# Addition of Mo in the Zn Based Alloy Coating in the Citrate Solution and Investigation of Its Corrosion Behavior

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## ABSTRACT

In this work, Zn-Co-Mo coatings were electrodeposited on mild steel substrate from a citrate solution at current densities of 5, 7.5 and 10 mA.cm$^{-2}$ and pH values of 4.5, 5, and 5.5. The coated samples were studied by scanning electron microscope and potentiodynamic polarization. The corrosion behavior of the coatings was related to the molybdenum content and formation of local anodes and cathodes. According to the results, a distinct range of current and pH was recognized to provide high quality and corrosion resistant coatings. The percentage of molybdenum as an alloying element plays an important role in the improvement of the corrosion properties of the coating. The formed coating at pH of 5.5 with 13 wt. % Mo showed the lowest corrosion current density with a value of 0.5 µA.cm$^{-2}$.The molybdenum coating also showed a passive-like behavior in the anodic region due to the presence of molybdenum in the coating composition.

## 1-Introduction

The application of alloy plating has expanded widely in many industries which has advantages over other coating methods such as sputtering, physical vapor and chemical vapor deposition methods [1-2]. The coating of Zn-M alloy where M can be Fe, Co or Ni has better properties than pure zinc, which is considered as a coating on steel to prevent corrosion and also an alternative to the toxic coatings containing chromium [3-4]. Rapid dissolution of zinc in zinc-containing coatings occurs over a short period of time due to the large difference in electronegativity of zinc and iron. Alloying of this element with iron group elements can enhance the coating potential, thus increasing the durability of the coatings [6-5]. Molybdenum as an alloying element can produce the desired hardness and corrosion properties. It is expected that this element will also have a positive effect on the corrosion properties of Zn coating [4, 7]. However, this metal cannot be deposited directly on a metal surface and requires the simultaneous precipitation with the aid of iron group metals. Molybdenum can be simultaneously deposited in a Zn coating with the help of alloying elements such as iron, nickel and cobalt [7]. The Zn-Co-Mo ternary coating can be electrodeposited in sulfate or sulfate-citrate electrolytes, which results in the formation of uniform coating in a narrow pH range. It has been recognized that Zn-Co-Mo coating, which has a small percentage of molybdenum and cobalt, includes better

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mechanical and corrosion properties than pure zinc coatings [4, 8, and 9]. A few studies have been carried out on the coating process of Zn-Co-Mo ternary alloy from a sulfate-citrate solution in the pH range of 5.5-5.9 [8-9]. The coatings produced so far contained little amount molybdenum [7]. In the previous work, the effect of permanent current density on the Mo content and corrosion behavior of Zn-Co-Mo was studied [8]. The main aim of this study is the deposition of Zn-Co-Mo ternary alloy from a simple solution of citrate with desirable molybdenum content at different current densities and pHs. In this study, also the effect of pH and current density on the morphology and corrosion properties of the coating was also investigated.

## 2. Experimental

The chemicals used in this study were $ZnSO_4$, $CoSO_4$, $Na_2MoO_4$, $Na_3C_6H_5O_7$, produced by Merck Company and used without further purification. The coating was deposited on the mild steel substrate with the composition of: Fe: 97.7, C: 0.19, Si: 0.415, Mn: 1.39, P <0.005, S <0.005, Cr: 0.026, Mo: 0.018, Co: 0.0559, Cu: 0.0429, Nb: 0.0481) which was polished by SiC sandpaper up to 1200. The deposition was performed using EG/G 273A potentiostat-galvanostat device using galvanostatic method with current densities of 5, 7.5, and 10 $mA.cm^{-2}$ and pH values of 4.5, 5, and 5.5. Surface morphology of electrodeposited coatings was studied using a Zeiss scanning electron microscope. Besides, elemental distribution of oxygen and sulfur was examined with the EDS detector. The corrosion properties of the coatings were investigated in a 0.1 M NaCl solution. The polarization experiment was performed by considering the calomel electrode as the reference electrode and platinum electrode as the counter electrode. Electrodeposited surfaces were regarded as the working electrode and masked with resin. The potentiodynamic polarization test was conducted from -300 mV to 700 mV with a scanning rate of 1 $mV.sec^{-1}$. Tafel extrapolation method was used to obtain polarization parameters including corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$),

