QUALITY REINFORCEMENT OF ELECTROPLATING ZINC COATINGSELECTRODEPOSITED FROM CYANIDE FREE ALKALINE SOLUTION BY POLYAMINE 70.000 AND POLYVINYL ALCOHOL 16.000

Truong Thi Nam[1, 2], Le Ba Thang[1, 2] , Nguyen Thi Cam Ha[3], Hoang Thi Huong Thuy[4, 5], Hoang Van Hung[4, *]

[1]*Institute for Tropical Technology, Vietnam Academy of Science and Technology 18 Hoang Quoc Viet, CauGiay, Ha Noi, Viet Nam*

[2]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18, Hoang Quoc Viet, CauGiay, Ha Noi, Viet Nam*

[3]*Faculty of Chemistry, the VNU University of Science - National University Ha Noi, 19 Le Thanh Tong, Hoan Kiem, Ha Noi*

[4]*Faculty of Chemistry, Hanoi National University of Education, 136 Xuan Thuy, Ha Noi*

[5]*Hong Duc University, 565 Quang Trung, Thanh Hoa City, Thanh Hoa Province*

[*]Email: *hunghv@hnue.edu.vn*

ABSTRACT

Zinc coatings have been deposited electrochemically from cyanine free alkaline solutions containing zinc ions with the presence of polyamine 70.000 and polyvinyl alcohol at different contents. The scanning electron microscope (SEM) images showed that the size of zinc grains decreased with the presence of polyamine 70.000 and polyvinyl alcohol with smoother surface of zinc coating. The polarization measurements also revealed that the coatings with the presence of polyamine or polyvinyl alcohol possessed higher value of polarity degree. This result is in good agreement with the result obtained from SEM images.

Keywords: zinc coating, polyamine, polyvinyl alcohol, alkaline cyanide free bath.

1. INTRODUCTION

Zinc coatings have been used extensively in different industrial fields as protective coatings for large quantities of items composed of steel such as wires, strips, sheets and tubes. These coatings commonly produced by electrode-position from alkaline cyanide-containing solutions, alkaline cyanide-free solution, or acidic solutions, offer a good protection for underneath metal even if the coatings were porous and a decorative appeal at low cost [1].

By the fact that the alkaline zinc cyanide-containing baths give a good coating. However, they are not universally applicable due to their effluent toxicity [2]. With the high conductivity, the acid zinc baths offer the high energy efficiency for zinc deposition. However, the critical pretreatment requirements and the low power lost of these solutions limit their use to plate the articles with the irregular shapes [3]. In recent years, zinc cyanide-free baths have been used to replace the cyanide solutions due to their low toxicity and low cost of effluent treatment though the energy efficiency for electroplating process is still low compared to the zinc cyanide-containing baths [4-8].The first work on alkaline cyanide-free zinc plating systems reported in the early 1960s due to the more stringent law on waste treatment. That was the beginning of the pressure to eliminate cyanide zinc plating. Many processes were then introduced into the market but did not prove to be viable plating processes. Among many processes, alkaline zinc cyanide-free baths shows the promising practical potentials in the field of zinc coatings, however this process still faces with a low power efficiency. Therefore, further study is needed to improve the power efficiency.

In general, alkaline zinc plating solutions contain zinc ions, water and hydroxide ions. At high pH, zinc baths without additive commonly produce a rough and spongy coating [3]. Thus, wide variety in procedures [9] and additives [4] were proposed for zinc electroplating to overcome the above drawbacks. In general, there are two main types of additives which can be added in alkaline zinc plating baths to achieve the desired bright and smooth surfaces [5]. These additives, commonly considered as carriers and brighteners in the electroplating bath, will increase the overpotential and nucleation rate of zinc, effectively inhibiting surface diffusion of zinc ions. However, the content and molar mass of additives (polymer) affect strongly on the properties of zinc coating.

In this work, we report the effect of polyvinyl alcohol with molecular weight of 16000amu (PVA16) and polyamine 70.000 amu (BT70) on alkaline non-cyanide plating process at different concentrations.

