IMPACT OF SINGLE AND DOUBLE ZINCATING TREATMENT ON ADHESION OF ELECTRODEPOSITED NICKEL COATING ON ALUMINIUM ALLOY 7075

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Article History: Received 17 January 2018; Revised 18 June 2018; Accepted 24 September 2018

ABSTRACT: The purpose of this investigation is to explore the relationship between various zincating treatments and coating adhesion. A modification on the conventional single zincating process has been made by extending the duration, with an objective to enhance the non-homogeneous deposition of zinc particles on the aluminium alloy 7075 (AA7075) substrate. To compare the impact of various zincating treatments on the coating adhesion, a double zincating process at various durations were also applied in this study. A scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive analysis of x-rays (EDX) were used to characterize the microstructural changes and composition of AA7075 during various zincating treatments at various durations. A scratch tester was used to investigate the coating adhesion of nickel deposits. A strong relationship between zincating duration and surface morphology of the zincated substrate has been observed in SEM results. The adhesion between the coating and substrate was improved at a longer single zincating duration, compared to conventional single and double zincating process. This finding suggests that the homogenous distribution and good coverage of zinc particles on the substrate have contributed to the improvement of the coating adhesion.

KEYWORDS: *Zincating; Nickel Coating; Electrodeposition; Scratch Test; Adhesion*

1.0 INTRODUCTION

Aluminium 7xxx alloys are key heat treatable engineering materials that are used in manufacturing aerospace and aircraft structures. Its application can be attributed to its superior strength to weight ratio over other series of aluminium alloys. Even though these alloys have good tensile properties, the alloying elements like copper contribute towards decreasing the corrosion resistance [1]. With regards to this drawback, pitting corrosion is a key damage mechanism impacting the alloy's integrity when employed without any surface protection [2]. Also, aluminium and its alloys with low wear resistance, low hardness and low corrosion resistance all need covering of the surfaces with a protective layer that is hard and wear- and corrosion-resistant.

Many research studies have been published regarding surface alteration of aluminium alloy by employing electroless techniques [3-5]. However, the electroless technique is laborious, costly, time consuming and results in additional waste disposal issues when compared with the electrodeposition technique. The electrodeposition technique is a much better option as being relatively cost-effective and useful technique to deposit different types of pure metals, composites and alloys to conduct high-rate production [6].

To date, most research works regarding the zincating process, instead of a single zincating process, were focused on double zincating treatment [7-11]. A granular zinc deposition was achieved via a single zincating process that includes dipping in the zincating solution only one time for less than a minute, which makes this surface inappropriate for the electrodeposition process [3-5, 12]. In a double zincating process, zinc stripping is conducted after the first zincating followed by a second zincating. Thereby yields a uniform and smooth zinc deposition layer, resulting in strong adhesion between deposit and substrate. Comparative studies were done by Hino et al. [3-4] regarding the impact of several zincating treatments performed on coating adhesion. They confirmed a role played by zincated samples' surface morphology in the adhesion process. They showed that double zincating treatments enhanced coating adhesion, where they obtained a dense and uniform layer of zinc deposits, whereas coarse zinc particles with a non-uniform layer were obtained with the single zincating treatment, which was not appropriate for the subsequent plating process.

However, many studies have demonstrated that the multiple zincating process is associated with various issues like making the process complex and excess dissolution of the aluminium substrate in a highly concentrated zinc stripping solution [12-13].

A comprehensive review of the literature did not show any report regarding the impacts of modification on the duration of single zincating to enhance the zinc particles deposition on 7xxx alloys. Thus, in this study, a homogenous distribution of zinc deposits was created to enhance the single zincating process, which also covers the whole substrate surface, by increasing the duration of the single zincating. It is considered that a uniform layer of nickel coating on the substrate can be produced with a homogenous deposition of zinc particles on the substrate, which improves the coating adhesion. The alloy studied is the widely used AA7075 alloy.