## 3. Results and Discussion

Fig. 1 shows the effect of pH and current density on the molybdenum content of the final coating. As can be observed, the molybdenum content of the coating increases with increasing pH at current densities of 5 and 7.5 $mA.cm^{-2}$. On the other hand, at the current density of 10 $mA.cm^{-2}$, maximum molybdenum content was observed at pH value of 5, which could be due to the simultaneous inefficiency of increasing pH and current density by increasing the molybdenum content of the coating. At a pH values less than 4.5, the molybdenum content of the coating obtained very low. At low pH values, zinc tends to precipitate more than other elements. Molybdenum is not found in the coating at acidic pH values due to the heterogeneous precipitation of zinc in acidic environments.

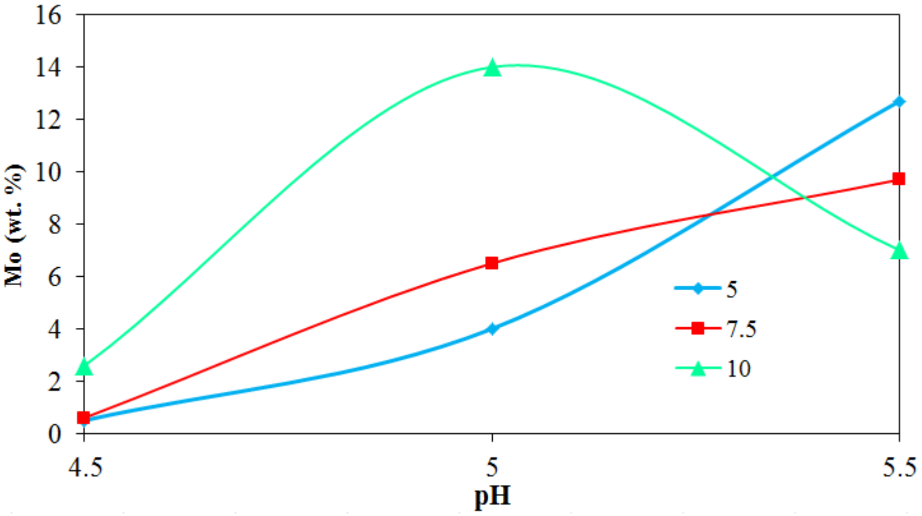

*Fig. 1: The relationship of molybdenum content in the coating and pH value at different current densities.*

The formation of zinc hydroxide is enhanced by electrode alkalizing due to hydrogen reduction at the interface, which led to the prevention of other elements deposition. Also, there exists the possibility of the formation of rare and complicated complexes of zinc, cobalt, and molybdenum at acidic pHs resulting the difficult reduction of these complexes on the surface of the metal [9]. At higher pH values, the deposition of zinc in the coating is limited which causes some disturbances for the simultaneous deposition of the three elements. Therefore, in order to create a coating that contains zinc, cobalt and molybdenum elements, it is necessary to adjust the pH value in a certain range. As can be seen in Fig. 1, the maximum molybdenum content was reported to be in the pH of 5 and 5.5.

Fig. 2 (a-c) shows the morphology of Zn-Mo-Co coatings at current densities of 5, 7.5 and 10 mA.cm$^{-2}$ at pH of 5, respectively, while Fig. 2 (d-f) shows the morphology of these coatings at current densities of 5, 7.5 and 10 mA.cm$^{-2}$ at pH of 5.5, respectively. At pH value of 4.5, the deposited molybdenum content was very low (Fig. 1), which is not shown in these figures. The lighter regions were identified rich in molybdenum. For example, in Fig. 2c, the molybdenum content was reported 42 wt. % in the bright region. As shown in Fig. 2, the molybdenum content increases by increasing the current density at pH = 5. This trend is reversed at pH = 5.5. This can be due to the formation of complexes with different charges at different pH values [9].