2. EXPERIMENTAL

2.1. Materials

Cyanide – free alkaline zinc plating solution was prepared as follows: 15 g of ZnO was dissolved in a solution containing 140 g of NaOHand PVA16 or BT70 with different contents. This mixture was then diluted to the volume of 1000 mL.20 % hydrochloric solution was used to pre-treat steel surfaces. All of chemicals used were of P grade and dissolved by deionized water.

2.2. Sample preparation

Low carbon steel plates (100 mm × 50 mm ×1.2 mm) were degreased by immersion in 60 g/L UDYPREP-110EC (Enthone) solution at 60 $^{\circ}$C for 10 min. After that the samples were immersed in 20 % HClsolution containing urotropine (3.5 g/L) at ambient temperature for 5 min.

Zinc electro-galvanizing process: all of samples were electrodeposited by DC supply with current stable device.

2.3. Characterization and analysis

The standard Hull cell with the volume of 267 mL was used to optimize the bath constituents and bath parameters. The steel plates were subjected to water wash and given bright dip in 1 % nitric acid for 3s prior to the electroplating process. The nature and appearance of zinc plating was carefully studied and recorded [10]. The cathodic polarization measurements were carried out at the scan rate of 2 mV/s using Autolab PGSTAT 30 connected with three-electrode cell in which silver/silver chloride and platinum sheet of 1.5 cm^2 were used as reference and counter electrodes, respectively, and steel electrode with area of 0.785 cm^{2}was used as working electrode. Morphologies of samples were evaluated using images obtained from scanning electron microscope (Jeol-JSM-6510LV, Japan)**.** Effect of BT70 and PVA16 on zinc coatings was analyzed with Hull, Haring-Blum and weight methods.The gloss of electrodeposited coating was determined by Progloss 3 (model 503, Germany) according to the ISO 2813 standard.

3. RESULTS AND DISCUSSIONS

3.1. Cathodic polarization curves

Polarization measurements are an important method to investigate electrochemical phenomena. These measurements can be used to study the reaction mechanism, and the kinetics of corrosion phenomena and metal deposition [11]. In general, polarization affects the electrodeposition processes therefore polarization measurements help us to understand the nature of electrodeposition. Figure 1a and 1b show the cathodic polarization curves of zinc coatings deposited from alkaline cyanide-free baths with different contents of PVA16 (a) and BT70 (b).
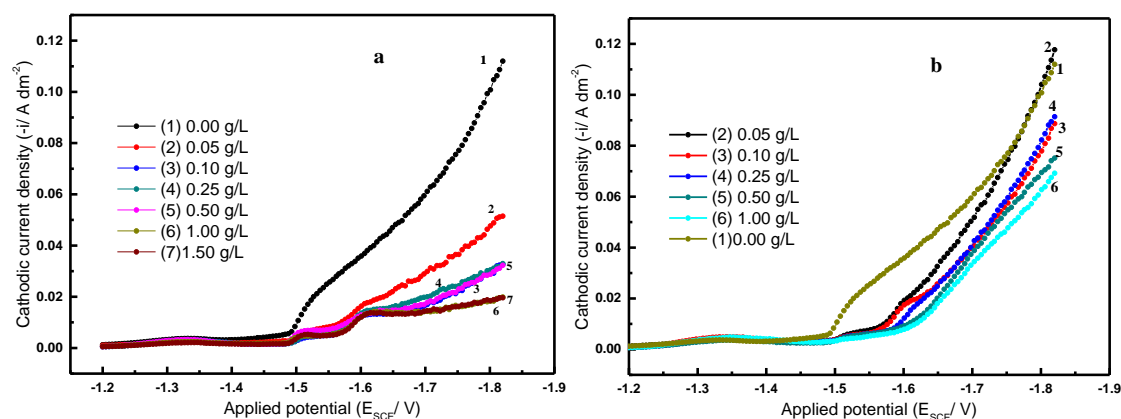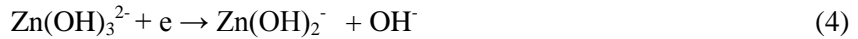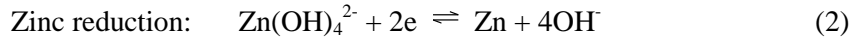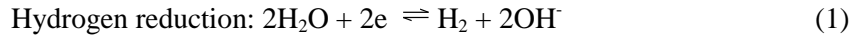

Figure 1. Cathodic polarization curves of zinc coatings deposited from alkaline non-cyanide baths with different contents of PVA16and BT70.

