Effect of Silver and Tin on the Corrosion Behaviour of Zinc Alloy in Alkaline Medium

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Abstract: The electrochemical and corrosion behaviour of Zn-20Sn and Zn-0.50Ag alloys in dishwasher detergent solution was investigated by Tafel plot and characterized X-ray diffraction (XRD) and Scanning Electrode Microscope (SEM). The measurements were conducted using different composition of elements addition (Ag: 0.03%, 0.27% and 0.50%, Sn: 1%, 8%, and 15%) under the same experimental conditions. The results showed that the addition of Ag led to decreased corrosion rate compared to Sn addition. The corrosion potential for Zn alloy with Ag addition are shifted towards more noble values compared to Zn alloys with Sn addition. By adding Ag, the current density is decreased and thus reducing the hydrogen evolution rate. The corrosion layer formed on Zinc sample in dishwasher detergent was investigated. The corrosion layer formed on Zn-20Sn-0.5Ag appeared more compact than other alloys. Zinc oxide (ZnO) and Zinc hydroxide (Zn(OH)₂) were formed on Zinc alloy surface. Probable mechanisms of Zinc corrosion products formation are presented.

Key words: Corrosion, zinc alloy, silver, tin, giftware, electrochemical, alkaline solution.

INTRODUCTION

Pewter alloy has long been used in the giftware industry to produce products such as tableware and dishware. However, the current price of the main element of pewter which is tin continues to rise and leads to high production costs. Zn alloys have been proposed to be a substitute for the pewter alloy because they have similar mechanical properties. A Zn alloy is one of the promising alternatives for Pewter alloy because of its low melting temperature. Other great advantages of the Zn alloy are its low cost and excellent mechanical properties, but it is susceptible to oxidation and corrosion ([1][2][3][4]).

The dishwasher detergent is a special detergent used to wash and clean the pewter-giftware products. The same cleaning method is applied for the alternative zinc alloy. The application of the dishwasher detergent on zinc alloy might produce stains and expose the metal to corrosive environments. Corrosion resistance is an important parameter for the choice of Zn alloys. Takemoto et. al. [5] established that the addition of Ag to the Zn alloy inhibits the anodic dissolution of zinc and enhances corrosion resistance. It has been shown that alloying Ag can slow down the corrosion rate and promote growth of the compact passive layer. However, the addition of Ag induces an increase of the melting point. Melting temperature is also an important characteristic for the development of Zn alloys. The addition of Sn to Zn alloy was found to provide a slight reduction of the melting temperature [6]. An Sn addition up to 20% to the Zn alloy reduced the melting point and improved the oxidation resistance.

Zn corrosion in alkaline solution is cathodic controlled, so the rate of the cathodic hydrogen evolution limits the Zn corrosion rate. Hence, the best way to slow down the corrosion process is to reduce the hydrogen evolution rate, which can be achieved by the introduction of a small amount of other metals (Ag and Sn into Zn alloy) [7,8]. However, there is a lack of information on the electrochemical corrosion behavior of ternary Zn-Ag-Sn alloy in dishwasher detergent solution. Lower corrosion resistance is representative of a lower current conductive effect and reduces the lifetime and appearance of the giftware product. This paper...
provides detailed information about the electrochemical behavior of zinc alloys. The objective of this work is to get more knowledge about the electrochemical and corrosion behavior of Zn-Ag-Sn alloy. Furthermore, the aim of this work is also to examine the effect of adding Ag and Sn as alloying elements on the corrosion of Zn.