2.0 EXPERIMENTAL

For the nickel electrodeposition, we employed AA7075 as a substrate. Initially, the substrates were cleaned in acetone and 10 wt.% sodium hydroxide (NaOH) solution for 10 seconds. Then, the substrates were immersed in a 50 vol.% nitric acid (HNO_3) solution for 20 seconds. The single zincating duration is increased from 1 to 5, 10, 15 and 20 minutes. In comparison, a double zincating process was also applied on the substrate in order to compare with the modified single zincating process. For the double zincating process, the first zincating duration was 60 seconds, while the second zincating was 10, 20, 30, 40 and 50 seconds. Between the consecutive zincating operations, acidic etching was performed in a 50 vol.% of HNO_3 solution for 20 seconds at room temperature. Zincated surfaces were studied using atomic force microscopy (Agilent 5500) in contact mode and scanning electron microscopy (JEOL JSM 6500 SEM). An Oxford Instruments INCA 300 EDS installed in the SEM was employed to study the composition of surface features. The zincating solution included sodium hydroxide (525 g/l), zinc oxide (100 g/l), potassium sodium tartrate (9.8 g/l) and ferric chloride (1 g/l). After every process, the samples were rinsed to avoid contamination from bath to bath. Then, the samples were introduced quickly in a modified nickel Watt's bath for electrodeposition process at a current density of 5 A/dm^2, for 1 hour at 45°C. The composition of the electrolyte is as follows: nickel sulphate hexahydrate (200 g/l), nickel chloride (20 g/l), sodium dodecyl sulphate (0.2 g/l), saccharin (3 g/l), boric acid (30 g/l) and 2-butyne-1, 4-diol (0.5 g/l).

Scratch testing (Teer Coating, ST-3001) was employed to examine the coating adhesions. A horizontal displacement rate (10 mm/min) and a loading rate (100 N/min) were maintained to perform the tests, which resulted in a 10 mm scratch. The tip had a radius of 200 µm and was a diamond Rockwell 'C' stylus indenter. On each specimen, the test was repeated eight times showing at least 2 mm scratch spacing, to get the standard deviation and mean values of critical loads. Optical microscopy was employed to analyse the failures, in order to find out the cohesion failure (*Lc1*) and adhesion failure (*Lc2*). The recorded AE signals during the test were analysed by looking at the significant changes in AE signals characteristics, such as number of AE events (N_{AE}). N_{AE} was determined by considering the number of AE signals which occurred higher than the background noise, which represented the coating failures on the track.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology and Composition Analysis

Zinc deposition on the substrate surface after conventional single zincating process at 1 minute and modified single zincating process at 5, 10, 15 and 20 minutes are displayed in Figure 1. Growth in the zinc particles, as well as increased in zinc density were observed after 5 minutes of zincating process (Figure 1 (b)). With duration increase from 5 to 15 minutes, the density of the zinc increased even more and most of the surface was covered by the particles, with the presence of few agglomerations at specific areas (Figure 1(d)). This result is in agreement with AFM's finding which display zinc particles stacking on each other until the dispersed zinc particles covers the surface of the substrate (Figure 2(a)). After 20 minutes, there was a steady growth of zinc particles and they started becoming connected with each other, as presented in Figure 2(b). The findings are in line with the studies of Arshad et al. [14] and Lin et al. [5], who found that zincating for more than a minute gave a high density and thick zinc layer, resulting in a rough surface. It is apparent from Figure 1 that zinc deposits obtained from zincating process at various durations show irregular grains. The similar finding was also reported by Yuan et al. [15].

