Different immersion periods and aqueous solutions effects upon the corrosion resistance of zinc and aluminium specimens

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Abstract

Several metallic materials form spontaneously an oxide film at the surface when is exposed in a corrosive environment. It is well known that the type of corrosive media may develop different results at the material corrosion resistance. The aim of the present paper is to investigate the influence of immersion periods and different solutions upon the corrosion resistance of pure Zn and Al specimens presenting different grain morphologies. The specimens were monitored for several periods in a 3 % NaCl solution at room temperature. Tests were also performed with variations of the 3 % NaCl solution modified by additions of acid and alkaline components. Both the electrochemical impedance spectroscopy (EIS) and polarization methods were applied.

Keywords

1. INTRODUCTION

The corrosion mechanism and corrosion behaviour for some metallic materials may be changed through active to the passive state when immersed in aggressive environment due to spontaneous oxide and/or hydroxide film formation. It has been reported that the oxide film grows when the metal is immersed either in acid, neutral or alkaline aqueous solutions. Obviously, the material corrosion behaviour considering both phenomena of oxide film formation and dissolution will present different performances depending on the characteristics of the solutions. It was suggested that the role of the corrosion behaviour in passive metals is strongly dependent on the oxide film formation and dissolution as well on its composition, morphological formation and thickness. As reported in previous papers, the electrolyte characteristic may affect the corrosion mechanism and corrosion behaviour. Obviously, there exist several other parameters affecting the materials corrosion behaviour.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Both commercially pure aluminum and zinc castings samples were obtained by using, respectively, a permanent steel mold which...
generates an equiaxed structure and a cooled vertical upward solidification system\textsuperscript{[13] and [14]} which generates a columnar structure. The chemical compositions for both pure metals were reported in a previous article\textsuperscript{[15]}. The working electrodes were ground by using a 600 SiC grinding paper and immersed in a Pyrex glass container with 200 ml of stagnant solution at room temperature. The specimens were kept in immersion in a 3 % NaCl solution and monitored for different periods: 20 min, 07 d (168 h) and 15 d (360 h). After each immersion periods the EIS and Tafel polarization techniques were also conducted in 3 % NaCl and in modified 3 % NaCl solutions. In order to conduct the tests, a potentiostat coupled to a frequency analyser system, a glass corrosion cell kit with the working electrodes, a plate platinum counter-electrode and saturated calomel electrode (SCE) were used.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the results of polarization and EIS tests performed respectively with zinc (Zn) and aluminium (Al) samples after different immersion periods.

A comparison is shown in figure 1 among the samples immersed for 20 min (impedance test) and those immersed for 7 d (168 h) and 15 d (320 h) both presenting oxide film formation: (a) and (b) show the comparison between different immersion times for the zinc equiaxed structure (ZES) and (c) and (d) for the zinc columnar structure (ZCE). By analyzing the results of the corrosion tests it is possible to observe that both types of structure immersed for 7 d have presented a considerable increase on the corrosion rate and a displacement of the corrosion potential toward the less noble side. On the other hand, both zinc structures

![Graphs showing polarization and EIS results](image-url)

**Figure 1.** Comparison between polarization curves (a) and (c) and EIS graphs (b) and (d) performed respectively with Zinc equiaxed (ZES) and columnar structure (ZCS) immersed in a 3 % NaCl solution after different immersion periods.

**Figure 1.** Comparación entre las curvas de la polarización (a) y (c) y los gráficos de EIS (b) y (d) realizados, respectivamente, para las estructuras del cinc equiaxial (ZES) y columnar (ZCS) en inmersión en 3 % NaCl después de diferentes tiempos de inmersión.
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immersed for 15 d have shown a considerable decrease on the corrosion rate and displacement of the corrosion potential toward the more noble side than those immersed for 7 d. These results permit to conclude that ZES presents a better corrosion behavior than ZCS \cite{16} due to oxide film formation.

Figure 2 (a-d) exhibits, a comparison between the aluminum coarse equiaxed (CES) and the fine equiaxed structures (FES).

The results presented in figure 2 show that the role of the immersion time upon corrosion behaviour for the aluminium specimens is similar to that observed for zinc specimens. It can also be observed an increase in the corrosion rate for an immersion period of 7 d and a decrease after a period of 15 d and a displacement of the corrosion potential toward the more noble side for both immersion periods due to oxide film formation.

Figure 3 shows a comparison of the corrosion behaviour of Al and Zn samples submitted to 4 different compositions: a basic 3 % NaCl solution; and modifications of this solutions obtained by adding 0.05 % acetic acid, 0.05 % hydrochloric acid and 0.5 % sodium hydroxide, respectively. It can be seen that both metals present a lower corrosion resistance in the alkaline solution (3 % NaCl + 0.5 % NaOH). Aluminium samples had their corrosion resistance decreased with tests performed in both acidified solutions. However, the more significant decrease is observed in presence of CI$^{-}$ ions. The zinc samples have presented a smaller corrosion rate in presence of COOH$^{-}$ ions, as is the case of HCl and acetic acid respectively.

Figure 4 shows micrographs of the oxide layers of zinc and aluminium samples which are corrosion products basically composed by ZnO and Zn(OH)$_2$ \cite{17-19} and Al$_2$O$_3$ and Al(OH)$_3$ \cite{18 and 19}.

Figure 2. Comparison between polarization curves (a) and (c) and EIS graphs (b) and (d) performed respectively with aluminium coarse equiaxed (CES) and fine equiaxed structure (FES) immersed in a 3 % NaCl solution after different immersion periods.

Figura 2. Comparación entre las curvas de la polarización (a) y (c) y los gráficos de EIE (b) y (d) realizados respectivamente para las estructuras del aluminio equiaxial grosera (CES) y equiaxial refinada (FES) en inmersión en 3 % NaCl después de diferentes tiempos de inmersión.
In figure 4, it can be seen that both zinc and aluminium coarser structures present a more homogeneous oxide layers than finer structures, indicating a higher influence upon the corrosion rate and corrosion potential. Zinc specimens have taken about 7 d to start the reaction against the corrosion phenomena. After this time, zinc samples have presented a reversion in behaviour, i.e., a decrease in corrosion rate and the displacement of the corrosion potential toward the noble side. On the other hand, aluminium samples clearly have taken more than 15 d to achieve its electrochemical reaction against the corrosion process. In general, each type of structural morphology has generated corrosion layers of different textures. The coarser structure has formed a more homogeneous corrosion product layer, a lower corrosion rate and its corrosion potential displaced toward the more noble side.

4. CONCLUSIONS

All zinc and aluminium specimens immersed for 168 h in a 3 % NaCl solution have presented a significant decrease in its corrosion resistances when compared with the results of tests performed in a period of 20 min, independently of the structural morphology.

Aluminium and zinc samples with coarser grain sizes exhibited more homogeneous oxide films and apparently free of porosity than the finer grain samples.

The corrosion kinetics was strongly influenced by electrolyte characteristics such as the presence of chlorides ions which can change considerably the corrosion behaviour for both metals.

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Figure 4. SEM micrographs of aluminum coarser (a) and finer equiaxed (b) and zinc coarser equiaxed (c) and finer structure (d) after immersion in a 3 % NaCl solution. Each micrograph presents in upper-right side a magnification of 1000 times.

Figura 4. Microscopio electrónico de estructuras del Al equiaxial refinado (a) y equiaxial grueso (b) y estructuras del Zn grueso (c) y refinada (d) después de inmersión en solución 3% NaCl. Las micrografías presentan una ampliación del 1000X.