EXPERIMENT

Materials and Solution Preparation
Zn-20Sn alloys with Ag addition (0.03%, 0.27% and 0.50%) and Zn-0.50Ag alloys with different Sn addition (1%, 8%, and 15%) were prepared by being melted in a crucible at 420 °C and casted. Zn alloy samples were cut from the prepared Zn alloys. The sample size was 10 mm x 10 mm x 2 mm. Samples were encapsulated in resin and only one surface was exposed to the solution. This approach facilitated the examination of corrosion morphology. Prior to studies, each sample surface was mechanically abraded using emery paper in successive grades from 300 to 1200 and mirror polished with the use of 1-0.05µm diamond paste. Samples were finally degreased with ethanol, ultrasonically rinsed with distilled water and dried. The electrolyte used to investigate the corrosion behavior of Zn alloy was a special dishwasher detergent with pH 13.6. A commercial dishwasher detergent was commonly used as a cleaning solution for the raw giftware product. This solution was used in order to facilitate the interpretation of the corrosion behavior observed in alkaline solution.

Electrochemical Test
The electrochemical test was performed on five samples of each alloy in a glass beaker. A three-electrode cell was used for the electrochemical studies. Platinum wire was used as the counter electrode (CE) with saturated calomel electrode (SCE) as reference electrode. The Zn sample was used as a working electrode. The electrochemical measurements were conducted using a PGSTAT302N Autolab potentiostat coupled with GPES software. The test was started immediately after the working electrode connected to the cell and the electrolyte was poured. The electrodes were kept immersed in the electrolyte. Tafel extrapolation technique was used to measure the corrosion rate, corrosion potential and current density. The extrapolation of anodic and cathodic Tafel lines was carried out in a potential range ±1V with respect to corrosion potential (Ecorr) at a scan rate of 0.01 V/s and step potential of 0.00106 V.

Characterization
To investigate the relationship between the alloying elements and the surface morphology, the surface was characterized using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) techniques. XRD measurements were performed using XRD-6000 Shimadzu diffractometer equipped with secondary monochromator and with a Cu radiation source. The XRD patterns were recorded in a continuous scanning mode. The 2θ range was recorded at scan speed of 2° min⁻¹ with 0.02° step. A scanning electron microscopy (JEOL JSM-5600) was used for the surface characterizations to examine the surface morphologies.

RESULT AND DISCUSSION
Polarization Behavior
The polarization studies provide further understanding of the corrosion behavior of the corresponding alloys. Fig. 1 shows the comparison of polarization curves of Zn-20Sn alloys, with Ag contents of 0.03, 0.27 and 0.50 wt.% Corrosion parameters were calculated based on cathodic and anodic potential vs current density characteristics in the Tafel potential region [9,10]. The values of the corrosion current density (Icorr) for reference alloy and Zn-based alloys were determined by extrapolation of the cathodic and anodic Tafel lines to corrosion potential (Ecorr). Both cathodic and anodic branches on the polarization curves of Zn-based alloys were shifted towards lower current densities as the content of Ag increased. This indicates that the rates of oxygen reduction and anodic dissolution decrease with increasing Ag content [11]. Zn-20Sn alloy with 0.50 Ag showed the lowest current densities while Zn-20Sn-0.03Ag showed the highest among all the alloys. A similar trend was observed between reference alloy and Zn-20Sn-0.50Ag alloy in the same concentration of alkaline solution. Thus, it can be suggested that alloy with addition of 0.50 wt.% Ag possesses similar characteristics to reference alloy. On the other hand, from the polarization curves, the corrosion potential (Ecorr) shifted positively with simultaneous addition of Ag content, indicating that the Ag addition increases the nobility and stability of Zn alloy approaching the corrosion potential of the reference alloy (Pewter). Zn-20Sn-0.03Ag shows the lowest corrosion potential value compared to other alloys. Although some studies mentioned the identification of the microgalvanic corrosion between the cathodic Ag:Sn compounds and the anodic Zn matrix [12,13], Cheng et al. reported that the Zn-rich phase disappear in the Sn matrix when 0.5 mass% Ag was added to the Zn-20Sn alloy, which shows that the Ag addition increases the solubility of Zn in Sn matrix [14]. It can also be ascribed to the lower polarizing action of Ag:Sn phase since hydrogen overpotential on particles of Ag:Sn phase might be lower. In general, it is observed that the intermetallic compound promotes the dissolution of the Zn-rich matrix [15]. Therefore, it is assumed that the corrosion resistance increases with
increase in Ag content. Zn-20Sn-0.50Ag can be assumed to have the highest corrosion resistance compared to other alloys. Thus, to improve the corrosion resistance of Zn-based alloy, higher Ag content will be more effective.

