ELECTRODEPOSITION OF NICKEL COATING ON AA7075 SUBSTRATE VIA MODIFIED SINGLE ZINCATING METHOD WITH ASSISTANCE OF COPPER ACTIVATION

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ABSTRACT: The established single zincating procedure leads to non-homogenous zinc deposition rendering the surface incompatible for successive electrodeposition, due to low adhesion between coating and the substrate. A combination of single zincating with copper activation was employed on an aluminium alloy 7075 (AA7075) substrate at prolonged zincating duration so as to incapacitate the shortcomings of the conventional single zincating process. Copper activation was applied to suppress the high dissolution of substrate in the highly alkaline solution during zincating process. The time-transition curve of open circuit potential (EOC) were recorded to study the dissolution of substrate in zincating solution. The composition and surface morphology of AA7075 substrate from copper activation procedure at diverse range of duration were distinguished by energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM). The progression of surface morphology of substrates was distinguished by characteristics pertaining to Atomic Force Microscopy (AFM) and SEM. The analysis of the coating adhesion of nickel deposits in the presence and absence of copper activation was conducted by a scratch tester. The adhesion breakdown of coating created from a single zincating process at 1 minute is diminished by the copper activation method. As reflected in the SEM results, the copper activation produces uniform size of zinc deposits and improves their distribution on the substrate. With prolonged zincating duration, there is sufficient time for the zinc deposits to growth and finally covered the whole surface without reveal the substrate. These results contributes to the uniform deposition of nickel coating, thus contribute to the improvement in the coating adhesion.

KEYWORDS: *Aluminium Alloy 7075; Nickel Coating; Copper Activation; Adhesion; Zincating*

1.0 INTRODUCTION

A 7075 series of aluminium alloy (AA7075) refers to a heat treatable wrought alloy that is necessary for the manufacturing of different aerospace and aircraft structures. This is primarily because this alloy exhibits excellence strength to weight ratio in comparison to other aluminium alloys series [1]. In spite of possessing high tensile characteristic and exceptional manufacturing properties, its constituent alloying elements such as copper can cause a decrease in corrosion resistance [2]. The strength of structural parts gets reduced due to corrosion, and thereby it is regarded as the key constraint for engineers in designing or manufacturing structural parts for aircraft [3]. Moreover, the low wear resistance, low corrosion resistance, and low hardness of aluminium and its alloys demand that their surfaces be shielded with a hard, corrosion-resistant, and wear-resistant protective layer.

A single zincating process constitutes of only single immersion of sample for less than 1 minute in the zincating solution, leading to granular zinc deposition, and rendering the surface not suitable for any successive electrodeposition [4]. Hence, so far researchers who have studied the zincating process have leaned towards supporting the double zincating treatment instead of the single zincating process. A double zincating process involves a first zincating that is subsequently followed by zinc stripping using high concentration of nitric acid (HNO_3) solution, and then a second zincating that results in a uniform and smooth zinc layer, causing the formation of strong adhesion between the deposit and the substrate [5]. Comparative studies conducted on the impact of multiple zincating treatments or processes on the strength of coating adhesion reveal that the surface morphology of the zincated samples have a significant role to play in determining the strength of adhesion [6-7].

However, multiple zincating process has a number of challenges such as the involvement of a complex process and production of an excess dissolution of aluminium substrate during the zinc stripping process in concentrated nitric acid solution [8]. A detailed observation of the aluminium bondpad surface formed after the zinc stripping process reveals that the zinc particles are completely removed after the first

zincating process, exposing the underlying pitting on the aluminium surface [9]. With regards to the measurement of electrochemistry, Azumi et al. [8] observed that there is a continuous dissolution of the aluminium alloys in the course of the first and second zincating process. When treated in a concentrated alkaline zincating solution, the aluminium substrate's high dissolution reaction has the potential to cause serious damage to the substrate [10]. The dissolution of substrates can be reduced and uniform distribution of zinc deposits can be achieved through the application of copper pre-treatment before the initiation of the zincating process [11-12].

