Physical, mechanical and corrosion properties of Zn-15Al alloy coating deposited at different voltage using thermal spray process

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Abstract. Steel is the most widely used metal on earth, cheap and found everywhere. It has good properties such as machinability, strength, ductility, and compatibility with other materials. However, it has weakness such as high corrosion rate which need to improve to achieve satisfying properties. The coating is one of the enhanced methods to improve the quality of steel coating methods are dipping and thermal deposition processes. Both processes have their own advantages and disadvantages. However, the thermal deposition method can produce a coating with better characteristics and performance. Zinc and aluminium are common metals to be used in the thermal spray process; however, a few parameters need to be concerned in the thermal spraying process. They include spraying voltage, spraying distance, deposition rate and applied current. The basic concept is that it melts the material and burst it to the substrate with high velocity. The purpose of this research is to evaluate the physical and corrosion properties of thermal sprayed pure zinc, aluminium and Zn-15Al alloy coating on a mild steel plate. The experimental procedures include roughness, thickness, adhesion, SEM with EDX, and EIS tests. The results show that at 30V, the surface roughness becomes lower, zinc’s decreases from 7.30μm to 6.55μm, Zn-15Al’s is from 8.52μm to 7.93μm. For aluminium, its surface roughness increases at higher voltage, from 13.10μm to 18.25μm. For coating thickness, the value of zinc, aluminium and Zn-15Al of 20V and 30V spraying voltage decreased from 629μm to 601μm, 486μm to 452μm, 541μm to 536μm respectively. The reason for sprays the material at higher velocity to the substrate; these findings depicted smooth and dense coating. Based on SEM/EDX analysis on the cross-sectioned samples, there is no gap between the coating and substrate and demonstrates good coating adhesion. The Daimler-Benz adhesion test shows all coating samples demonstrate good adhesion as no failure at the indentation boundary. In the EIS corrosion test, the frequency range 0.1Hz to 100kHz in 3.5wt.% NaCl solution, the highest impedance shown by zinc, aluminium and Zn-15Al at 20V are 21, 2122 and 49ohms; at 30V, they possess 11, 1347 and 20ohms. It illustrates those coatings with lower spraying voltages demonstrate better corrosion resistance due to the higher coating thickness. Hence, the coating which owns the best properties in all aspects is pure aluminum coating.

Keywords: Wire Arc Thermal Spray, Steel Protection, Physical Properties, EIS.
1. Introduction
Steel is one of the principal metals used today in many industries due to its outstanding properties and low cost. With the discovery of new materials and steel processing technology, its properties can be changed and alter into different functions. Its advantages include high strength, easy to fabricate and produced, high machinability and durable product [1]. Metal coating techniques like thermal spray and dipping are important processes to enhance the properties of steel. Thermal Spraying demonstrated better quality than other coating processes because it provides dense and uniform coating, is portable, and requires less energy input to melt the material [2].

Corrosion, buckling issue and lack of function under high temperature is severe issue of steel product. So, the surface coating becomes essential. Zinc and aluminium are two common coating metals, but zinc does not provide good barrier protection, and aluminium does not provide cathodic protection. The hot dipping process is cheap; however, possesses some limitation like heat distortion, only on-site process available, and the disability to coat on a particular part of the substrate [3].

The study aims to determine the characteristic of pure zinc, aluminium and Zn-15Al coating deposited by wire arc thermal spray of 20V and 30V. It includes coating thickness, surface roughness, coating adhesion, SEM/EDX observation, and corrosion test using Electrochemical Impedance Spectroscopy (EIS).

1.1 Protection of Steel by Coating
A protective coating like paint acts as barrier to steel substrate to protect against corrosion. It is also soft and vulnerable to the atmosphere, so a duplex coating technique combines it with a metal coating. Its corrosion resistance is known to be 1.5-2.3 times of both the methods combined. Besides thermal spray and hot dipping, the electro-galvanising process and coating in a vacuum are also good metal coating techniques [4].

1.2 Coating Materials
1.2.1 Polymer Coating
It has low strength in general, needs time to dry or cure after applied and the temperature resistance is about 280°C. Its advantage is cheap and easy to apply. Some common types of polymers are nylon, alkyds and acrylics, polyurethane [5].

1.2.2 Ceramic Coating
They are good insulator with great abrasive resistance and hardness. Ceramic can be coated using plasma spray, detonation gun, oxygen acetylene powder, rod and CVD [6].

1.2.3 Metallic Coating
Metalizing means applying a metal coating on the substrate. It enhances the physical and corrosion resistant of the component, its friction characteristic can also be improved [7]. Some common types of coating materials are zinc (good cathodic protection), aluminium (good barrier protection), chromium, nickel and NiCoTef.

1.3 Methods of Coating
1.3.1 Dipping
Dip coating consists of 3 stages: immersion, dwell time (film formation) and withdrawal. The rate of withdrawal, and viscosity determine the quality of coating.