As shown in Fig. 1, these curves were swept from the rest potential (zero current potential) towards cathodic direction with a scan rate 10 mV/s. There is a clear difference between the curves of the coatings with and without PVA16 or BT70. The polarization curve for coating without additive (PVA16 or BT70) increases significantly after the rest potential due to the zinc reduction (see reaction 2). With the presence of PVA16 or BT70, there are two peaks which can be seen in all polarization curves. The first one appears at around 1.52 V assigned to the zinc reduction (see reaction 2) and the second one at about 1.62 V [7]. In general, the cathodic curve can be divided into different regions. The range from -1.30 V to greater than -1.50 V is the region where hydrogen reduction reaction is taking place (see reaction 1) and the range from -

1.50 to -1.60 V is the region where reduction reaction forming zinc is occurring (see reaction 2). This reaction occurred with several steps proposed by P.J. Mitchell group (from reaction 3 to 6) [12]

$$\text{Hydrogen reduction: } 2H_2O + 2e \rightleftharpoons H_2 + 2OH^- \tag{1}$$

$$\text{Zinc reduction: } Zn(OH)_4^{2-} + 2e \rightleftharpoons Zn + 4OH^- \tag{2}$$

$$Zn(OH)_4^{2-} \rightleftharpoons Zn(OH)_3^{2-} + OH^- \tag{3}$$

$$Zn(OH)_3^{2-} + e \rightarrow Zn(OH)_2^- + OH^- \tag{4}$$

$$Zn(OH)_2^- \rightleftharpoons ZnOH + OH^- \tag{5}$$

$$ZnOH + e \rightarrow Zn + OH^- \tag{6}$$

when PVA16 or BT70, a compound containing an atom (oxygen or nitrogen) with a high value of electronegativity and a lone pair electron, is present in the electroplating bath, they act as an inhibitor to form a barrier that can hinders zinc deposition. In addition, PVA16 or BT70 can be replaced H_2O molecule present in the complex $Zn(OH)_3(H_2O)^-$ according to the following process:

$$Zn(OH)_3(H_2O)^- + PVA16/BT70 \rightleftharpoons Zn(OH)_3(PVA16/BT70)^- + H_2O \tag{7}$$
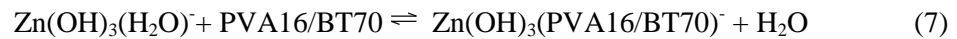
Hence, more energy is needed to break the PVA16 or BT70 complex for depositing zinc on steel surface with a barrier of additive. It might be the reason of appearance of the peak II in our case.

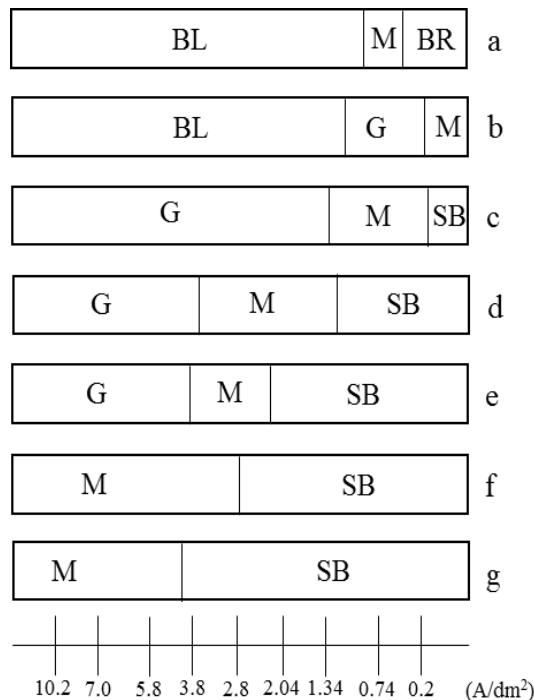## 3.2. Effect of PVA16 and BT70 on zinc electrodeposited coating surfaces