Hence, the purpose of this study is to enhance the conventional or established single zincating process by prolonging the duration of immersion of the substrate in the zincating solution. It is believed that a homogenous deposition of zinc particles on the substrate will lead to a uniform layer of nickel coating, thereby improving the strength of adhesion of the coating. Moreover, before the initiation of the conventional and modified single zincating processes, copper activation was applied to avert high dissolution of AA7075 in the zincating solution.

2.0 EXPERIMENTAL PROCEDURE

Aluminium alloy 7075 (AA7075) provided by British Aluminium Limited (Birmingham, United Kingdom) was used as the cathode, and nickel plate provided by Advent Research Materials Limited (Oxford, United Kingdom) was used as the anode. To begin with, the AA7075 substrates were cleaned in 10 wt. % sodium hydroxide (NaOH) and acetone for 10 seconds, followed by 50 vol.% HNO_3 for 20 seconds. After this, the substrate was dipped in an etching solution of 0.5 M H_2SO_4 + 3.13×10^{-4} M $CuSO_4$ for 10 minutes at room temperature to realise the copper activation process. Then, the conventional single zincating process constitutes of immersing the substrate in the zincating solution was held for 1 minute, while for the modified single zincating process, the zincating duration was extended to 5, 15, 10 and 20 minutes. The current density used for the electrodeposition process was 4 A/dm^2 under direct current mode at 45˚C. The electrolyte was stirred at 300 rpm with the total time of electrodeposition set at one hour. Table 1 presents the chemical concentration for both zincating solution and modified nickel Watt's electrolyte.

Table 1: Chemical concentration in modified Nickel Watt's electrolyte and zincating solution

Chemical compound	Concentration (g/L)
Modified Nickel Watt's electrolyte	
Nickel sulphate hexahydrate, $NiSO_4.6H_2O$ (>99.0%)	200
Sodium chloride, NaCl (99.5%)	20
Sodium dodecyl sulphate, $C_{12}H_{25}SO_4Na$	0.2
Saccharin, $C_7H_5NO_3S$ (>99.0%)	3
Boric acid, H_3BO_3 (99.5%)	30
2-butyne-1,4-diol, $C_4H_6O_2$	0.5
Zincating solution	
Zinc oxide (ZnO) (≥ 99.0%)	100
Sodium hydroxide (NaOH) (97%)	525
Ferric chloride (FeCl) (97%)	1
Potassium sodium tartrate ($KNaC_4H_4O_6{\cdot}4H_2O$)(ACS reagent)	9.8

Atomic force microscopy (Agilent 5500) and scanning electron microscopy (JEOL JSM 6500 SEM) were employed to observe the surface morphology of copper activated and zincated substrates. The scratch tester (Teer Coating, ST-3001) was then used to examine the coating adhesions. Creation of a scratch was done on the coating by drawing a diamond stylus (Rockwell 'C', 120° cone with a 200 μm radius) over the coating's flat surface by maintaining constant horizontal displacement rate (10 mm/min) and loading rate (100 N/min), given the test conditions were unchanged during the testing period. Then, in each scratch track, specific levels and kinds of progressive damage could be seen by employing an optical microscope (Olympus BH2-UMA).

3.0 RESULTS AND DISCUSSION

3.1 Open Circuit Potential (EOC) of AA7075 Substrates during the Single Zincating Process with Copper Activation

Figure 1 exhibits the variation of E_{OC} with immersion time during single zincating process with various copper activation durations at 5, 10 and 15 minutes. The measured curves could be segmented into three phases: dissolution, deposition and steady state. An identical trend of E_{OC} variation was observed with the specimens derived from copper activation at 5 and 10 minutes. In the first phase, a gradual reduction in the E_{OC} values was observed for both specimens. Then, in the second phase, there was a gradual rise in the E_{OC} values for both specimens towards a noble direction, which eventually reached the steady state of potential pertaining to the third phase at around -1.603

V post 1,000 seconds. A continuous dissolution pertaining to the substrate in the zincating solution was occured on increasing the copper activation duration further to 15 minutes, until a steady state was reached at almost -1.607 V.

