Comparative Evaluation of Chemical Deposition Parameters of an Induced Zn/Al-Zn and their Interfacial Characteristic Trend on Mild Steel

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A statistical study and matlab evaluation has been made on the deposited Zn/Zn-Al alloy on mild steel. The deposition was performed to obtain a better surface adherent coverage using electroplating technique with developed zinc and aluminum powder particle. SEM/EDX was used to examine the morphological adhension phenomena. The methodology values obtained were processed using statistical package for social scientists (SPSS) software to compare all electrodeposition variables of the plating treatment values by analysis of variance (ANOVA) and Pearson Correlation Index with matlab tool. The results obtained from these statistical evaluations indicate positive improved correlations between all the groups of deposition considered in this work. The alloy deposition proved better than the single phase deposition of zinc coating.

1. INTRODUCTION

Steel remain the most widely used material in all application due to its excellent properties but its weaknesses cannot be over emphasis in term of corrosion and mechanical deterioration [1-3]. Due to these disadvantages, many protective methods have been adopted to improve the service life of steel against corrosion attacks [2-5]. Among these, electroplating method with metallic thin films of various interests has been worked upon. The improvement from single bath additive system to binary deposition such as Zn-Co, Zn-Fe, and Zn-Ni have so much gained a wider range of applications in both manufacturing and marine industries lately as a better substitute for ordinary zinc plating [3-6].

Comparative measure to clearly define the extend of modification, improvement and adhesion phenomena of this bath formulated coatings against the single plate as necessitate this study using statistical tool and matlab technique. Statistical method has been reported by Popescu et al [7] and Thangaraji et al [11] as a tool that helps to explain results of a given treatment and large results of analysis especially for efficient and effective comparisons. In this present study, the experimental results from the anomalous co-deposition measurement of Zn and Zn-Al from our previous work [3,4-5] by varying coating parameter such as, the coating voltage, time of deposition, and coating thickness were examined from the various deposition variable using statistical package for social scientists (SPSS) software to generate data and compare the characteristic by analysis of variance (ANOVA) and Pearson Correlation Index of the coating interface deposited

2. EXPERIMENTAL METHOD

2.1 Material

The substrate used in this work is mild steel which was obtained in the market and examined with spectrometer at the NFL, Ilupeju, Lagos, Nigeria. The per cent compositions are 0.200C, 0.007Ni, 0.006P, 0.168Si, 0.390Mn, 0.012S, 0.080Cu, 0.024Al, Balance is Fe.

2.2 Test Media

All Chemical and powders used in this work are of Analar grade obtained from MERCK and SMM chemical laboratory South Africa.

2.3 Preparation of Admixed Solution

Zn and Zn-Al bath were prepared according to Popoola et al [2] with electroplating cell consisting of three electrodes. Locally sought mild steel of (40 mm x 20 mm x 1 mm) sheet was used as substrate and zinc sheets (30 mm x 20 mm x 1 mm) were used as anodes. The samples were polished with different grades of emery. Acid pickling operation in 20% 0.5 M HCl was used for descaling and finally activated. Cathode and Anodes were connected to the D.C. power supply through a rectifier at 2 A. Electrodeposition was carried out at varying applied voltage between 0.6-1.0 V for 20 minutes. The bath contain 50 g each of 98.5 % pure aluminum and 98.8 % zinc powder which were put into a 250 ml bottom flask and dissolve in with other additive. Morphological study of the Zn-Al and Zn powder coating deposited at different applied potential was investigated using (SEM/EDS). Equally, Zn and Zn dispatched Al at different metallurgical process were processed using (SPSS) software and compare all the coating per unit area, weight gained, thickness of deposition with time of deposition and applied potential values by analysis of variance (ANOVA), Pearson Correlation Index and matlab computation.