Figure 2. Hull cell pattern obtained from alkaline non-cyanide bath containing PVA16 with various concentrations namely: 0 g/L (a), 0.05 g/L (b), 0.1 g/L (c), 0.25 g/L (d), 0.5 g/L (e), 1 g/L (f), 1.5 g/L (g). Abbreviations for Hull Cell figures: BR-bright, M-matte, BL-black, G-grey, SB-semi-bright.

Hull cell is often used to test a plating station. Because a Hull cell can produce a deposit with different regions obtained from various current densities within the operating range of a particular system, and it allows experienced operators to determine multiple process parameters.

Hull cell patterns obtained from alkaline non-cyanide bath containing PVA16 and images of zinc coatings obtained plating bath with TB70,at different concentrations were presented on the Fig. 2 and Fig. 3.
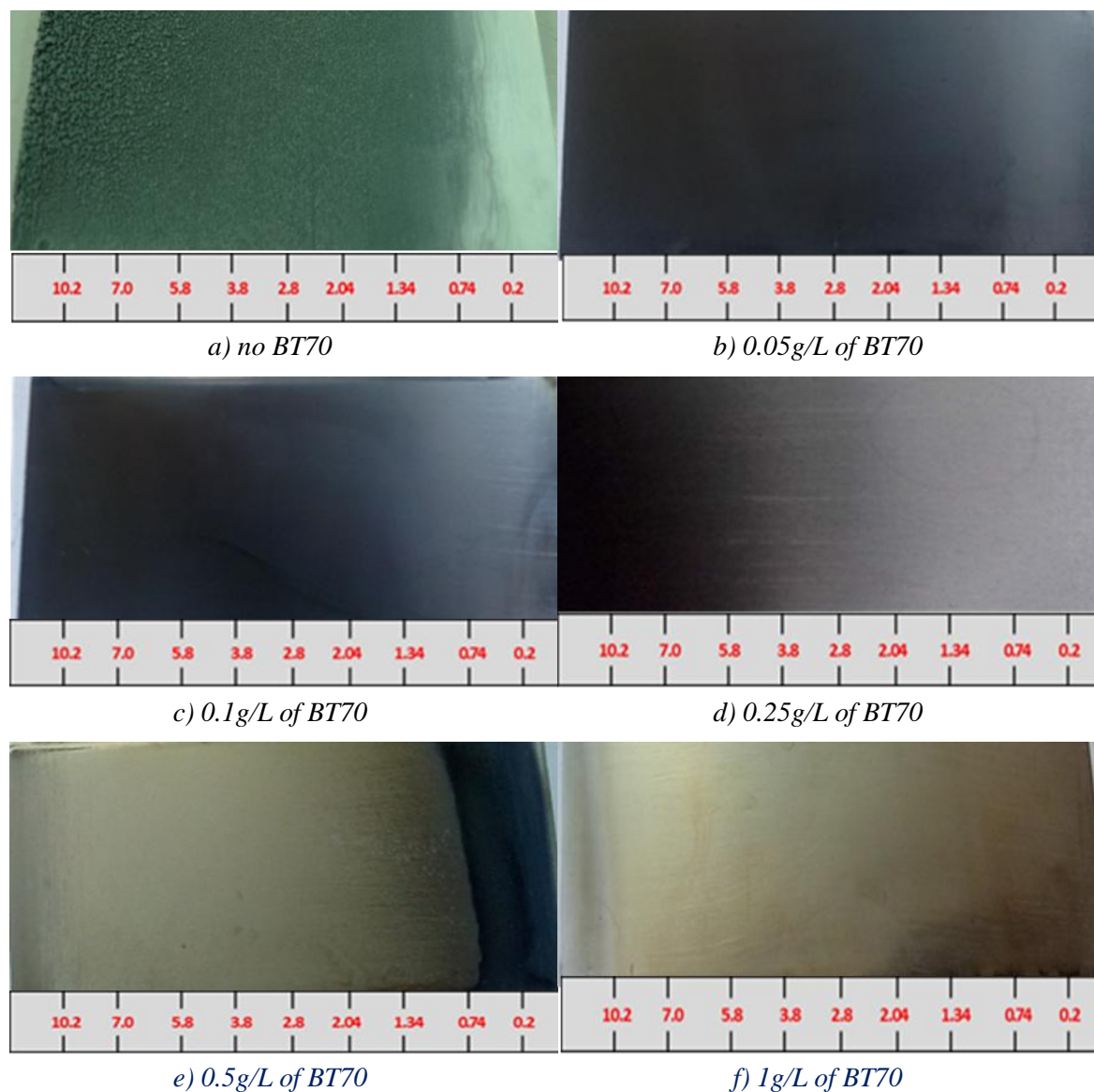

