β_c) are listed in Table 2.

According to Fig. 1, the Al−Zn−Si−RE coating and Zn−15Al coating show φ_{corr} values of −0.965 V and −1.112 V, respectively. These values are approximately 300 mV more negative than that of steel substrate (−0.643 V), which indicates that both the coatings can

Fig. 1 Potentiodynamic polarization curves of Al−Zn−Si−RE coating, Zn−15Al coating and bare steel in 3.5% NaCl solution