3. RESULTS AND DISCUSSION

3.1. Statistical Evaluation of Deposited Parameter for Zn Coated Mild Steel

The results of the post hoc test in a multiple-comparism chart (Tables 1 & 2) for Zn deposition on coating thickness and weight gained indicates that the mean difference is significant and visible within the deposition voltage and time with standard error bars ranged from ± 0.92 to ±2.59. At 0.9 and 1.0 V, the highest coating value of the Zn deposition was achieved. This was also observed for weight gained evaluation with standard bar error significant at ± 0.26 to ±0.25 an indication of an appreciable difference between the groups. Since different applied voltage and time as maximum influence on the plating efficiency, the post hoc test result indicates that deposition at 1.0 V compare to other voltage value even at constant time and vice versa are not significant to each other. Hence, one could say that the significant effect is notable to some extend at 1.0V in 20 minutes and this can be linked to the adhesion and structural modification of the plated sample in line with the parameter of deposition since [8] affirm that the use of a statistical approach allowed us to see individual and/or interaction effects of deposition parameters in order to obtain alloy powders with a desired composition and to determine the optimum experimental conditions that lead to the maximization of current/ potential efficiency.

Table 1. Post Hoc Tests for zinc coating thickness at different voltage
Multiple Comparisons
Dependent Variable: Coating thickness (Zn) LSD

(i)group	(j)group	Mean Difference (I-J)	Std. Error	Sig	95% Confidence interval	
					Lower Bound	Upper Bound
0.6	0.7volts	-2800	2.37386	.907	-4.6718	5.2318
	0.8 volts	-1.0120	2.37386	.674	-5.9638	3.9398
	0.9 volts	-8.1080*	2.37386	.003	-13.0598	-3.1562
	1.0 volts	-7.3320*	2.37386	.006	-12.2838	-2.3802
0.7	0.6volts	-2800	2.37386	.907	-5.2318	4.6718
	0.8 volts	-1.2920	2.37386	.592	-6.2438	3.6598
	0.9 volts	-8.3880*	2.37386	.002	-13.3398	-3.4362
	1.0 volts	-7.6120*	2.37386	.004	-12.5638	-2.6602
0.8	0.6 volts	-1.0120	2.37386	.674	-3.9398	5.9638
	0.8 volts	-1.2920	2.37386	.592	-3.6598	6.2438
	0.9 volts	-7.0960*	2.37386	.007	-12.0478	-2.1442
	1.0 volts	-6.3200*	2.37386	.015	-11.2718	-1.3692
0.9	0.6 volts	8.1080*	2.37386	.003	3.1562	13.0598
	0.8 volts	8.3880*	2.37386	.002	3.4362	13.3398
	0.9 volts	7.0960*	2.37386	.007	2.1442	12.0478
	1.0 volts	.7760	2.37386	.747	-4.1758	5.7278
1.0	0.6 volts	7.3320*	2.37386	.006	2.3802	12.283/8
	0.8 volts	7.6120*	2.37386	.004	2.6602	12.5638
	0.9 volts	6.3200*	2.37386	.015	1.3682	11.2718
	1.0 volts	-.7760	2.37386	.747	-5.7278	4.1758

- The mean difference is signification at the .5 level

Table 2. Post Hoc Tests for zinc weight gained at different voltage.
Multiple Comparisons
Dependent Variable: Coating thickness (Zn) LSD

(i)group	(j)group	Mean Difference (I-J)	Std. Error	Sig	95% Confidence interval	
					Lower Bound	Upper Bound
0.6	0.7 volts	-0236	.11412	.838	-.2144	.2616
	0.8 volts	-.0464	.11412	.689	-.2844	.1916
	0.9 volts	-.3508*	.11412	.006	-.5888	-.1128
	1.0 volts	-.3662*	.11412	.004	-.6042	-.1282
0.7	0.6 volts	-.0236	.11412	.838	-.2616	.2144
	0.8 volts	-.0700	.11412	.547	-.3080	.1680
	0.9 volts	-.3744*	.11412	.004	-.6124	-.1364
	1.0 volts	-.3898*	.11412	.003	-.6278	-.1518
0.8	0.6 volts	-.0464	.11412	.689	-.1916	.2844
	0.8 volts	-.0700	.11412	.547	-.1680	.3080
	0.9 volts	-.3044*	.11412	.015	-5424	-.0664
	1.0 volts	-.3198*	.11412	.011	-5578	-.0818
0.9	0.6 volts	.3508*	.11412	.006	.1128	.5888
	0.8 volts	.3744*	.11412	.004	.1364	.6124
	0.9 volts	.3044*	.11412	.015	.0664	.5424
	1.0 volts	.0154	.11412	.894	-.2534	.2226
1.0	0.6 volts	.3662*	.11412	.004	.1282	.6042
	0.8 volts	.3898*	.11412	.003	.1518	.6278
	0.9 volts	.3198*	.11412	.011	.0818	.5578
	1.0 volts	.0154	.11412	.894	-.2226	.2534

- The mean difference is signification at the .5 level

3.2 Statistical Evaluation for Deposited Parameter of Zn-Al Coated Mild Steel.

A multiple-comparative chart for Zn-Al deposition is indicated below in Tables (3&4). From all indication the mean difference is significant within the deposition voltage and time with standard error bars ranging from ± 0.04 to ±0.11.