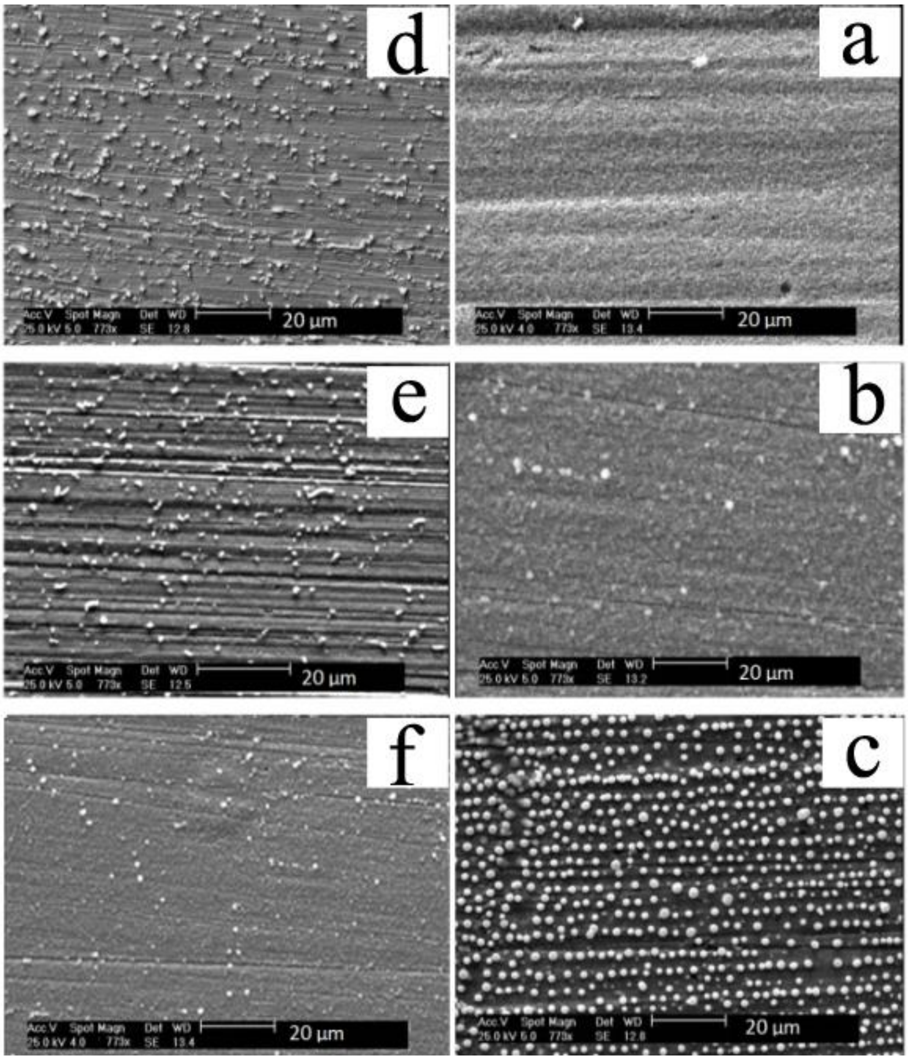

Fig. 2 : Morphology of Zn-Co-Mo coatings at different current densities and pH values.

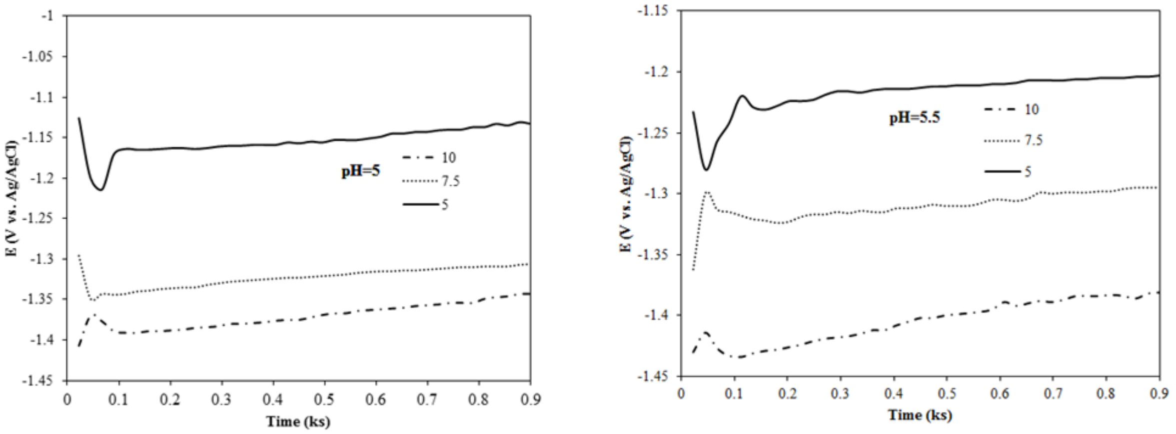

Fig 3: Potential changes during coating process at different current densities and pH values.

