Research Article

Corrosion Behaviour of Zn-10Al-1.5Cu Alloy

C. N. Panagopoulos and A. G. Tsopani

Laboratory of Physical Metallurgy, National Technical University of Athens, Zografos, 15780 Athens, Greece

Correspondence should be addressed to C. N. Panagopoulos, chpanag@metal.ntua.gr

Received 24 August 2010; Revised 2 December 2010; Accepted 11 January 2011

Academic Editor: Michael J. Schütze

Copyright © 2011 C. N. Panagopoulos and A. G. Tsopani. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The corrosion behaviour of Zn-10Al-1.5Cu alloy in NaCl solution was examined. The used NaCl solution concentrations were 1M, 0.3M, and 0.003M for a constant temperature values of 7°C or 25°C or 45°C. The corrosion behaviour of this alloy was investigated under potentiodynamic corrosion conditions. The surface of the corroded alloy specimens was studied with the aid of scanning electron microscopy and X-ray diffraction techniques. It was observed that the increase of NaCl concentration in the corrosion solution for a constant value of temperature led to lower corrosion resistance of the alloy. For a constant value of solution concentration, the increase of solution temperature also led to the decrease of corrosion resistance of the same alloy.

1. Introduction

The Zn-10% w.t Al-1.5% w.t Cu alloy is a metallic material that has not been widely studied. This alloy is mainly used for aeronautical and marine applications. Its corrosive resistance is an important factor for those applications. The corrosion is well established as an important factor in the damage and failure of metallic materials.

The surface of an alloy plays an important role in its corrosion performance and in the growth of good quality thin anticorrosion films. It is necessary before any experiments to prepare the specimen surface carefully in order to generate a clean surface, free of particles, poor in surface oxides. Some recent reports concerning the corrosive behaviour of zinc alloys are presented below.

Panagopoulos et al. [1] investigated the abrasive wear behaviour of zinc in environments containing various concentrations of NaCl and water solution. It was found that the corrosive action of the solutions led to a decrease in the wear rate of zinc. Furthermore, NaCl solutions were found to be more effective than H₂O in decreasing the wear rate, when the pH of the contact solution was close to alkaline values.

Guerrero et al. [2] examined the corrosion behaviour of Zn-20% w.t Al-3% w.t Cu alloy in NaCl solutions. These investigators prepared the surface of the zinc alloy with the aid of mechanical polishing and electropolishing techniques.

After corrosion, they found that there was a difference in atomic concentration ratio of Al/Zn in oxides grown on the surface layers of the alloy.

Rosalbino et al. [3] investigated the effect of rare earth metal additions on the corrosion behaviour of Zn-5% w.t Al Galfan alloy in a 0.1 M Na₂SO₄ solution. They examined the corrosion behaviour of this alloy, Zn-5Al-1Ce, Zn-5Al-1Er, and Zn-5Al-1Y by various electrochemical techniques such as corrosion potential measurements, polarization curves, and electrochemical impedance spectroscopy. They observed that rare earth additions improved the corrosion behaviour of the above alloy.

Yildiz and Kaplan [4] studied the corrosion behaviour of zinc-based alloys in 1 N HCl solution. These investigators found that the corrosion behaviour of Zn-based alloys in acidic solutions greatly depended on the concentration of aluminium in the alloy, since it is believed that aluminium forms a compact surface oxide which decreases the corrosion of the alloy.

Osorio et al. [5] investigated the effect of microstructure on the corrosion resistance of Zn-Al alloys. These investigators studied the influence of the dendrite arm spacing on the corrosion resistance of this alloy. They have also investigated the mechanism and the kinetics of solute redistribution and dendrite arm size in order to understand the cathodic and anodic reaction rates.

FIGURE 1: Microstructure of Zn-10% Al-1.5% Cu after the annealing.

The present work examines the corrosion behaviour of Zn-10Al-1.5Cu alloy under different experimental conditions. The corrosive behaviour of the alloy was studied in different NaCl solutions (1 M, 0.3 M, and 0.003 M) and under different temperatures (7°C, 25°C, and 45°C). The pH of the solution was always 5.5.