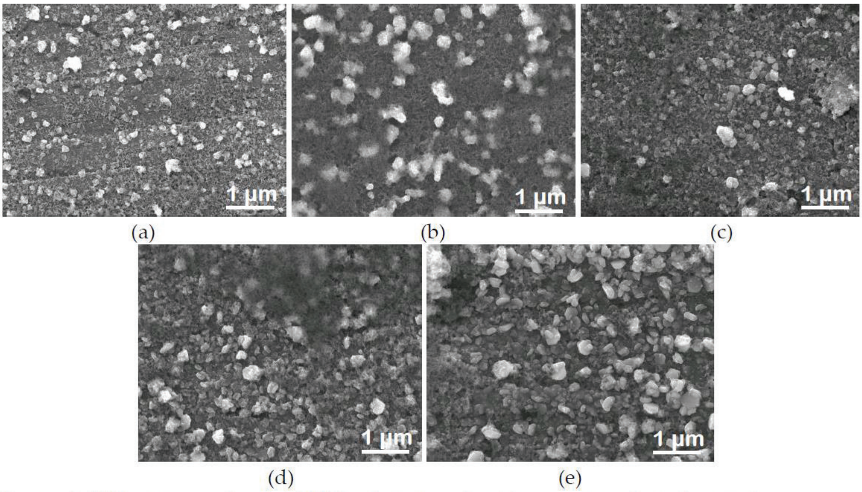

Figure 1: SEM micrographs of AA7075 substrates after (a) conventional single zincating process at 1 minute and modified single zincating process at various durations: (b) 5, (c) 10, (d) 15 and (e) 20 minutes

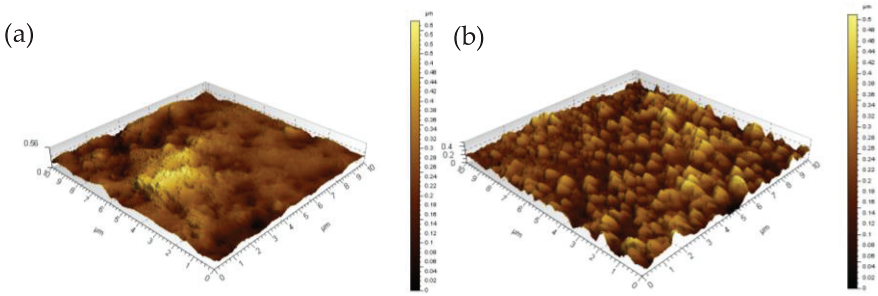

Figure 2: AFM images of AA7075 substrate after (a) conventional single zincating process at 1 minute and (b) modified single zincating process at 20 minutes

AA7075 substrates' SEM micrographs after the double zincating process at different durations are displayed in Figure 3. The first zincated sample's morphology in the double zincating process was found to be identical with the conventional single zincated sample, after using the same duration for both processes. As observed in Figure 3, a smoother and more uniform zinc layer resulted on the samples' morphology of double zincated samples, which included more refined zinc particles versus the conventional and modified single zincating processes. A smooth zinc layer was achieved with the sample exposed to double zincated at 60/10 seconds, which had zinc particles that were small sized (Figure 3(a)). Even after this process, the zinc particles did not fully cover the surface, as evident from the cavities covering the surface. After carrying out double zincating process for 60/20 seconds, there was a decrease in size as well as the number of the previously observed cavities (Figure 3(b)).

Post 60/30 seconds, the surface enhanced by giving a uniform and smooth zinc layer without voids on the surface (Figure 3(c)). The figure shows that during this duration, there was development of another layer of zinc particles. With rise in duration increased from 60/30 to 60/50 seconds, the zinc particles' initial layer turned denser and more uniform (Figures 3(d-e)). Moreover, the density of the zinc particles was also increased. Post zinc stripping process, the sample's AFM images and sample's SEM morphology showed that the zinc particles were almost completely removed (Figure 3(f) and Figure 4(b)).