1.3.2 Thermal Spray
The material is melted and the atomization jet will accelerate it to the surface in high speed. Nearly all materials are available for this method. There is minimal thermal distortion of the component because no high energy input is needed. Some different characteristics of thermal spray processes are shown in Figure 1.
1.4 Corrosion Test (Electrochemical Impedance Spectroscopy, EIS)

The concept EIS is by applying low AC signal to an electrode in the electrolyte, then the electrode (sample) response is analysed by comparing the phase shift and measuring their amplitudes. The dynamic of moving charges of the interface can be determined, which resembles corrosion mechanism. Then, the properties of metal can be represented by electronic circuit with impedance under alternating current (AC), the results can be expressed in Ohm’s law.

From the Nyquist plot, the larger the diameter of the semicircle, the higher the resistance and hence, the lower the corrosion rate. The impedance at low frequency response was related to the charge transfer process, considering that the response at high frequencies was attributed to the presence of a surface film [9]. Environment with high resistivity such as concrete can be measured. It is non-destructive testing, can monitor the evolution of the passive or active state over time. It is accurate and quick to get the results [10].

2. Materials and Methods

In this experiment, wire arc of 2mm diameter of pure zinc, aluminium and Zn-15Al were deposited on a mild steel plate, spraying voltage of 20V and 30V were tested, on 6 specimens altogether.

2.1 Mechanical Testing

Surface Roughness Test was carried out using Mitutoyo-SJ310 profilometer and Daimler-Benz Adhesion Test was taken by Rockwell-C indenter with 100kg load.

2.2 Morphology, Microstructure and Chemical Phase Analysis

Sample preparation was carried out by cross-sectioning the sample using CNC, hot mounting, grinding using sandpaper of 300 to 1200 roughness, polishing and etching. Then, the coating thickness was measured under optical microscope. Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray (EDX) analysis was used to determine the microstructure and surface adhesion between the coating and substrate to confirm the element content of the materials.

2.3 Corrosion Test

Electrochemical Impedance Spectroscopy (EIS) method in VersaSTAT was used by determining its coating impedance when different frequency of current is applied. To simulate marine condition, 3.5wt.%
NaCl solution was used as electrolyte as shown in Figure 2. Start and End Frequency applied were 100kHz and 0.1Hz respectively with 10s measurement delay. The result was plotted in Nyquist plot and Bode Diagram.

![EIS setup for corrosion test](image)

**Figure 2: EIS setup for corrosion test**

3. Results and Discussion

3.1 Surface Roughness

It shows a trend of decreasing surface roughness as the voltage of thermal spraying increases, except pure aluminium coating as 30V is not the optimum voltage to melt the material, as shown in Table 1. High voltage means high energy uses to melt and pump the coating material at a higher velocity; hence, the size of the droplet of the melted material would be smaller [11].

| Type of coating | Spraying Voltage | Surface Roughness(μm), Average Roughness (Ra) | Average |
|-----------------|------------------|---------------------------------------------|---------|
| Pure Zinc       | 20V              | 7.708, 7.212, 6.969                         | 7.296   |
|                 | 30V              | 6.610, 6.186, 6.838                         | 6.545   |
| Pure Aluminium  | 20V              | 12.844, 13.499, 12.960                       | 13.101  |
|                 | 30V              | 17.349, 17.8751, 9.514                       | 18.246  |
| Zn-15Al         | 20V              | 8.103, 9.543, 7.906                         | 8.517   |
|                 | 30V              | 6.312, 7.988, 9.490                         | 7.930   |

3.2 Daimler-Benz Adhesion Test

Figure 3 presents the adhesion quality of pure zinc, in which Zn-15Al coating is HF3, while aluminium is HF2. Referring to the Daimler-Benz Adhesion chart if it is under HF5 and HF6 it means that the coating quality and adhesion are poor. Using a thermal spray, they all have good bonding with the substrate with minimal cracks and delamination. For aluminium, it possesses the best adhesion quality without delamination. Spraying voltage does not seem to have any effect on them.
3.3 Coating Thickness

A trend of coating thickness is shown in Table 2 when the higher the spraying voltage, the lower coating thickness. In fact, the high voltage provides higher energy to melt and spray the materials in smaller particles so there is a lower mass of them deposited on the surface. Also, the lightest coating material which is aluminium deposited on the surface, followed by Zn-15Al and zinc [12].

| Type of coating | Spraying Voltage | Coating Thickness (μm) | Average |
|----------------|------------------|------------------------|---------|
| Pure Zinc      | 20V              | 645 634 609            | 629     |
|                | 30V              | 592 603 607            | 601     |
| Pure Alum      | 20V              | 460 468 529            | 486     |
| Aluminium      | 30V              | 402 500 455            | 452     |
| Zn-15Al        | 20V              | 535 556 532            | 541     |
|                | 30V              | 537 527 543            | 536     |
3.4 Coating Surface Morphology and Composition

3.4.1 Scanning Electron Microscope (SEM)

The coating morphology in Figure 4 shows dense and good bonding with the steel substrate. There are no porosity and cracks at the interface between the coating layer and substrate of pure zinc and aluminium. The Zn-Al alloy shows irregular and not uniform patterns because the content element is more complicated. There are differences in atomic size and melting point.
Figure 4. SEM microstructures and element mapping on the cross section. (a) pure zinc, (b) pure aluminium. (c) Zn-15Al.