Figure 1 Polarization curves of Zn-20Sn with different Ag content and reference alloy tested in alkaline solution.

Fig. 2 shows the polarization curves of Zn-0.50Ag with different Sn content (1%, 8% and 15%) respectively. There are distinctive passivation regions for Zn-0.50Ag-xSn alloy, which means the passive films forming on the surface of alloys are stable and protective. It is observed that the curves of current density shift to the left side with increasing Sn content, indicating that the current density decreases with increased Sn content. The polarization curves illustrate the current density values determined from the polarization curves, showing the formation of protective passive films with Sn addition. Zn-0.50Ag with the addition of 15 wt.% Sn shows the lowest value of current density. It has been reported that when active-passive metal was exposed to a corrosive medium and the current density of the metal was lower than about 100 µA/cm², the metal would spontaneously passivate [16]. On the other hand, the polarization curves in Fig. 2 illustrates that the corrosion potential increases positively with increasing Sn content. The corrosion resistance increases with the addition of Sn because the Ag₃Sn appears in the Zn matrix [17]. Zn-0.50Ag-15Sn shows the highest corrosion potential value (Ecorr), which indicates that Zn-0.50Ag-15Sn is more noble and stable than Zn-0.50Ag-8Sn and Zn-0.50Ag-1Sn alloy. The Zn-0.50Ag alloy with Sn addition exhibits passive responses, indicating that the alloy surface is passivated with protective layer in the alkaline medium. Adding Sn will produce the intermetallic compound of Ag₃Sn. Furthermore, the compound of Ag₃Sn improves the corrosion resistance of the Zn alloy as reported by Yu et. al. [18], hence the appearance of Ag₃Sn and Zn-rich phase is another important factor for the better corrosion resistance of the Zn alloy. This suggests that the Sn content is the major cause of the microgalvanic corrosion in the Zn alloys. It is assumed that the presence of Ag₃Sn phase in the alloy acts as cathodic sites on the alloy surface. It is concluded that increasing Sn content will increase the corrosion resistance of Zn alloy and alloy with addition up to 15% Sn will produce better corrosion resistance.

Figure 2 Polarization curves of Zn-0.50Ag with different Sn content and reference alloy tested in alkaline solution.

Table 1 summarizes the results obtained from the evaluation of the corrosion potential of the alloys. The presence of alloying element of Ag and Sn results in a displacement of the corrosion potential (Ecorr) in positive direction: Ecorr(pewter) > Ecorr(0.50Ag) > Ecorr(0.27Ag) > Ecorr(0.03Ag) > Ecorr(15Sn) > Ecorr(8Sn) > Ecorr(1Sn). This positive shift in Ecorr is attributed to the stability and nobility of Zn alloy.

Table 1 Corrosion potentials obtained from Tafel polarization of the alloys in alkaline solution.

| Alloy                      | Ecorr (V) vs SCE |
|----------------------------|------------------|
| Pewter (reference)         | -0.760           |
| Zn-20Sn-0.03Ag             | -1.009           |
| Zn-20Sn-0.27Ag             | -0.968           |
| Zn-20Sn-0.50Ag             | -0.773           |
| Zn-0.50Ag-1Sn              | -1.453           |
| Zn-0.50Ag-8Sn              | -1.368           |
| Zn-0.50Ag-15Sn             | -1.283           |