a) no BT70

b) 0.05g/L of BT70

c) 0.1g/L of BT70

d) 0.25g/L of BT70

e) 0.5g/L of BT70

f) 1g/L of BT70

Figure 3. Photos of samples from plating solutions containing various BT70 contents: a) no BT70, b) 0.05 g/L, c) 0.1 g/L, d) 0.25 g/L, e) 0.5 g/L, f) 1 g/L.

For deposit obtained from plating bath without PVA16, the surface of zinc coating is very harsh and only bright at the current density less than 0.2 A/dm^2. The coating becomes rougher and darker as the increase of current density. At the current density greater than 2.8 A/dm^2, the

coating becomes black and exists in the form of large grains leading to rough surface. These results indicated that zinc deposited coatings from the plating solution in absence of additive have a low distribution in all range of current density. In general, grain size of zinc coating depends on the current density. Grain size increases as the current density increases [9]. This dependence can be explained based on the mechanism as mentioned above, in which reaction (4) is the rate determining step. In plating solution without PVA16, reaction (4) becomes:

$$Zn(OH)_3(H_2O)^- + e \rightarrow Zn(OH)_2^- + OH^- + H_2O \qquad (8)$$
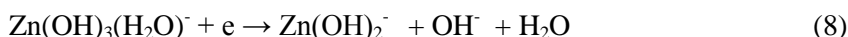
If the rate of reaction (8) occurred faster than the rate of transport of electroactive species to the site of discharge, powdery non-adherent deposits result. The addition of an additive to the plating solution can reduce the reaction rate of reaction (8) producing a brighter coating [7, 9].

When PVA16 is added to plating bath, smoothness of the coating surface increases as the PVA16 content increases. This can be explained as the following: with presence of PVA16, the reaction (8) was modified and a barrier is formed from additive molecules on the surface of metal. This barrier will slowdown the deposition process. In addition, additive can also replace water molecule as the reaction (7). These reasons make the grain size reduced [7].

In the case of adding BT70 to plating bath, at the same current density the formation of zinc coating is slower than the formation of zince coating with the presence of PAV16, the coating becomes smoother at the BT70 content of 0.05g/Land 0.1g/L and has a better distribution without semi-gloss scope (see Fig. 3b and 3c). When the content of BT70 reaches the value of 0.25 g/L, the semi-gloss scope starts to appear and goes up with the increase of BT70 content. At the content of 1.0 g/L, the whole sample becomes gloss (see Fig. 3 d, 3e and 3f). It is clear thatBT70 has strong effect on the gloss and semi-gloss scope of deposited coatings but there were the range of samples at either low or high current density which were dark grey and not shown here. Effect of additives on the zinc plating process is revealed easily with Hull method. However full of effect needs further studies with the non-cyanide alkaline plating bath.