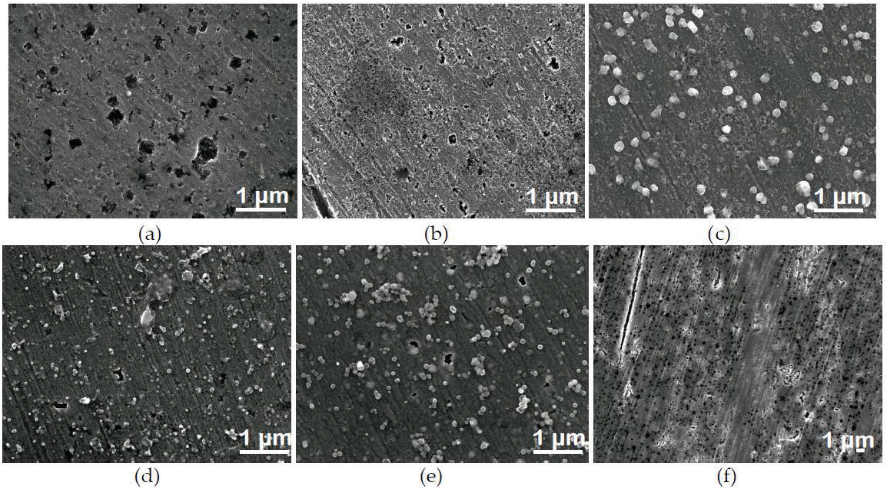

Figure 3: SEM micrographs of AA7075 substrate after double zincating process at various durations (a) 60/10, (b) 60/20, (c) 60/30, (d) 60/40, (e) 60/50 seconds and (f) zinc stripping process

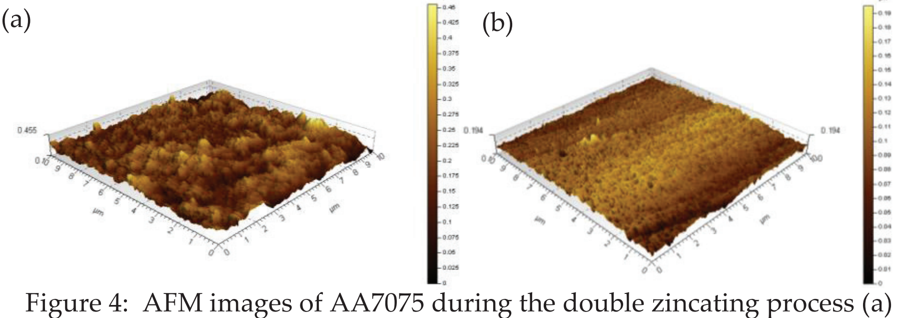

Figure 4: AFM images of AA7075 during the double zincating process (a) after first zincating at 60 seconds and (b) after zinc stripping

This result was in line with the EDX analysis (Figure 5), which shows a reduction in the zinc composition from 10 wt.% (the first zincating process) to 5.9 wt.% (the zinc stripping process). Based on Lin et al. [5], post the first zincating process, any zinc stripping process carried out will resulted in refining of the zinc nodules that were previously deposited or a favourable dissolving of zinc nuclei that had sizes smaller than the critical nucleation radii.

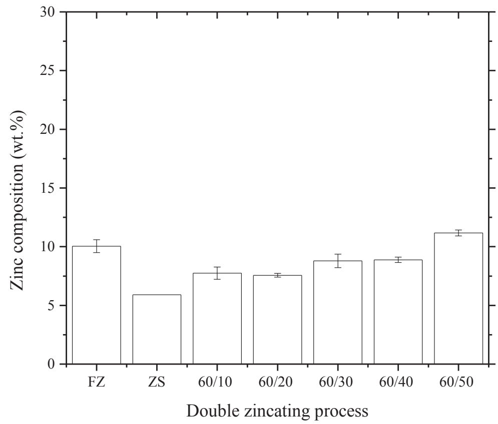

Figure 5: EDX analysis of zinc composition (wt. %) after various double zincating durations where FZ: first zincating process and ZS: zinc stripping process