Table 3. Post Hoc Tests for Zn-Al coating thickness at different voltage
Multiple Comparisons
Dependent Variable: coating thickness (Zn-Al) LSD

(I) Group	(J)Group	Mean Difference (I-J)	Std. Error	sig	95% confidence Interval	
					Lower Bound	Upper Bound
0.6 volts	0.7 volts	2640	2.37322	0.913	-4.6864	5.2144
	0.8 volts	-1.0080	2.37322	0.676	-5.9584	3.9424
	0.9 volts	-8.1140	2.37322	0.003	-13.0644	-3.1636
	1.0 volts	-7.3550	2.37322	0.006	-12.3164	-2.4156
0.7 volts	0.6 volts	-2640	2.37322	0.913	-5.2144	4.6864
	0.8volts	-1.2720	2.37322	0.598	-6.2224	3.6784
	0.9 volts	-8.3780	2.37322	0.002	-13.3284	-3.4276
	1.0 volts	-7.6300	2.37322	0.004	-12.5804	-2.6796
0.8 volts	0.6 volta	1.0080	2.37322	0.676	-3.9424	5.9584

(I) Group	(J) Group	Mean Difference	Std. Error	Sig	Lower Bound	Upper Bound
	0.7 volts	1.2720	2.37322	0.598	-3.6784	6.2224
	0.9 volts	-7.1060	2.37322	0.007	-12.0564	-2.1556
	1.0 volts	-6.3580	2.37322	0.756	-11.3084	
0.9 volts	0.6 volts	8.1140	2.37322	0.003	3.1636	13.0644
	0.7 volts	8.3780	2.37322	0.002	3.4276	13.3284
	0.8 volts	7.1050	2.37322	0.007	2.1556	12.0564
	1.0 volts	0.7480	2.37322	0.756	-4.2024	5.5984
1.0 volts	0.6 volts	7.3550	2.37322	0.006	2.4156	12.3164
	0.7 volts	7.6300	2.37322	0.004	2.6795	12.5804
	0.8 volts	6.3580	2.37322	0.014	1.4076	11.3084
	0.9 volts	-0.7480	2.37322	0.756	-5.6984	4.2024

The highest standard error bars was also found at 0.9 and 1.0 V, which are the highest coating parameter for the Zn-Al deposition

Table 4. Post Hoc Tests for Zn-Al weight gained at different voltage.
Multiple Comparisons
Dependent Variable: Weight gain (zn-Al) LSD

(I) Group	(J)Group	Mean Difference (I-J)	Std. Error	Sig	95% Confidence Interval	
					Lower Bound	Upper Bound
0.6	0.7 volts	0.0212	0.11396	0.854	-0.2165	0.2589
	0.8 volts	-0.0464	0.11396	0.688	-0.2841	0.1913
	0.9 volts	-0.3520	0.11396	0.008	-0.5897	-0.1143
	1.0 volts	-0.3700	0.11396	0.004	-0.6077	-0.1323
0.7	0.6 volts	-0.212	0.11396	0.854	-0.2539	0.2165
	0.8 volts	-0.0676	0.11396	0.560	-0.3053	0.1701
	0.9 volts	-0.3732	0.11396	0.004	-0.6109	-0.1355
	1.0 volts	0.3912	0.11396	0.003	-0.6289	-0.1535
0.8	0.6 volts	0.0464	0.11396	0.688	-0.1913	0.5897
	0.7 volts	0.0676	0.11396	0.560	-0.1701	0.3053
	0.9 volts	-0.3056	0.11396	0.014	-0.5644	-0.0679
	1.0 volts	-0.3236	0.11396	0.010	-0.5613	-0.0859
0.9	0.6 volts	0.3520	0.11396	0.008	0.1143	0.5897
	0.7 volts	0.3732	0.11396	0.004	0.1355	0.6109
	0.8 volts	0.3056	0.11396	0.014	0.0679	0.5433
	1.0 volts	-0.0180	0.11396	0.878	-0.2557	0.2197
1.0	0.6 volts	0.3700	0.11396	0.004	0.1323	0.6077
	0.7 volts	0.3912	0.11396	0.003	0.1535	0.6289
	0.8 volts	0.3236	0.11396	0.010	0.0859	0.5613
	0.9 volts	0.180	0.11396	0.878	-0.2197	0.2557