Thus, the duration of copper activation was set at 10 minutes in this study, which led to less dissolution pertaining to the substrate as well as fast deposition of the zinc particles when exhibiting the zincating process. Setting the copper activation duration at 10 minutes is also backed by the SEM micrographs, as presented in Figure 3. A homogeneous surface with no cavities was observed based on the SEM micrograph of substrate for copper activation set at 10 seconds, which was different from other durations. A homogenous coverage was seen with the copper seeds, along with certain agglomerations on the substrate.

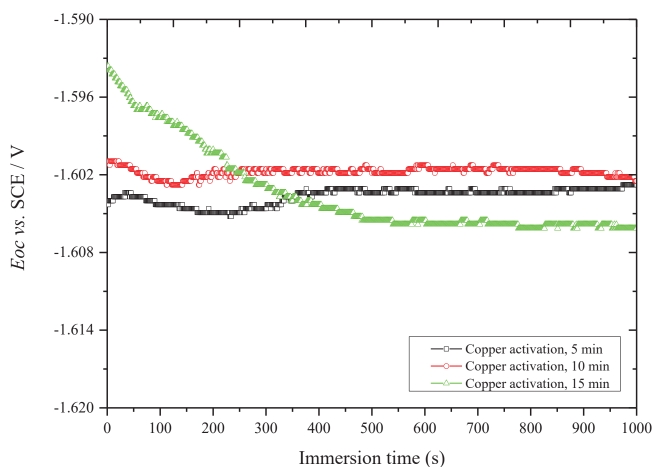

Figure 1: Changes in EOC of copper activated substrates prepared from various copper activation durations during a single zincating process

Figure 2 presents a comparison pertaining to E_{OC} with that of immersion time curves for different specimens without or with copper activation during the single zincating process. A more noble potential was seen with the curve measured for the specimen that had copper activation versus single zincating without copper activation, which suggests a passive dissolution pertaining to copper pre-treated substrate that was present in the zincating solution. The figure also demonstrated the occurrence of fast zinc deposition over the copper pre-treated substrate. These copper deposits act as nucleation sites for zinc deposition during the zincating process and produce a uniform and dense layer of zinc deposits which almost completely cover the substrate surface [12].

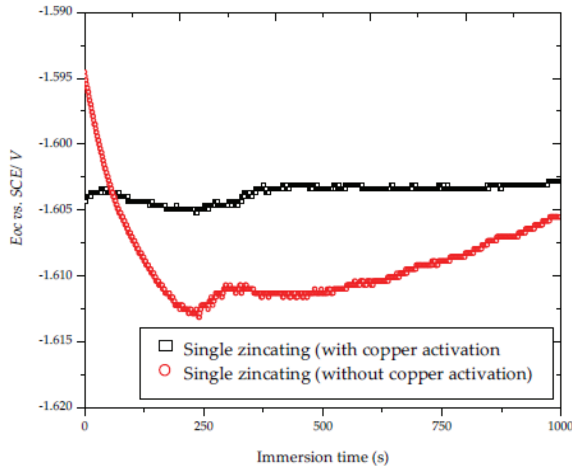

Figure 2: Changes in EOC of substrates with and without copper activation during a single zincating process

3.2 Effects of Copper Activation on Surface Morphology and Element Composition of AA7075 Substrate

Figures 3 presents the surface morphology as well as element composition of AA7075 substrates post copper activation process at various durations. Post copper activation at 5 minutes, it can be seen that only a few copper seeds' nucleation is on the surface,as highlighted by the bright spots shown in Figure 3(a). Based on Figure 3(b), after 10 minutes of copper activation, it was seen that there was a homogenous coverage of copper seeds, along with certain agglomeration on the substrate. However, when the duration was further increased up to 15 minutes, there was a rise in copper seeds population, along with certain agglomeration seen on the surface (Figure 3(c)).