3.4.2 Chemical Composition Analysis by EDX

**Pure Zinc.** The chemical composition of zinc is shown in Figure 5. The presence of the silicon is due to silicon carbide from SiC paper that contaminated during grinding process. The EDX result confirmed that the coating is pure zinc.

![EDX spectrum of zinc coating](image)

**Figure 5.** Elemental composition of zinc coating.

**Pure Aluminium.** The carbon could be from the steel substrate or impurity of aluminium and the oxygen content is the oxides of aluminium. Hence, the result in Figure 6 shows it is pure aluminium coating.

![EDX spectrum of aluminium coating](image)

**Figure 6.** Element content of aluminium coating.
**Zn-15Al.** The chemical composition of Zn-15Al is shown in Figure 7. It consists of all the elements of impurities and bulk materials, the iron is expected from the substrate.

| Element | At. No. | Line s. Netto | Mass [%] | Mass Norm [%] | Atom [%] | abs. error [%] | abs. error [%] | abs. error [%] | re (1 sigma) | re (2 sigma) | re (3 sigma) |
|---------|---------|---------------|----------|--------------|----------|----------------|----------------|----------------|--------------|--------------|--------------|
| Aluminium | 13 | K-Serie 45672 | 5.13 | 50.14 | 43.40 | 0.27 | 0.53 | 0.80 |
| Carbon | 6 | K-Serie 3588 | 1.68 | 16.38 | 31.84 | 0.30 | 0.61 | 0.91 |
| Zinc | 30 | K-Serie 8952 | 1.56 | 15.28 | 5.46 | 0.08 | 0.16 | 0.24 |
| Oxygen | 8 | K-Serie 5235 | 0.83 | 8.14 | 11.88 | 0.15 | 0.31 | 0.46 |
| Silicon | 14 | K-Serie 5409 | 0.80 | 7.80 | 6.48 | 0.06 | 0.12 | 0.18 |
| Iron | 26 | K-Serie 278 | 0.23 | 2.26 | 0.95 | 0.04 | 0.08 | 0.13 |

**Figure 7.** Element content of Zn-15Al coating.

3.5 Corrosion Test by Electrochemical Impedance Spectroscopy, EIS

3.5.1 Nyquist Plot

According to Figure 8, the first curve represents the coating and the second one is the substrate. The spraying voltage of 20V exhibits a bigger semicircle which means it has better corrosion-resistant properties, theoretically higher voltage produces a denser and more compact coating that protects the substrate from corrosion. The result is the opposite due to its more increased thickness, which avoids contact and dissolution with NaCl solution.

![Nyquist plot from EIS of different material: (a) pure zinc. (b) pure aluminium and (c) Zn-15Al.](image-url)
3.5.2 Bode Diagram
The impedance is inversely proportional to the frequency applied, as shown in Figure 9. High frequency with high penetrating power can detect coating properties without affecting by the deposition of corrosion products on the surface. Generally, the impedance of coatings with 20V is only slightly higher than 30V, except for zinc at low frequency, which is more significant [13].

In conclusion, the effect of coating thickness is more significant than the coating density. The corrosion resistance of each material arranges in ascending order in such a way Zn < ZnAl < Al. The formation of dense aluminium oxide protects the substrate from the contact with the electrolyte for corrosion process. At the same time, the zinc acts as a sacrificial anode that is more prone to corrosion than the steel substrate.

![Bode Diagram](image1)
![Bode Diagram](image2)
![Bode Diagram](image3)

**Figure 9.** Bode diagram of impedance as function of frequency of each specimens (a) pure zinc, (b) pure aluminium and (c) Zn-15Al.

4. Conclusions
For surface roughness, the result shows a trend of decreasing roughness as the voltage increases for pure zinc and Zn-15Al coating. The 30V spraying voltage provides more constant and denser surface properties. For pure aluminium, it is the opposite. The reason is that 30V is not the optimum voltage to melt and spray the aluminium to the substrate. In Daimler-Benz Adhesion Test, all coatings on the samples are accepted as good adhesion bonding to the substrate. The pure aluminium coating shows the best quality without significant defects such as delamination and crack. About coating thickness, the
coating becomes thinner and denser when the spraying voltage increases from 20V to 30V. Higher voltage melts and sprays the materials at higher velocity to the substrate, making more a compact coating. For microstructure and chemical composition, the interface between coating and substrate is observed. The coating quality is good without porosity. There are porosity and microcrack in the Zn-15Al layer due to the content of more complex elements. In EDX, the coating materials’ content consist of a small number of impurities, except Zn-15Al. In the corrosion test (Electrochemical Impedance Spectroscopy, EIS), the aluminium coating has the highest corrosion resistance, followed by Zn-15Al and zinc coating by analysing the Nyquist plot. Generally, lower spraying voltage provides better corrosion resistance because the more increased thickness provides more barrier protection for the substrate.

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