The dependent variable with mean difference is more pronounced and significant at 1.0 V in 20 minutes likewise. Notably, at these points, 95% confidence level: lower bound and upper bond values are the highest compared to others within the group of analysis from descriptive coating thickness. Obviously it is assumed that the surface adhesion properties exhibited by the Zn-Al deposited, was a function of the firmly bond thin film. It is also worthy to note that deposition at 0.8 and 1.0 V still remained the peak adhered conditions for this plating parameter. This may probably account for insignificant occurrence associated at this deposited condition.

Comparing the significant effect of Zn and Zn-Al from *Tables 4 and 5* especially with deposition at 20 minutes, there is no much significant different at 1.0 V. This may be expected because according to Popoola et al [2, 4] adhesion mechanism and surface improvement is not a direct influence of weight gained produced from the codeposition, rather the number of electrons involved in the electrochemical reaction to produce a stable thin film. In this regards, weight gain does not in all cases influence proper adhesion as affirmed from this statistical evaluation study.

Moreso, the overall analyses of summarized variance between the groups better explain details of the trend as in table 5 with lower bound of 2.0968 for Zn compare to 2.1029 for Zn-Al. Equally, the thickness value is obvious even for Zn-Al particulate from a maximum condition at 95% in which we have 8.43 for Zn-Al deposited compare to zinc at 8.40.

Table 5. Mean thickness of deposition from Zn and Zn-Al deposition at different voltage.
Thickness of deposition

| | N | Mean | Std. Deviation | Std. Error | 95% Confidence Interval for Mean | | Minimum | maximum |
					Lower Bound	Upper Bound		
Zn	5	5.4000	2.66027	1.18971	2.0968	8.7032	3.09	8.40
Zn-Al	5	5.4420	2.68922	1.20266	2.1029	8.7811	3.12	8.43
Total	10	5.4210	2.52191	.79750	3.6169	7.2251	3.09	8.43