EDX analysis using 'point ID' mode was conducted based on the agglomeration of particles post the process of copper activation (as shown in Figure 4). Finding from this study is line with Tang and Azumi [11] and Azumi et al. [8], who reported obtaining a dispersed copper deposition in etching solution that include a low concentration of Cu^{2+} ions, because of substitution reaction pertaining to aluminium substrate. Therefore, the copper deposits behave as nucleation spot to facilitate zinc deposition during zincating process, which yields a thin, dense and fine zinc deposition layer.

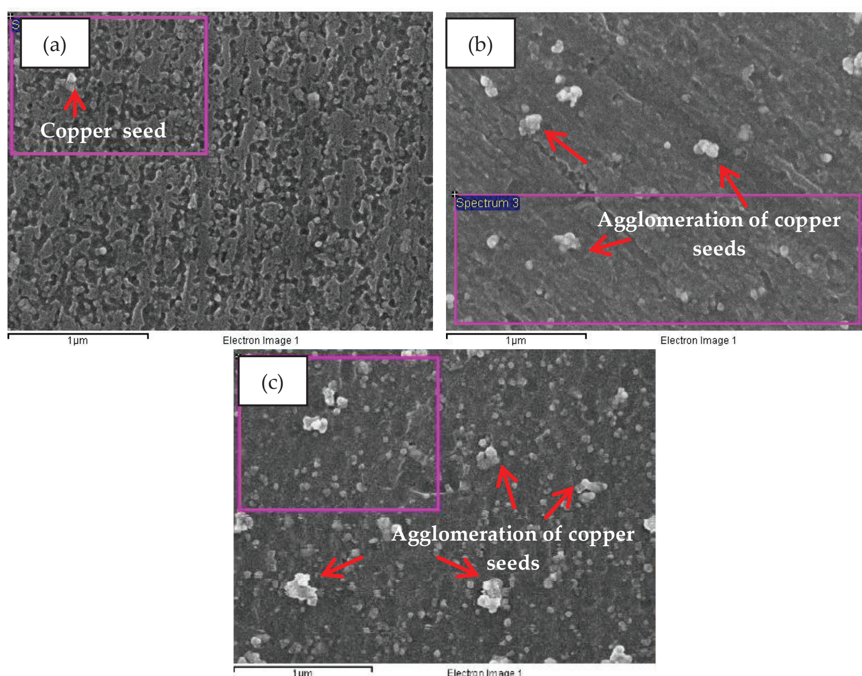

Figure 3: EDX analyses of AA7075 substrates after copper activation process at (a) 5, (b) 10 and (c) 15 minutes

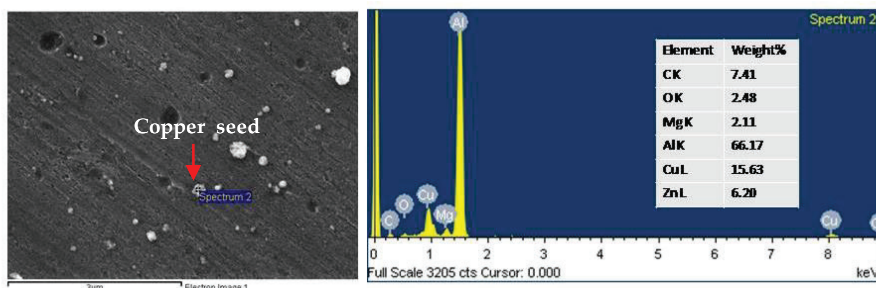

Figure 4: EDX analysis of the particles formed after copper activation

3.3 Effects of Conventional and Modified Single Zincating Process with Copper Activation at Various Durations on Surface Topography and Roughness of AA7075 Substrate

Different sizes of zinc particles were seen, which were non-homogenously deposited on the substrate without a copper activation process (Figure 5(a)). Based on Figure 5(b), it was clear that copper activation resulted in homogenous distribution of zinc particles with uniform particle size. When zincating was further carried out, growth could be seen with the zinc particles with increase in density after

keeping in the zincating solution for 10 minutes (Figure 5(c)). By lengthening the zincating duration to 20 minutes, it can be seen that there is rise in the size and density of zinc particle along with few agglomeration on the substrate (Figure 5(d)). As presented in Figure 5(d), the zinc particles were seen to take the hexagonal shape. As per AFM images in Figure 6 that included longer zincating durations, the zinc particles were seen to stack upon each other as well as encompass the whole surface. The findings were in line with the work of Lee et al. [13], who discovered that on further deposition, zinc deposits were seen to result in creating hexagonal platelets, which eventually would grow and begin stacking on each other. A roughened surface would appear due to this longtime deposition [14].