EDX analysis was employed to investigate the element composition when the single and double zincating processes were performed at different durations (Figure 6). Initially, 6.69 wt.% of zinc was achieved with the as-received AA7075 substrate (Figure 7). Following the conventional single zincating process performed for 1 minute, ~10 wt.% zinc was obtained, which is almost double that of the AA7075 zinc content. However, between conventional single zincating for 1 minute and modified single zincating process for 5 minutes, there was no significant difference in the zinc composition. However, a gradual rise in the zinc composition from ~10 to ~25 wt.% was seen when extending the zincating duration from 5 to 20 minutes (Figure 6(a)). There was a gradual reduction in the aluminium element from ~86 to ~68 wt.%, with extending of the single zincating duration from 1 to 20 minutes. Figure 6(b) displays the zinc and aluminium composition based on the double zincating duration. On extending the duration from 60/10 to 60/50 seconds, an increase in zinc composition from 7.7 to 11.17 wt.% was observed. The aluminium composition displayed a gradual decrease on increasing the duration from 60/10 to 60/30 seconds. A fluctuation pattern in the aluminium composition was observed on further extending the duration to 60/50 seconds.

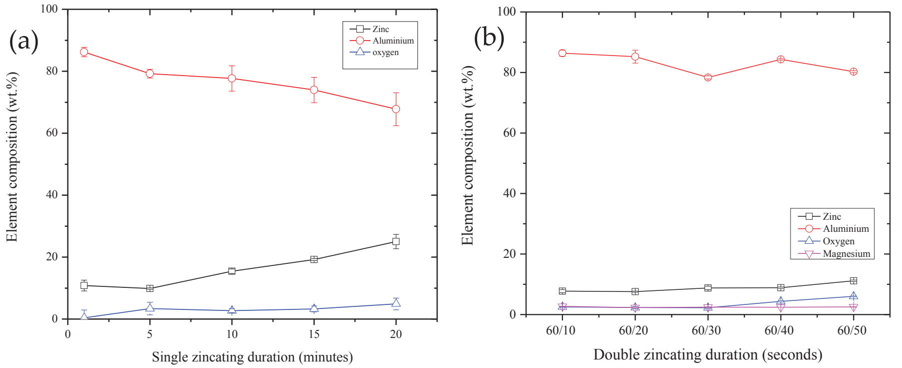

Figure 6: EDX analysis of substrate surfaces after (a) single and (b) double zincating process at various durations

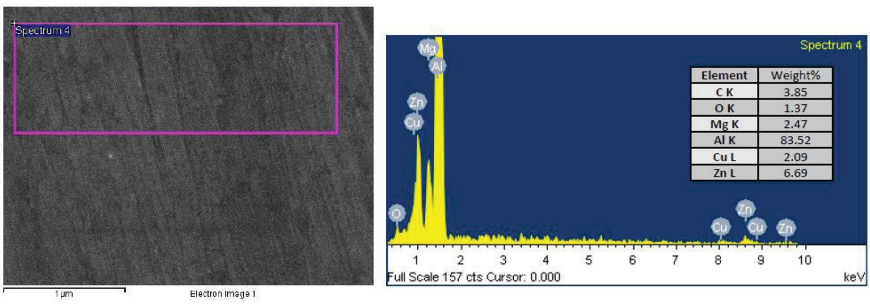

Figure 7: EDX analysis on as- received AA7075 substrate

3.2 Coating Adhesion

Figure 8(a) presents how the nickel coatings' critical loads (L_{C1} and L_{C2}) get affected by different single zincating durations. L_{C1} is when the first cracks occur on the scratch tracks, while L_{C2} indicates the adhesion failure. The lowest L_{C1} was achieved with the conventional single zincating process applied at 1 minute. L_{C1} enhanced up to 78.4 N when a zincating process was applied for 5 minutes. After that, there was a gradual decrease in L_{C1} values with increase in duration of single zincating from 5 to 20 minutes. Moreover, the adhesive failure mode or L_{C2} value at 84.5 N could be seen only with the conventional single zincated sample, as presented in Figure 8(a). In contrast, consistent trends were not seen with the nickel coatings' L_{C1} and L_{C2} values at different double zincating durations (Figure 8(b)). All double zincated samples show the L_{C2} values, which indicate that the samples are having adhesive failure. Therefore, there is a need for sufficient zincating duration to yield zinc particles that are not only dense by also increase the covering of the substrate by the zinc intermediate layer.