3.3 Effect of Plating Time on Coating Per Unit Area for Zinc and Zinc-Aluminum:

Figures 1-2 show the effect of plating time against the coating per unit area of zinc and zinc-aluminum deposited sample using matlab plot. It was observed that, coating thickness increases proportionally as the plating time increases. However, not much difference is shown when compare to zinc deposition in term of coating thickness but significant difference is seen with the appearances and adhesion from surface structure which is also paramount to this study. Investigation by proven researchers affirmed the significant of little improvement. Quibo, [10] pointed out that the incorporation of metallic additive in the coating always lead to improvement in the crystal size, good surface adhesion. [9,10] reported from their studies that the surface homogeneity deteriorated as the thickness of the layer/coating increased, possibly due to mass transport limitations or occurrence of local electrocrystallization events within the layer from the electrolyte bath. With this, conclusion can be drawn that the significant of surface film protection is not only for surface weight gain/ thickness but also for close adhesion and resistance to degradation. Hence, The Al uniformly distributed within zinc based is for the enhancement, blocking tendency of surface point rather than improving excessive weight.
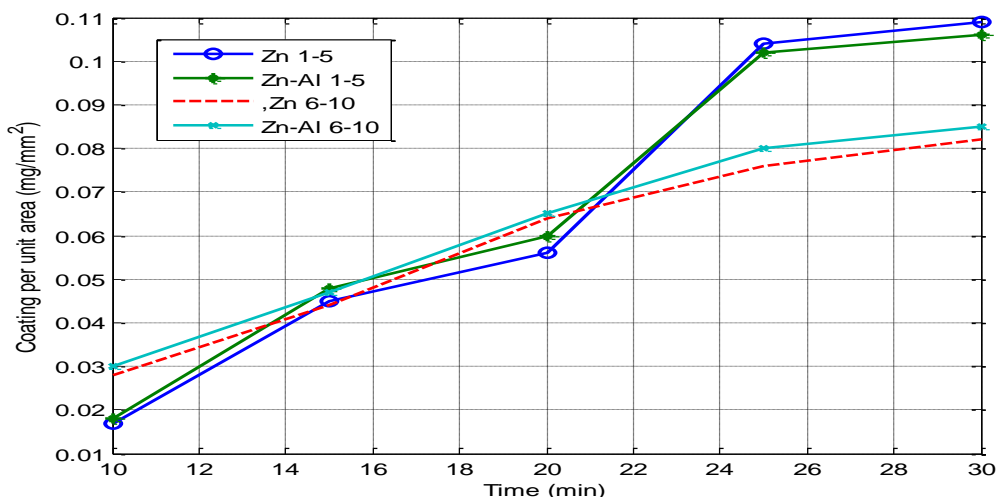
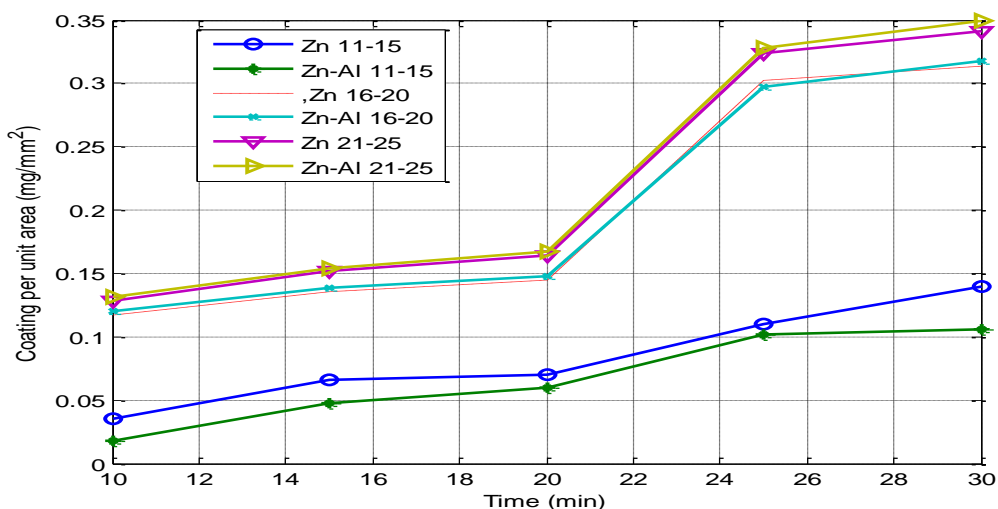**Figure 1.** Variation in coating per unit area with time of deposition

Figure 2. Variation in coating per unit area with time of deposition

In addition, an assumption have been made that the difference observed on Zn-Al to that of Zn is a function of Al ion migration into the zinc interface which produces the strong metallurgical bond during morphological and mechanical study.

Hence, an empirical formula to predict or describe this relationship can be written as

Zn 1-5: $T = -339.1667 V^3 + 840.2143V^2 - 666.3012V + 173.8329$

Zn-Al 1-5: $T = -357.5000V^3 + 883.8571V^2 - 700.1964V + 182.4534$

Where T=Thickness of deposition

V= voltage.