Fig. 3 and 4 show the relation of corrosion current density with the corrosion rate of Zn alloys. The addition of Ag tends to lower down the corrosion rate. Zn-20Sn alloy with 0.50Ag possesses the lowest corrosion rate among others. By comparing with the reference alloy, the addition of 0.50 wt% Ag reduces the corrosion rate by 10%. In addition, the Zn-20Sn with the addition of 0.50Ag shows an activity close to Pewter.
Secondly, as the Sn content is higher, passive phenomena are clearly found as the potentials are more positive than their corresponding $E_{\text{corr}}$. Moreover, the corrosion rate is decreasing by raising the Sn content, and Zn-0.50Ag-15Sn shows the lowest corrosion rate. In addition, the lower current density values indicate that the rate of dissolution is lower and better anticorrosive ability of alloy for the attack of $\text{OH}^-$.

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$$  \hspace{1cm} (2)

In the cathodic polarization curves, characteristic behavior of processes controlled purely by diffusion. This process is associated with the reduction of oxygen in the electrolyte (alkaline) solution [22]. The anodic polarization curves exhibit an active/passive transition. In the active region, the dissolution current increases linearly with the applied potential then followed by the appearance of peak, which can be associated with the active dissolution of Zn to Zn(II) species according to reaction (2) and:

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2$$  \hspace{1cm} (3)

While small anodic peak appears may be related to the dehydration of $\text{Zn(OH)}_2$ to ZnO as the following reaction:

$$\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}$$  \hspace{1cm} (4)

Elemental Composition of Corrosion Product

The passive layer formed on the surface of Zn alloys with Ag and Sn addition after anodic polarization treatment in alkaline solution. The passive electrode was withdrawn carefully, washed with distilled water, dried and finally examined by XRD.

$$\text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-}$$  \hspace{1cm} (5)

Or

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-}$$  \hspace{1cm} (6)

When the electrolyte in the immediate vicinity of the alloy becomes supersaturated with [Zn(OH)$_4$]$^{2-}$, Zn(OH)$_2$ precipitates on Zn surface to form a porous or nodular film. Dissolution proceeds according to the reaction (5) and (6) until the ZnO is insoluble. At this stage, the alloy surface is passivated because of the surface formation of a thin compact ZnO layer. It is well known that an oxide or hydrated oxide is formed on zinc when immersed in alkaline solution of NaOH. These insoluble zinc salts (ZnO or Zn(OH)$_2$) cover the surface of the corroded zinc.

Several studies on the corrosion behavior of zinc in alkaline solutions have been carried out, whereby the corrosion of zinc proceeds via two partial reactions: The cathodic reaction corresponds to the reduction of oxygen [19].

$$\text{O}_2 (g) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$$  \hspace{1cm} (1)
Zn(OH)$_2$ as a minor constituents. Presence of Sn and Ag$_3$Sn phases were identified with the increased in Ag content. Moreover, these results also indicate that the peak potential of Zn in alkaline solution is related to the formation of ZnO and Zn(OH)$_2$ system on the electrode surface. Comparison between X-ray data for the presence ZnO and Zn(OH)$_2$ amounts on the surface of the alloys reveals that a large amount of ZnO or Zn(OH)$_2$ is formed at low current density compared with those amounts formed at high current density. This provides that at high current density (Zn-20Sn-0.27Ag and Zn-20Sn-0.03Ag), most ZnO dissolves in alkaline solution and leads to reactivation of the electrode surface. Therefore, XRD results are in good agreement with polarization measurements, which indicate that the Ag addition retards the formation of ZnO and Zn(OH)$_2$ by the presence of Ag$_3$Sn phase.

In conclusion, the main corrosion products formed on the Zn alloy surface treated in alkaline solution are ZnO and Zn(OH)$_2$.