2. Experimental Procedure

The material used in this study was obtained from a bulk zinc alloy casting with the following chemical composition: 88.5% wt. Zn, 10% wt. Al, and 1.5% wt. Cu. The specimens had surface dimensions 3 cm × 10 cm and thickness 3 mm. A stress relief annealing was performed at 200°C for two hours. This procedure was conducted in THERMAWATT furnace with argon atmosphere. The hardness of Zn-10Al-1.5Cu alloy was found to be 96 HVN. The alloy specimens were also etched in a solution containing 100 gr Cr₂O₃, 7.5 gr. Na₂SO₄, and 500 ml H₂O with 20°C for 15 sec.

The potentiodynamic corrosion experiments were conducted in 1 M, or 0.3 M, 0.003 M NaCl solution at 7°C, or 25°C, 45°C (pH=5.5), with the aid of an EG & G Potentiostat-Galvanostat Instrument. The reference electrode was a Normal Hydrogen electrode (NHE) while the cathode was a Graphite Electrode. The scan rate of the applied potential was 0.2 mV/sec. This scan rate has been used in our laboratory since it does not belong to the extremes potential scan rates.

After each potentiodynamic corrosion experiment, the alloy specimens were observed with the aid of a Jeol JSM 6380-LV Scanning Electron Microscope (SEM), which was connected with an Oxford Inca Energy 250 Premium Resolution LN₂ (EDAX). A Siemens D 5000 X-ray diffractometer with Cu K_α radiation, Cu filter, and a graphite monochromator was also used for the structural study of the specimens. Also Electron Back Scatter Diffraction (EBSD) technique was used to identify.

It should be noted that each experiment was performed three times and the mean values are given in the graphs presented.

3. Results and Discussion

A typical metallographic structure of Zn-10Al-1.5Cu alloy obtained with the aid of the SEM microscope is presented in Figure 1. The Zn matrix (area 1 is solid solution of Al in Zn, phase η), Al (area 2, is solid solution of Zn in Al rich or metastable Al, phases α and α'), and CuZn₄ (area 3, phase ϵ) precipitates were detected by using XRD and EDAX technique. In order to examine the crystallographic texture of the zinc alloy, EBSD technique was used. Figure 2(a) shows a typical area of the zinc alloy which was investigated with EBSD technique. EBSD analysis in area (1) of Figure 2(a) showed the Kikuchi lines projection of Al solid solution in Zn and the orientation of the crystals (Figure 2(b)). The solid solution of Zn in Al or metastable Al is presented in Figure 2(c) for area (2) and lastly, in Figure 2(d) the presence of the CuZn₄ precipitate was also detected in area (3). The pattern of Kikuchi lines of all the phases on the phosphor screen is electronically digitized and processed to recognize the individual Kikuchi lines. It is also important to mention that the Kikuchi lines project the crystal structure, and the tracing criterions are particle and grain boundary misorientation distribution factor. This data is used to identify the phase and to determine the orientation of the crystal from which the pattern was generated.

In Figure 3, the corrosion curves of Zn-10Al-1.5Cu alloy under potentiodynamic conditions in 0.3 M NaCl solution, at different temperature are given. According to the last figure, the open circuit potential of the alloy at 7°C has more positive value compared to the other two plots for temperatures of 45°C and 25°C [6]. In addition, the anodic polarization curves show clearly that the corrosion current is higher during the corrosion of the alloy in 45°C and lower in 7°C. From above, two important observations that is, the lower open circuit potential and higher corrosion current of the alloy in the solution of 45°C, might be attributed to the higher absorption and incorporation of the chloride ions into the surface layers of the alloy in this temperature [7]. The result of those assumptions is the higher interaction of chloride ions with the solid phases leading to the higher corrosion of parent metallic alloy. In the anodic polarisation curves, the occurrence of some pits and repassivation of them can be observed.

From Figure 4, it can be observed that the specimen is corroded mainly intergranularly and several cracks developed across grain boundaries. In the same figure, EDAX analysis was performed and observed a loss of zinc in the surface layer of corroded zinc alloy in comparison to the original zinc alloy. The found content of the various elements was the following: 11% w.t Zn, 24% w.t Al, 3% w.t Cu, and 60% w.t O (Figure 5). The observed high decrease of zinc concentration is due to the dezincification effect [8]. This phenomenon selectively removes several zinc atoms from the alloy surface layers leaving behind micropores. In the case here, the dezincification occurs because of the zinc presence, the high chloride ion content, and the pH value of the corrosion solution.