Fig. 3 shows the potential-time plots at constant pH value and different current densities of 5, 7.5 and 10 mA.cm$^{-2}$. It can be seen that by increasing the current density, the potential shifts to more negative values. The increase of the current density up to 10 mA.cm$^{-2}$ led to increase the hydrogen production and created cavities in the coating. It seems that the decrease in pH value generally cause alkalization of the cathode surface due to an increase in the amount of hydrogen exhaustion. This will cause the availability of higher oxygen and the deposited zinc oxidizes is enhanced [10-12]. This will prevent simultaneous deposition of other elements, especially molybdenum. This phenomenon, which is called anomalous deposition, has also been reported by other researchers [13-16]. This system is found in baths containing simple and complex ions, and its characteristic is the more deposition of active metal than the noble one, and as a result, the percentage of the active metal in the alloy coating becomes higher [9].

Pourbaix diagrams and probable reactions in this system were studied in order to investigate the behavior of the alloy during electrodeposition process. According to Fig. 4, it can be concluded that it is necessary to apply a voltage higher than -1 V for the simultaneous deposition of these three elements. In order to deposit Zn in metal state it requires a voltage more negative than -1 V. On the other hand, at high pH values, it is possible to form hydroxide and oxide compounds which will result in a defect in the coating. Therefore, the pH value was maintained at 5-5.5 range in order to prevent the formation of adverse compounds. The charge of zinc complexes from changes from $[ZnHcit]^-$ to $[Zn2cit]^0$ by increasing pH from 5 to 6 at a concentration of 0.1 M citrate [9]. According to the above-mentioned figure, it is not possible to express a definitive statement about the possibility of elemental deposition, since the complex compounds of the elements available in the solution can also react together. On the other hand, as can be seen for the case of molybdenum, it has a negative charge in the entire range of the process that is not suitable for the coating, but the reaction with other complexes can change the behavior of this ion and provides its deposition in the coating. Depending on the amount of precipitates containing alloying elements, it seems that the deposition of zinc, cobalt and molybdenum is under the control of various kinetic regimes. Since zinc has the most active potential of reduction and its deposition process is more convenient, it seems that its deposition process is diffusion controlled, while the deposition of cobalt and molybdenum may be controlled by activation [8, 9]. However, it seems that the deposition of these three elements is related to each other. The presence or absence of a complex compound in a solution in addition to pH, complexing agent concentration, and the amount of alloying element in the solution is also related to the potential or current applied in the process.