3.3. Morphologies of zinc deposited coatings from alkaline non-cyanide bath containing PVA16 and BT70

Due to the different rate electrodeposition of zinc on steel from plating bath with the presence of PVA16 and BT70,the current density of 2 A/dm^2 and 5 A/dm^2 were chosen for solutions with PVA16 and BT70, respectively. The morphology of zinc deposited coatings are displayed Fig. 4 and Fig. 5.

As can be seen from Fig. 4a, the zinc deposition produced from alkaline non-cyanide bath in absence of PVA16 was in form block with diameter approximately 5 μm. However, the zinc deposition was in form slice if it was produced from plating bath with the presence of PVA16 (see Figs. (4b – 4g). The zinc particles become smaller as the PVA16 concentration increases. There was little difference among zinc coatings from plating bath at the PVA16 concentration ranging from 0.5 g/L to 1.5 g/L.

It could say that PVA16 affects to zinc deposition producing in the alkaline non-cyanide zinc plating process. PVA16 makes zinc coating brighter and smoother at even high current density and at PVA16 concentration of greater or equal 0.5 g/L.

Figure 5 shows images of zinc coatings obtained from solutions with the presence of BT70 at different contents. Similar to coatings formed from solutions containing PVA16, coatings formed from solution with the presence of BT70 are brighter and smoother.

As can be seen from Fig. 5, the morphology of zinc deposited coatings depends on the BT70 content.For coating formed from solution without BT70, the zinc grain size is in the range from10 to 30 μm. However, with the addition of BT70, the zinc coating surface becomes smoother with smaller and better distribution as the increase of BT70 content.
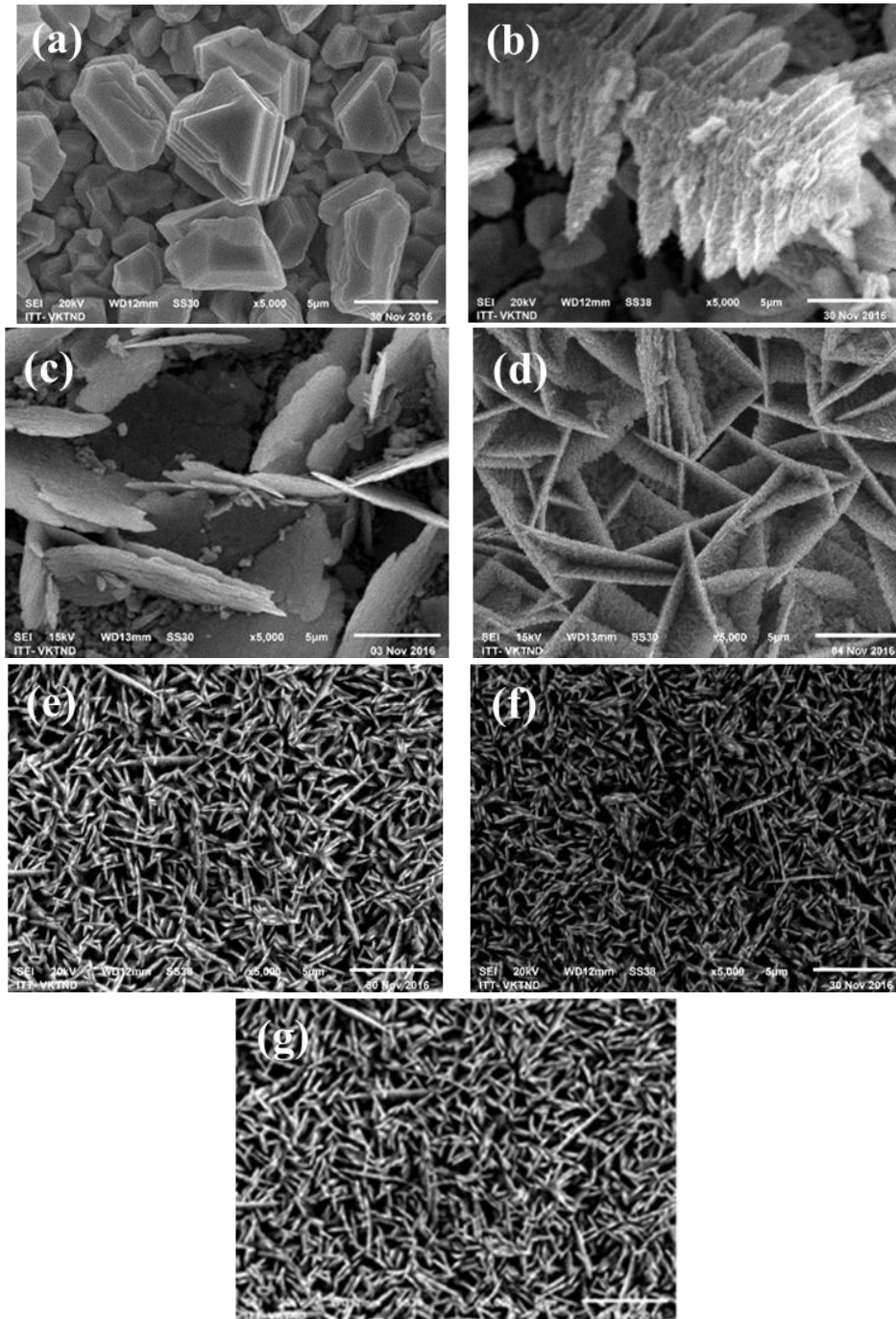