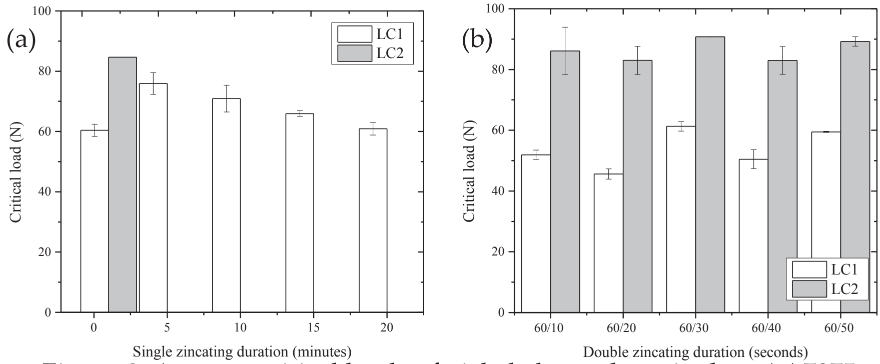

Figure 8: Average critical loads of nickel electrodeposited on AA7075 produced at various (a) single and (b) double zincating durations

Figure 9 demonstrates the correlation existing between the number of AE events (N_{AE}) and the durations of the zincating process. As presented in Figure 9(a), the highest N_{AE} value was achieved with the nickel coating generated via the conventional single zincating at 1 minute. An interesting thing to note in this figure is that there is a considerable decrease in the N_{AE} value from ~130 to ~25, when the duration of zincating is extended from 1 to 5 minutes. However, when the duration was extended further to 20 minutes, significant differences in the N_{AE} values were not observed. There were no consistent trends observed with the N_{AE} values in the case of double zincating process at different durations as well as no considerable decrease in N_{AE} could be seen when the duration of double zincating was extended (Figure 9(b)). Meanwhile, no surface damage was seen on the scratch tracks before the L_{C1} point (Figure 10).

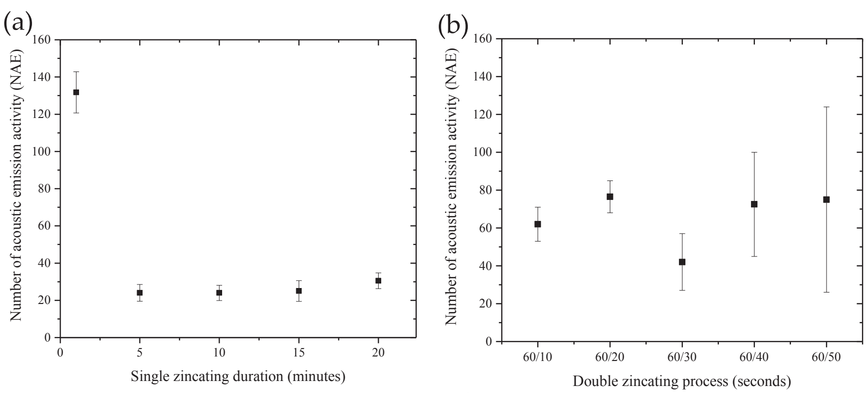

Figure 9: Correlation between number of acoustic emission activity (N_{AE}) and various (a) single zincating durations and (b) double zincating durations