**Surface Morphology**

Fig. 7 shows the micrographs of the anodic passive film formed on the surface of Zn-20Sn alloys with different content of Ag in alkaline solution with magnification of 1000X. Some typical images clearly revealed that the Zn alloy surface is well covered by a layer of corrosion products. Fig. 7a shows SEM micrographs of Zn-20Sn-0.50Ag alloy. It is observed that the surface is almost completely covered by adhered passive oxides. Two layers are observed on the electrode surface. The crystals of the upper layer exhibit different shapes and partially cover the underneath surface by smaller nodular crystals compared with those observed in Fig. 7b and 7c. The second layer seems to lie below the upper layer and their crystals sizes are bigger. The upper layer might be related to AgSn, while the underneath layer is due to ZnO/ Zn(OH)$_2$ formation. This indicates that the presence of Ag as alloying element retards the formation of ZnO and Zn(OH)$_2$ on the alloy surface.

For the Zn-20Sn-0.27Ag electrode surface in Fig. 7b, a layer of the oxide crystals appeared on the alloy surface. It was observed that the nodular product
on the upper layer vanished while the amount of the crystals at the underneath layer decreased and became more distant apart than those in Fig. 7a. The quantity of the oxide crystals in the underneath layer decreases with smaller size. Whereas the crystals of the layer become loosely bound to the alloy surface and an amount from this layer dissolves in the bulk of solution. In addition, the crystals of the underneath layer are distorted. This observation may be attributed to the partially dissolving ability of OH$^-$ ions on the crystal of the oxides film.

It would be recognized in Fig. 7c that the oxide film formed on treated Zn-20Sn-0.03Ag alloy surface is less than that formed at more positive potential (Fig. 7a and 7b). The treated surface is not partially covered by the passive layer so that the electrode surface can still be seen. The nodular oxide crystals exhibit different shapes and become smaller compared with those Zn alloys in Fig. 7a and 7b. Therefore, the addition of 0.50Ag in Zn-20Sn will produce the passivation layer that will stop the corrosion activity.

Fig. 8 shows the micrographs of the anodic passive films formed on the surface of Zn-0.50Ag alloys with the addition of 1, 8 and 15Sn in alkaline solution at passive region with a magnification of 1000X. It may appear from Fig. 8a that the surface of Zn-0.50Ag-15Sn is almost completely covered by thick nodular layer of corrosion product and loosely bound to the metal surface. In addition, the attack begins at the surface defects which are in the polishing scratch. The crystals of this layer exhibit different shapes that might related to the mixture of ZnO and Zn(OH)$_2$. However, the photograph of Zn-0.50Ag-8Sn treated anodically shown in Fig. 8b shows that the crystal size is smaller than that at less positive potential, while for Zn-0.50Ag-1Sn, the crystal size is the smallest and lesser than other alloys when the potential is the lowest. The crystals of the layer become more adhered on the surface and not compact. Thus most parts of the alloy surface show more empty space. This is the reason why the potential curve did not show the passivation curve. Therefore SEM results support the measurements; the addition of Sn enhances passivation activity.

The results shown in Fig. 7 and 8 indicate the differences in the morphology developed on the surface of the Zn alloy with the addition of Ag and Sn. It seems that the coverage and the morphology developed on the Zn alloy surface with the addition of Ag is preferable, supporting the electrochemical studies indicating that the addition of Ag is superior in reducing the corrosion rate of the Zn alloy and induce the passivation.

CONCLUSION
Corrosion behavior of zinc alloy with the addition of silver and tin has been investigated experimentally. The Zn-20Sn-0.50Ag alloy exhibited good anti-corrosive properties in alkaline medium. The addition of Ag shifted the anodic and cathodic branches to lower currents densities and corrosion potential (Ecorr) to more noble values compared to Sn addition. The corrosion rate of zinc alloy with Ag addition is reducing to lower value that resulted in better corrosion resistance. The presence of corrosion products, ZnO and Zn(OH)$_2$ reduced with increasing Ag and Sn. The passive films of the passivated surface are presence on the alloy with lower corrosion rate.

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