A third order polynomial is used so that the error between the actual and the predicted values will be at least 0.9.
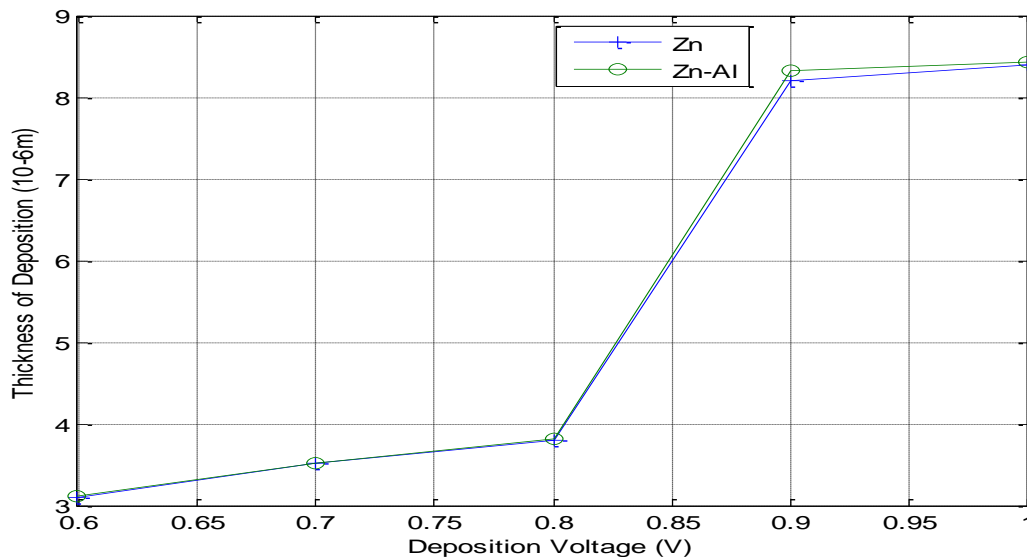
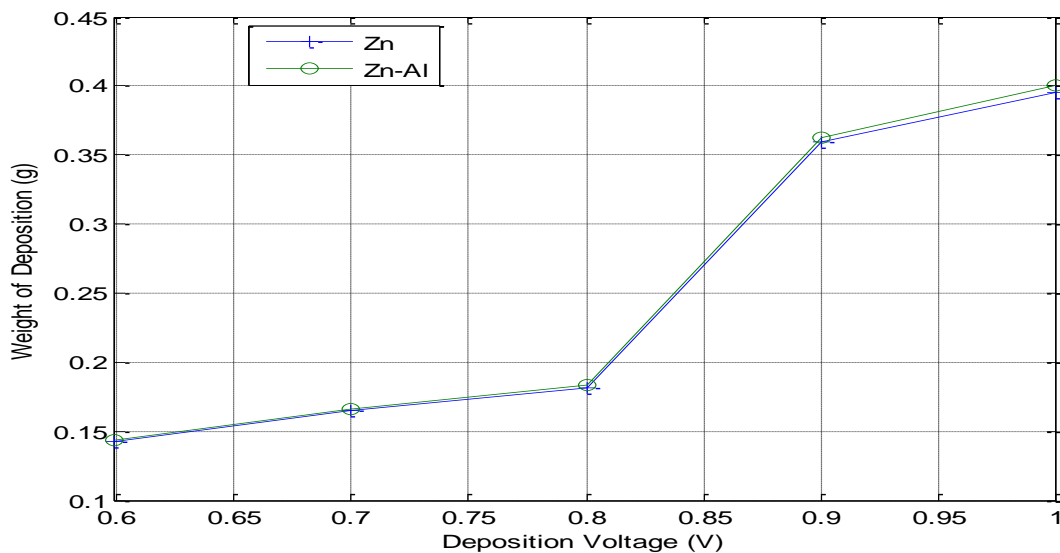**Figure 3.** Variation in thickness of deposition with applied voltage

Figure 4. Variation in weight of deposition with deposition voltage

3.4 Morphological Examination on the Influence of Voltage Variation on Weight Gain/Thickness behavior of Zinc and Zinc-Alloy Deposition:

Figure 5a and b show the FIB-SEM micrographs of the two different depositions under investigation, the electrodeposition of Zn-Al reinforcement brought about good surface finish compared to zinc coated
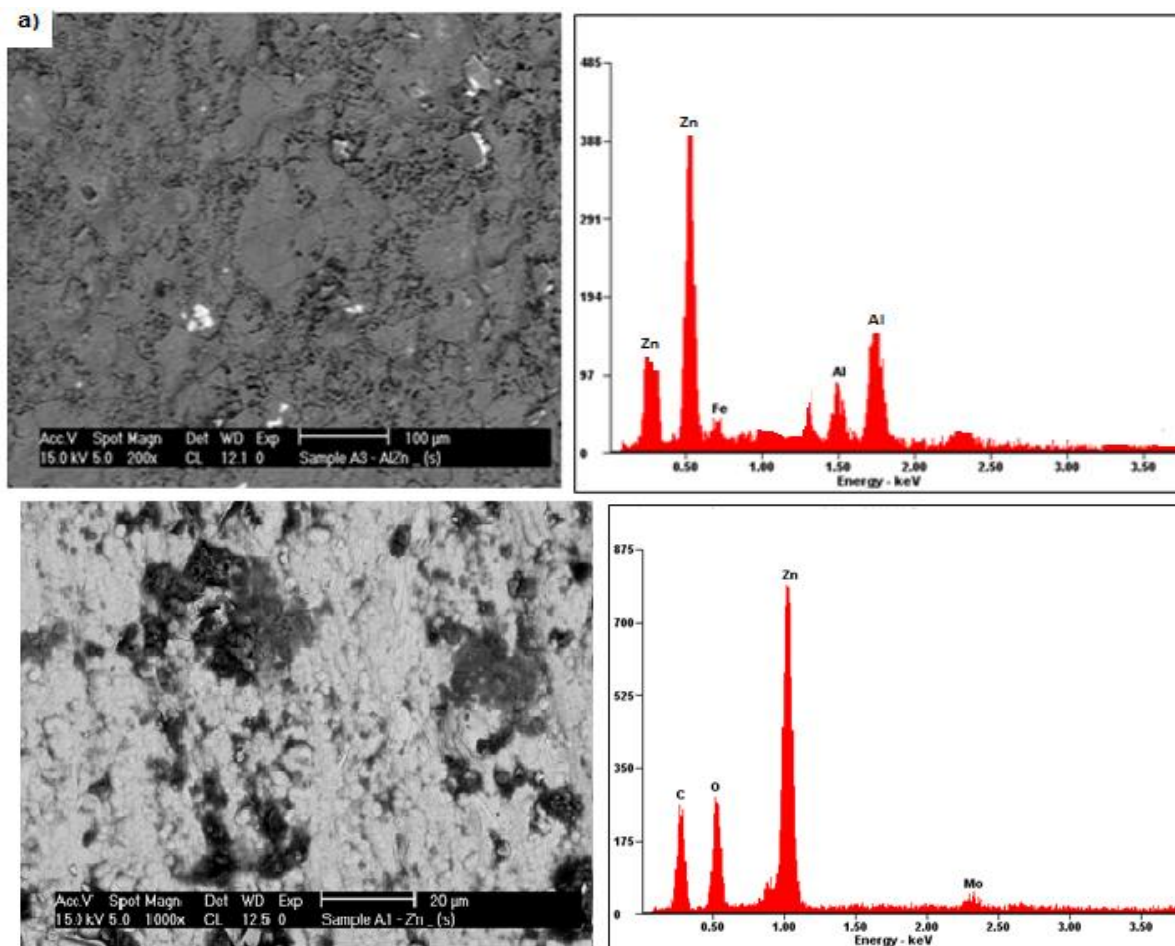
Figure 5. SEM Morphological examination of the deposited a) Zn/Al and b) Zn.

In the case of zinc deposition, the dispersion was quite uniform but microstructure had some few solid crystals embedded at the surface of the substrate. Al distribution within the zinc matrix resulted in good surface finish; and its high affinity for oxygen resulted in Al_2O_3 oxide film on the surface which led to good resistance to corrosion attack and finer microstructure. [2, 9] affirmed that it is impossible for crystal growth to be completely free from inhibiting species, and some species such as hydrogen and hydroxide exist in most electroplating, and they play a major role in crystal growth. Hence, little change in weight gain could gain a long way to redefine the morphological characteristic of a coating. More so, weight gain observed might also be due to the bonding properties and electron transferring of Al ion. Since, aluminum being a light metal displayed faster transfer of the Al^{3+} much more than Zn^{2+} ion with formation of stable properties.

4. CONCLUSIONS

- The results obtained from these statistical evaluations indicate positive correlations between all the deposited condition and adhesion evaluation considered in this study.
- Statistical assessment of the coated materials under electrodeposited studied parameter, showed coating variable has a major significant impact on the coating.

- The higher fractions of the adhesion in co-deposition are explained by voltage and time of deposition.

- It can be seen that statistical method and matlab evaluation results of the test agree with each other.

- From the statistical and matlab evaluation, the Al distribution within the zinc matrix resulted in good surface finish; and a better improved trend which are meant to provide good resistance to corrosion attack and mechanical properties.

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