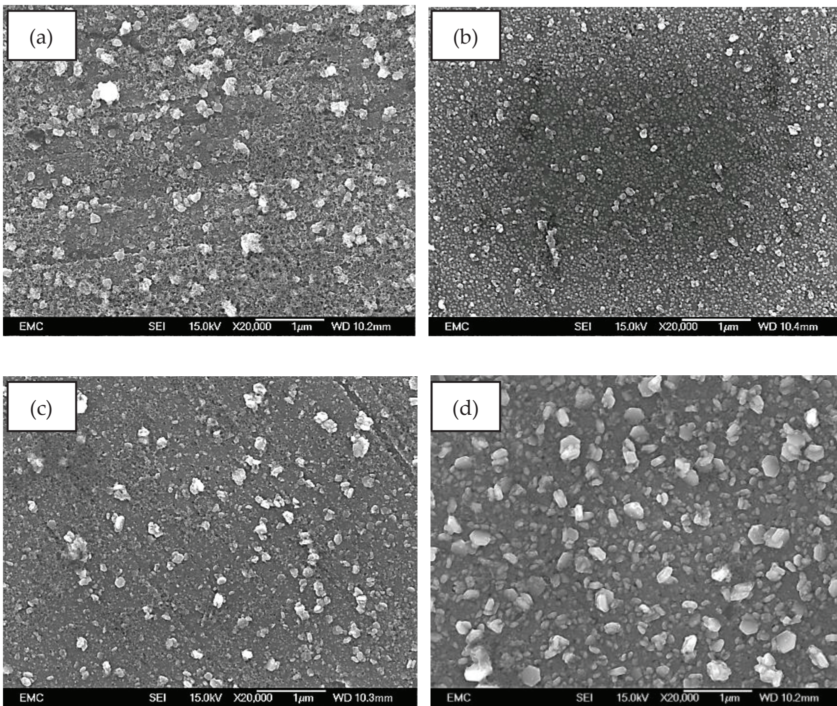

Figure 5: SEM micrographs of AA7075 substrates after conventional single zincating process for 1 minute with (a) without a copper activation, (b) with copper activation and various modified single zincating durations with (c) 10 and (d) 20 minutes with copper activation

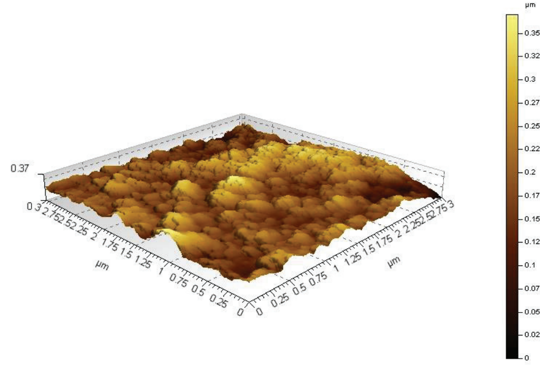

Figure 6: AFM images of AA7075 substrate after modified single zincating durations for 20 minutes with copper activation

3.4 Effects of Conventional and Modified Single Zincating Process with Copper Activation at Various Durations on Adhesion Properties of Nickel Coatings

Based on Figure 7, all samples were seen to demonstrate a series of ductile tensile cracking near the scratch track's centre, which can be regarded as a kind of through-thickness cracking that can be classified as cohesive failure modes. Labelling is done for the first crack as L_{C1}, which occurs on the scratch tracks. With progressive continuation pertaining to the applied load on the coatings, the stylus produces more cracks. Based on the sample generated via the conventional single zincating lacking copper activation, the coating was seen to rupture as well as would get detached from the substrate towards the scratch track end (Figure 7(a)). This failure that has been recognised as adhesion failure is labelled as L_{C2}. This suggests the existence of a poor bonding between substrate and the coating. Applying the copper activation process prior to conventional single zincating allows enhancing of the coating adhesion to the substrate (Figure 7(b)). Samples that were yielded from modified single zincating process with copper activation showed only cohesive failure with progressive rise in the applied load, there was no adhesive failure seen along the track (Figure 7 (c-f)). This suggests that the coatings have been well adhered towards the substrate.