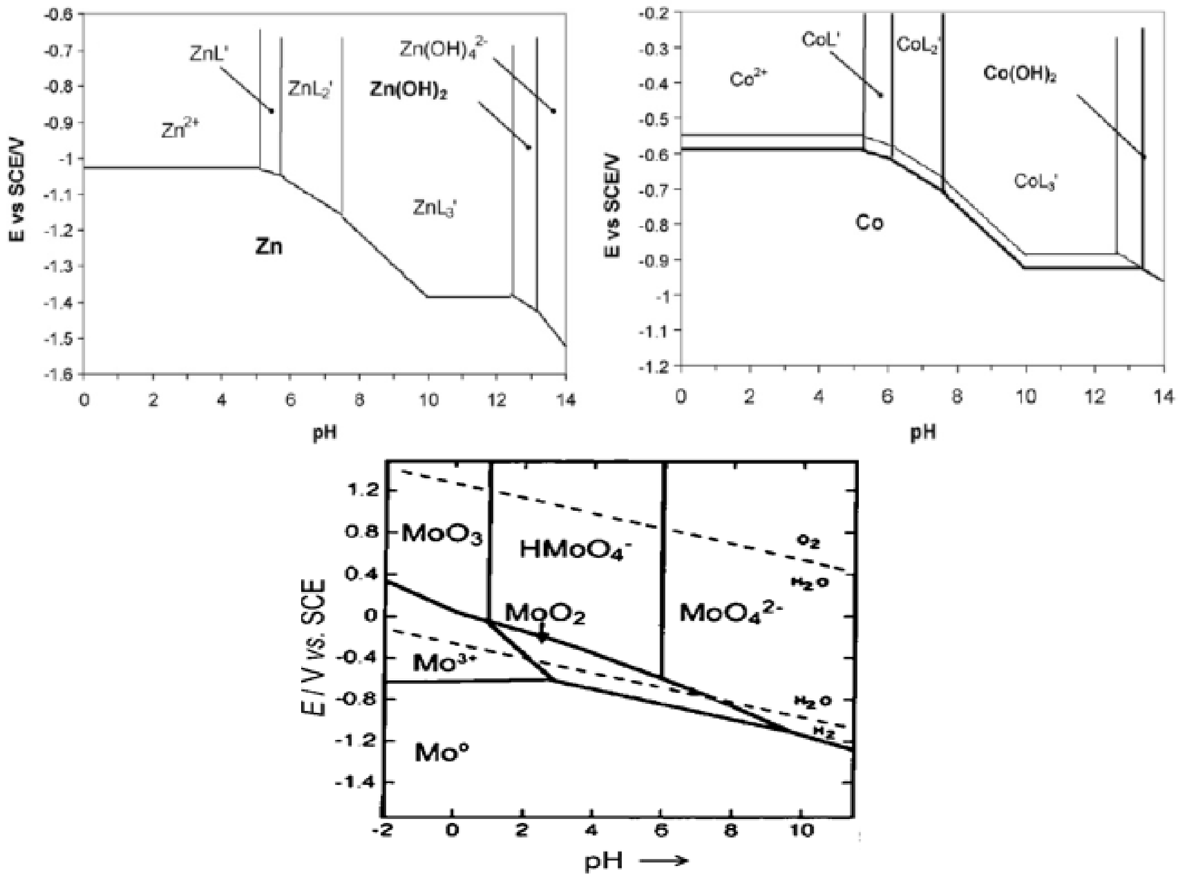

*Fig. 4: Pourbaix diagram of Zn, Co and Mo metals [17].*

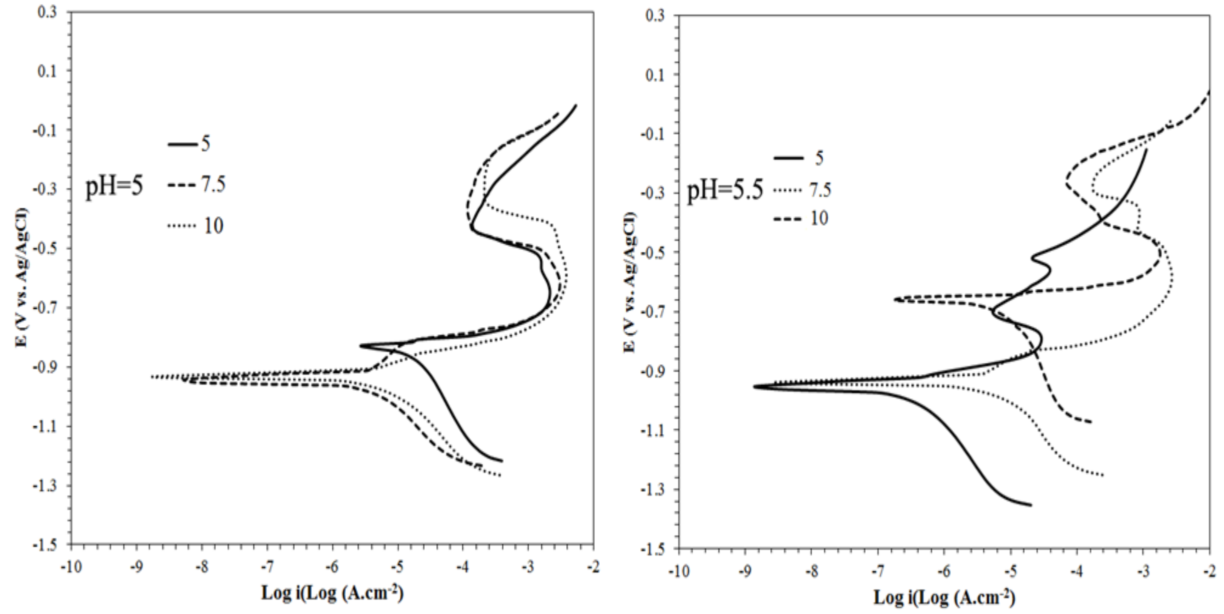

Fig. 5: Polarization curve of the obtained coatings in 0.1 M NaCl solution.

Table 1: Parameters obtained from the polarization curve.

| pH | Current Density (mA.cm$^{-2}$) | Mo percent (wt. %) | $i_{corr}$ (µA.cm$^{-2}$) |
|---|---|---|---|
| 5 | 5 | 4 | 20 |
| 5 | 7.5 | 7 | 2 |
| 5 | 10 | 14 | 4 |
| 5.5 | 5 | 13 | 0.5 |
| 5.5 | 7.5 | 10 | 4 |
| 5.5 | 10 | 7 | 10 |

For example, the potential change can change the stability of single valence zinc and its complex that will change the amount of zinc-molybdenum complexes, which eventually the amount of created alloying elements in the coating will change. As the zinc content of the most coatings is higher than 80%, the main matrix is the zinc alloy. On the other hand, the alloy does not have a complete solid solution in any range and includes different phases. According to the phase diagrams of these elements, the probable intermetallic compounds during coating deposition can be $MoZn_{22}$, $MoZn_7$, $CoZn_4$ and a combination of zinc-containing matrix [18].

Fig. 5 shows the potentiodynamic polarization curve of the coatings produced at pH = 5 and 5.5 at the current densities of 5, 7.5 and 10 mA.cm$^{-2}$. The corrosion current density and corrosion potential of the coatings are presented in Table 1.

As can be seen, the coatings exhibit a passive-like behavior in the anodic region, which can be due to molybdenum present in these coatings [7, 8]. The corrosion current density at pH =5 and current densities of 5 (molybdenum content equal 4 wt. %), 7.5 (molybdenum content equal to 7 wt. %) and 10 mA.cm$^{-2}$ (molybdenum content equal to 14 wt. %) was obtained 20, 2 and 4 µA.cm$^{-2}$, respectively. In the case of the coatings created at pH = 5.5 and current densities of 5 (molybdenum content is 13 wt.