Figure 4. Morphology of zinc plated coatings' surfaces obtained from alkaline non-cyanide bath with PVA16 in various contents: 0 g/L (a), 0.05 g/L (b), 0.1 g/L (c), 0.25 g/L (d), 0.5 g/L (e), 1 g/L (f), 1.5 g/L (g).
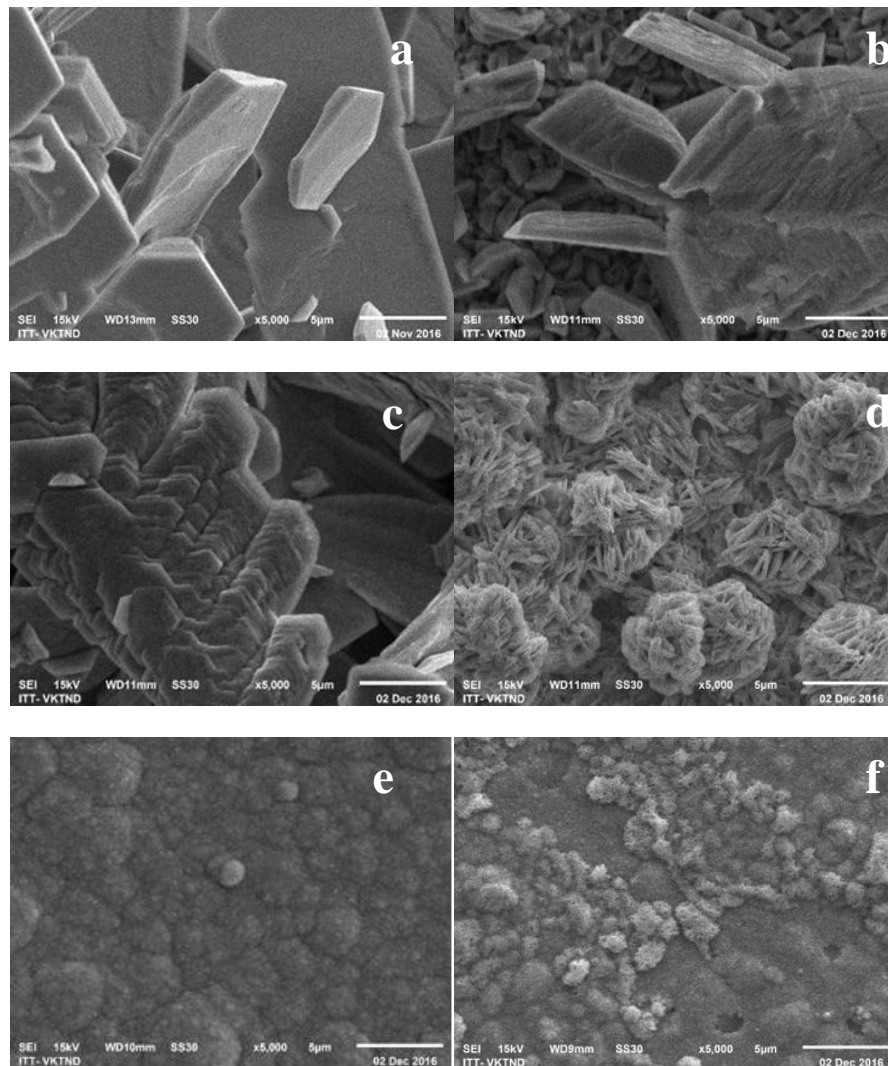
Figure 5. SEM images of zinc deposited coatings from plating solutions containing various BT70 contents: blank (a), 0.05 g/L (b), 0.1 g/L (c), 0.25 g/L (d), 0.5 g/L (e) and 1.0 g/L (f) at the current density of 5A/dm^2.