A poor adhesion between substrate and nickel coating may have caused the adhesive failure pertaining to conventional single zincated sample lacking a copper activation process. During the process, the poor coverage pertaining to zinc particles resulted in weak adhesion with regards to the substrate coating. The study results corroborated with the work of Yang et al. [15], who reported the zinc coverage was

closely associated with the coating adhesion. As per their study, if the zincating duration is very short, part of the substrate surface tends to remain uncovered, while if the zincating duration is very much extended, excess zinc gets deposited on the substrate [15].

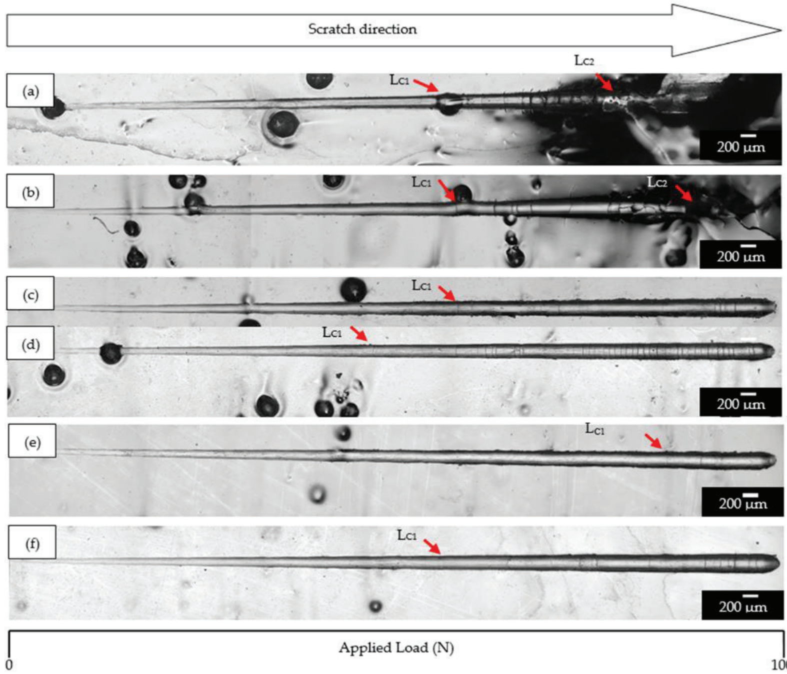

Figure 7: Optical micrographs of the scratch tracks of nickel coatings generated by conventional single zincating process for 1 minute: (a) without and (b) with copper activation and various modified single zincating durations at (c) 5, (d) 10, (e) 15 and (f) 20 minutes with copper activation

4.0 CONCLUSION

In this study, the effect of various single zincating durations with copper activation on the properties of coating was investigated and the following conclusion can be made:

i. The electrochemistry measurements show that specimen generated from single zincating along with copper activation efficiently suppress the dissolution of substrate in the zincating solution.

ii. The SEM morphologies show that zinc particles' size and density increased with the extension of the zincating duration. The

copper activation process enhanced the zincating layer's uniformity.

iii. The optical microscopy images from the scratch tests show that nickel coating produced from single zincating process for 1 minute exhibited poor coating adhesion due to occurrence of cohesive and adhesive failures, while single zincated samples with copper activation experienced only the cohesive failure.

iv. Overall, the study results demonstrated the significance of the zincating duration and copper activation in terms of controlling the zinc layer's morphology, thus enhancing the coating adhesion.