%), 7.5 (molybdenum content is 10 wt.%) and 10 mA.cm$^{-2}$ (molybdenum content is 7 wt.%), the corrosion current density values were obtained equal to 0.5, 4 and 10 µA.cm$^{-2}$, respectively. As can be seen, the coatings with more molybdenum content have the least corrosion current density at both pHs, which can be due to the presence of molybdenum with more electrochemical nobility than that of zinc and cobalt. However, the coating with the highest molybdenum content did not have the highest corrosion resistance (pH = 5 and current density of 10 mA.cm$^{-2}$), which could be due to the formation of galvanic couples between the cathodic and anodic regions of the coating.

As can be seen, the coatings with molybdenum content of 7-10 wt. % have the highest corrosion resistance that can be due to the presence of molybdenum and its ability to form passive films. However, the highest reported values of Mo (14% for the coating at pH = 5 and current density of 10 mA.cm$^{-2}$) did not have the highest corrosion properties, which could be due to the formation of severe anodic and cathodic regions which can be observed obviously in Fig. 3a.

## 4. Conclusion

In this study, Zn-Co-Mo coatings were electrodeposited on a mild steel substrate in a citrate bath using electrochemical deposition at pH values of 4.5, 5 and 5.5 where the molybdenum content was higher in the coatings with higher pH values. As the molybdenum content of the coating increases by about 10 wt. %, the corrosion resistance of the coating increases, while with increasing molybdenum up to about 14 wt. % led to decrease the corrosion resistance of the coating. It could be due to the formation of galvanic cells between anodic and cathodic regions.

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