In Figure 6, it can be seen that the cracking begins from the surface of the corrosion product and continues as

FIGURE 2: EBSD identification of phases. (b) solid solution of Al in Zn, (c) solid solution of Zn in Al rich or metastable Al, and (d) CuZn_4 precipitates.

FIGURE 3: Potentiodynamic curves of Zn-10% Al-1.5% Cu at 0.3 M NaCl solution for $T = 25^\circ\text{C}$, 45°C , or 7°C .

intergranular corrosion across the grain boundaries of the surface layers of zinc alloy. This intergranular corrosion is believed to act intensively due to the presence of precipitates along the grain boundaries of the zinc alloy.

The X-ray diffraction pattern of the corroded Zn-10Al-1.5Cu in different solution temperatures showed that the surface presents different oxides, Zn solid solution, and Al metastable, respectively. In this spectrum, the presence of Al_2O_3 (aluminium oxide) and ZnO (zinc oxide) is evident. At 45°C and 25°C , the presence of ZnOH_2 , ZnO, and Al_2O_3 oxides was observed. The detected peaks of two oxides from the corroded surface of the alloy at 25°C and 45°C show that the intensity of the ZnO peaks is lower than the intensity of Al_2O_3 peaks. However, at 7°C temperature, only Al_2O_3 oxide was observed (Figure 7).

In Figure 8, the corrosion curves of Zn-10Al-1.5Cu alloy under potentiodynamic conditions in different NaCl solutions at 25°C are given. By analysing the last figure, it can be seen that the corrosion of the alloy is higher in 1 M NaCl solution in comparison to other two solution concentrations. This observation could be explained by the assumption that the higher concentration of NaCl solution which destroys more easily the protective passive film of the zinc alloy surface results in higher corrosion [9]. In the same figure, it can also be observed that the open circuit potential of the alloy in 0.003 M NaCl solution is more noble when compared to both 1 M NaCl and 0.3 M NaCl solutions. Furthermore,

FIGURE 4: Surface morphology of Zn alloy after anodic polarization in 0.3 M NaCl solution at $T = 25^\circ\text{C}$.

the corrosion current (I_{corr}) of the alloy specimen increases with increasing NaCl solution concentration. The higher NaCl solution concentration is believed to lead to the higher I_{corr} value. In addition, the lower NaCl solution concentration has lower I_{corr} value. It can also be observed that all the anodic branches of the potentiodynamic curves showed several micropits and repassivation. This phenomenon is more evident during the anodic polarisation of the Zn-alloy in the solutions with the two higher concentrations of chloride ions.

With the aid of X-ray diffraction technique, patterns of the corroded alloy in different solution concentrations at 25°C were obtained and given in Figure 9. From these patterns, the following observations could be given.

- (1) At 1 M NaCl solution concentration, Al_2O_3 , ZnO , ZnOH_2 , and Al and Zn from their solid solution were recorded.
- (2) For both the solution concentration of 0.3 M NaCl and 0.003 M NaCl, the presence of ZnO was not detected. This might be due to the dezincification phenomenon which is explained previously on the low content of ZnO in the surface film.
- (3) At 1 M NaCl solution concentration, the presence of ZnO and Al_2O_3 was identified. The intensity of the detected peaks for the Al_2O_3 were found to be higher than the ZnO .

In Table 1, the corrosion current and the corrosion potential obtained from the different potentiodynamic corrosion curves are given. According to this table, the solution with the higher concentration gives higher values for the corrosion current (I_{corr}) and lower values of the corrosion potential (E_{corr}) for the Zn-alloy.

4. Conclusions

The main conclusions of this study are given below.

- (1) The dezincification phenomenon appears in all the corrosion experiments.
- (2) The solution with the lower concentration is less corrosive of the Zn-alloy in comparison to the

FIGURE 5: EDAX Analysis of previous Figure 4.

FIGURE 6: Cross section of the corroded Zn-10 Al-1.5 Cu alloy.

TABLE 1: Comparison table between the three different concentrations (1 M, 0.3 M, and 0.003 M NaCl) with I_{cor} and E_{corr} .