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REFERENCES

[1] M.J. Starink, B. Milkereit, Y. Zhang, and P.A. Rometsch, "Predicting the quench sensitivity of Al-Zn-Mg-Cu alloys: a model for linear cooling and strengthening", *Materials & Design*, vol. 88, pp. 958-971, 2015.

[2] S.V. Oleynik, Y.A. Kuzenkov, S.A. Karimova, and T.I. Tararaeva, "Non-chromate conversion coatings on A7075 aluminum alloy after various thermal treatment", *Protection of Metals and Physical Chemistry of Surfaces*, vol. 47, no. 7, pp. 889-894, 2011.

[3] C. Bocking and A. Reynolds, "Mechanism of adhesion failure of anodised coatings on 7075 aluminium alloy", *Transactions of the Institute of Metal Finishing*, vol. 89, no. 6, pp. 298-302, 2011.

[4] M. Hino, K. Murakami, Y. Mitooka, K. Muraoka, R. Furukawa, and T. Kanadani, "Effects of zincate treatment on adhesion of electroless Ni-P coating onto various aluminum alloys", *Transactions of Nonferrous Metals Society of China*, vol. 19, no. 4, pp. 814-818, 2009.

[5] M. Schwankl, J. Wedler and C. Korner, "Wrought Al- cast Al compound casting based on zincate treatment for aluminium wrought alloy inserts", *Journal of Materials Processing Technology*, vol. 238, pp. 160-168, 2016.

[6] M. Vijayanand and R. Elansezhian, “Effect of different pretreatmetns and heat treatment on wear properties of electroless Ni-B coatings on 7075-T6 aluminium alloy”, *Procedia Engineering*, vol. 97, pp, 1707-1717, 2014.

[7] A. Farzaneh, M. Sarvari, M. Ehteshamzadeh and O. Mermer, “Effect of zincating bath additives on structural and electrochemical properties of electroless Ni-P coating on AA6061”, *International Journal of Electrochemical Science*, vol. 11, pp. 9676-9686, 2016.

[8] K. Azumi, S. Egoshi, S. Kawashima, and Y. Koyama, “Effect of copper pretreatment on the double zincate process of aluminum alloy films”, *Journal of the Electrochemical Society*, vol. 154, no. 4, pp. D220-D226, 2007.

[9] D.A. Hutt, C. Liu, P.P. Conway, D.C Whalley and S.H. Mannan, “Electroless nickel bumping of aluminum bondpads - Part I: Surface pretreatment and activation”, *IEEE Transactions on Components and Packaging Technologies*, vol. 25, no. 1, pp. 87-97, 2002.

[10] S. Egoshi, K. Azumi, H. Konno, K. Ebihara, and Y. Taguchi, “Effects of minor elements in Al alloy on zincate pretreatment”, *Applied Surface Science*, vol. 261, pp. 567-573, 2012.

[11] J.W. Tang, and K. Azumi, “Effect of copper pretreatment on the zincate process and subsequent copper electrodeposition of AZ31 magnesium alloy”, *Journal of the Electrochemical Society*, vol. 158, no. 9, pp. D535-D540, 2011.

[12] J.W. Tang, and K. Azumi, “Effect of copper pretreatment on the zincate process and subsequent electroplating of a protective copper/nickel deposit on the AZ91D magnesium alloy”, *Electrochimica Acta*, vol. 56, no. 24, pp. 8776-8782, 2011.

[13] S.K. Lee, J.H. Lee, and Y.H. Kim, “Nucleation and growth of zinc particles on an aluminum substrate in a zincate process”, *Journal of Electronic Materials*, vol. 36, no. 11, pp.1442-1447, 2007.

[14] K.L. Lin, and S.Y. Chang, “The morphologies and the chemical states of the multiple zincating deposits on Al pads of Si chips”, *Thin Solid Films*, vol. 288, no. 1-2, pp. 36-40, 1996.

[15] Y. Yang, J. Cai, S. Wang and S. Jia, “The impact of zincation on the electroless nickel UBM for low cost flip technology" in 6th International Conference on Electronic Packaging Technology, Shenzhen, China, 2005, pp. 229-233.