4. CONCLUSION

It was proved that additives (PVA16 and BT70) affect to zinc deposited coatings formed from alkaline non-cyanide zinc plating bath. The current density of zinc deposition reduced with the presence of additives because these additives replace H_2O present in complex $Zn(OH)_2(H_2O)^-$. The presence of additives also made zinc deposited coatings smoother and brighter. The morphology of zinc deposited coating surfaces showed that the size of zinc particles produced depends on content of both additives. The better coatings will be obtained when the additive content reaches 0.5 g/L or higher.

REFERENCES

1. Ramesh Bapu G. N. K., Devaraj G., Ayyapparaj J. - Studies on non-cyanide alkaline zinc electrolytes, Journal of Solid State Electrochemistry **3** (1998) 48-51.

2. Darken J., Trans. Inst. Met. Finish - Recent Progress in Bright Plating from Zincate Electrolytes, The international Journal of Surface Engineering and Coatings **57** (1) (1979) 145-151.

3. Müller C., Sarret M., Benballa M. - Complexing agents for a Zn–Ni alkaline bath J. Electroanal. Chem. **519** (1-2) (2002) 85-92.

4. Haque U., Khan A., M. U. Ahmad, Additives for bright zinc deposition, J. Chem. Soc. Pak., **29 (**4) (2007) 373-378.

5. Hsieh J. C., Hu C. C., Lee T. C. - Effects of polyamines on the deposition behavior and morphology of zinc electroplated at high- current densities in alkaline cyanide- free baths, Suface and Coatings Techno. **203** (20-21) (2009) 3111-3115.

6. Aparicio J. L. O., Meas Y., Trejo G., Ortega R, Chapman T. W, Chainet E. - Effects of organic additives on zinc electrodeposition from alkaline electrolytes, J. Appl. Electrochem **43** (3) (2013) 289-300.

7. Chandrasekar M. S., Srinivasan S., Pushpavanam M. - Structural and textural study of electrodeposited zinc from non-cyanide alkaline electrolyte,J Mater. Scie.*,* **45** (5) (2010) 1160-1169.

8. Ortiz-Aparicio J. L., Meas Y., Chapman T. W., Trejo G., Ortega R., Chainet E. - Electrodeposition of zinc in the presence of quaternary ammonium compounds from alkaline chloride bath*,* J. Appl. Electrochem. **45** (1) (2015) 67-78.

9. Kh. Saber, C.C. Koch, P. S. Fedkiw - Pulse current electrodeposition of nanocrystalline zinc, Mater. Sci. Eng. **A341** (2003) 174 - 181.

10. Shanmugasigamani and Pushpavanam M. - Role of additives in bright zinc deposition from cyanide free alkaline baths, Journal of Applied Electrochemistry **36** (3) (2006) 315-322.

11. Stern M. and Geary A. L. - Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves, Journal of electrochemical society **104** (1) (1957) 56-63.

12. Nakano H. - Effects of plating factors on morphology and appearance of electrogalvanized steel sheets, Transactions of Nonferrous Metals Society of China **19** (4) (2009) 835-841.