1 M	$I_{\text{corr}} (\mu\text{A})$	$E_{\text{corr}} (\text{mV})$
$T = 7^\circ\text{C}$	26.2	-988.4
$T = 25^\circ\text{C}$	121.7	-1046
$T = 45^\circ\text{C}$	529	-996.3
0.3 M	$I_{\text{corr}} (\mu\text{A})$	$E_{\text{corr}} (\text{mV})$
$T = 7^\circ\text{C}$	10.2	-885
$T = 25^\circ\text{C}$	10.7	-979
$T = 45^\circ\text{C}$	117.4	-900.4
0.003 M	$I_{\text{corr}} (\mu\text{A})$	$E_{\text{corr}} (\text{mV})$
$T = 7^\circ\text{C}$	6.8	-796.3
$T = 25^\circ\text{C}$	9.9	-864.4
$T = 45^\circ\text{C}$	7.3	-816.9

other two solutions with different concentrations under potentiodynamic conditions for a constant temperature.

- (3) The higher corrosion of the Zn-10Al-1.5Cu alloy was found to occur in the higher temperature for a constant value of solution concentration.
- (4) The X-ray diffraction pattern of the corroded Zn alloy gave the phases of ZnO and Al_2O_3 and solid solution of Zn and Al; these phases were only detected in the high temperature and in the high solution concentration. The two lower temperatures and solutions concentrations gave only the phases of the Al_2O_3 and the solid solution of Zn and Al.

FIGURE 7: X-ray diffraction pattern of the Zn-10Al-1.5Cu alloy in 0.3 M NaCl, at (a) 45°C, (b) 25°C, and (c) 7°C solution temperature.

FIGURE 8: Potentiodynamic curves of Zn-10% Al-1.5% Cu alloy at 25°C under three different solutions concentration of 1 M, 0.3 M, and 0.003 M NaCl.

FIGURE 9: X-Ray diffraction pattern of the Zn-10Al-1.5Cu alloy at $T = 25^\circ\text{C}$ and (a) 1 M NaCl, (b) 0.3 M NaCl, (c) 0.003 M NaCl.

Acknowledgment

The authors would like to thank Helena Kyriakopoulou for experimental assistance

References

- [1] C. N. Panagopoulos, V. D. Papachristos, and A. El Amoush, "Abrasive wear of zinc in various environments," *Surface and Coatings Technology*, vol. 89, no. 1-2, pp. 151–157, 1997.
- [2] R. Guerrero, M. H. Farias, and L. Cota-Araiza, "Surface analysis of the environmental corrosion of zinalco (Zn-22Al-2Cu) alloy," *Applied Surface Science*, vol. 195, no. 1–4, pp. 137–145, 2002.
- [3] F. Rosalbino, E. Angelini, D. Macciò, A. Saccone, and S. Delfino, "Influence of rare earths addition on the corrosion behaviour of Zn-5%Al (Galfan) alloy in neutral aerated sodium sulphate solution," *Electrochimica Acta*, vol. 52, no. 24, pp. 7107–7114, 2007.
- [4] A. K. Yildiz and M. Kaplan, "Corrosion behaviour, microstructure and phase transitions of Zn-based alloys," *Bulletin of Materials Science*, vol. 27, no. 4, pp. 341–345, 2004.
- [5] W. R. Osório, C. M. Freire, and A. Garcia, "The effect of the dendritic microstructure on the corrosion resistance of Zn-Al alloys," *Journal of Alloys and Compounds*, vol. 397, no. 1-2, pp. 179–191, 2005.
- [6] V. Ashworth and D. Fairhurst, "The effect of temperature on the behaviour of a zinc-mild steel couple in a solution containing chloride ions," *Corrosion Science*, vol. 15, p. 669, 1975.
- [7] M. M. Ahmed, "Corrosion behaviour of Zn-Al-Cu alloy in HCl solution and its inhibition," *Portugaliae Electrochimica Acta*, vol. 24, pp. 1–22, 2006.
- [8] M. N. Kuperman and H. E. Troiani, "Pore formation during dezincification of Zn-based alloys," *Applied Surface Science*, vol. 148, no. 1, pp. 56–63, 1999.
- [9] E. E. Abd El Aal, "On the pitting corrosion currents of zinc by chloride anions," *Corrosion Science*, vol. 46, no. 1, pp. 37–49, 2004.