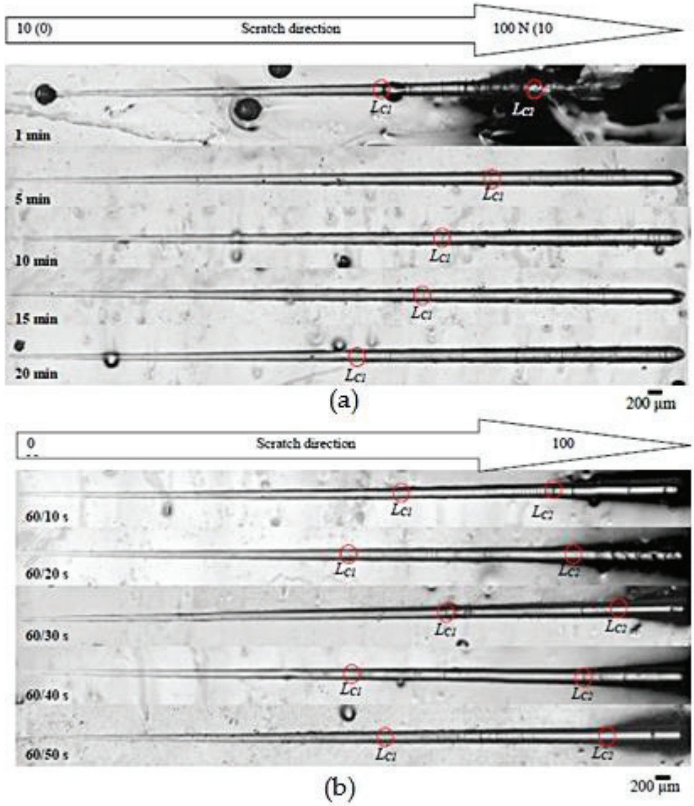

Figure 10: Optical micrographs of the scratch tracks of nickel electrodeposited on AA7075 substrate produced with (a) single zincating process and (b) double zincating process at various durations

The OM images in Figure 10 depict the samples that were exposed to single and double zincating process with varying durations. They demonstrate a series of ductile tensile cracking mostly at the centre of the scratch track, which considered a kind of through-thickness cracking categorised under cohesive failure modes. For the entire samples, continuing scratch followed by applying of loads on the coatings progressively producing more cracks by the stylus. Ruptured coating was seen with the sample yielded via the conventional single zincating duration, which got separated from the substrate near the end of the scratch track in the wedge spallation failure mode (Figure 10(a)). This failure is determined as an adhesion failure and tagged as L_{C2}, which signified a poor bonding between the coating and the substrate.

When observed with the optical microscopy for double zincated samples, a black region appeared for the delaminated coating's raised portion near the end of the scratch track, while the bright region represented the coating surfaces and scratch track (Figure 10(b)). This is due to the multiple focus points at various positions on the delaminated coating. The coating pile-up on these samples towards the end of the scratch track confirms the occurrence of adhesive failure (L_{C2}). A possible reason for this could be low composition of zinc particles on the substrates caused by the rapid immersion in the zincating solution. Thus, the covering of all substrate surfaces is incomplete leaving some of the parts uncovered. The study findings are in line with those of Palaniappa et al. [16], who found increased adhesion between aluminium surface and nickel with the uniform zinc layer as well as sufficient coverage of the aluminium substrate surface by zinc particles.

4.0 CONCLUSION

For both single and double zincating processes, SEM morphologies demonstrated that the zinc particles' composition and size increased with increasing zincating duration. Around 25 wt.% of zinc on the surface was achieved by employing the modified single zincating process for a longer duration (20 minutes), which is almost double the value than with the double zincating process. During scratch testing a decrease in the acoustic emission activity was seen for samples obtained from the single zincating process, which was from ~130 to ~20, with extension of the zincating duration from 1 to 20 minutes. However, there was no consistent trend observed in the acoustic emission activity when the double zincating process was employed. The zincating duration was a key parameter that can impact zinc particles' morphology and deposition on the substrate, which makes it a strong influencer for the coating's adhesion process for the substrate. The adhesion between the coating and substrate was improved at a longer single zincating duration, compared to conventional single and double zincating process.

ACKNOWLEDGMENTS

The authors would like to thank Ministry of Higher Education Malaysia (KPT(BS)810526086238) for sponsoring this research. Also, thanks to Faculty of Engineering and the Environment, University of Southampton for the laboratory facilities and the chemical supplies.

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