JOURNAL OF MATERIALS SCIENCE **40** (2005) 805–807 LETTERS

Effect of microstructure on the corrosion behavior of a zinc–aluminium alloy

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Zinc and zinc die casting alloys exhibit relatively good corrosion resistance in atmospheric exposure, immersion services, in soils, and in a wide range of chemical environments. However, there is a lack of specific corrosion data of ZA alloys, and their corrosion resistance has been based on the well-established performance of zinc and zinc die casting alloys [1]. The corrosion rate of the ZA alloys in water increases considerably below pH 6.0 and above pH 11.5 [1, 2]. The corrosion rate of ZA27 has been found to be 1/3rd that of the other alloys. This is probably because ZA27 has a larger amount of the Al-rich phase, while the attack occurs mainly on the Zn-rich phase [3]. In practice it is often found that the general corrosion rate of zinc and zinc alloys in service is much less than in simulated conditions. This is because many naturally occurring substances act as inhibitors [3]. The choice of alloy is unlikely to be affected by the difference in levels of general corrosion [3].

Zinc aluminium alloys are known to possess excellent bearing properties particularly at high load and low speeds. Improvement in wear behavior of Zn–Al alloys has also been reported with additions of Ni at higher sliding speeds [4]. It has been shown in an earlier paper [4] that the presence of nickel improves the adhesive wear resistance as well as the friction characteristics of the zinc–aluminium alloy. For practical applications, the corrosion resistance of casting alloys is as important as other properties. The present paper investigates the effect of Ni, Ti and Sr addition on the corrosion behavior of ZA27 alloy in the as-cast condition.

Alloys were prepared by conventional melting and casting route. The addition of Ni was done to the extent of 0.3, 0.9 and 2.0 wt%. 0.1 wt% each of Ti and Sr were added in the form of master alloys. Corrosion behavior of the alloys was studied by both immersion corrosion as well as potentiodynamic polarization tests. The tests were carried out at room temperature by suspending the samples in a closed atmosphere for a period of twenty days in a medium of 3.5% NaCl solution. After the completion of the tests, the adherent corrosion product and salt deposit were removed by scrubbing with a rubber stopper under running tap water. The corrosion rate was calculated by the weight loss method, using the formula:

$$\text{Corrosion rate (in mpy)} = (KW)/(ATD) \quad [5],$$

where mpy is abbreviated for mils per year, (one mil is one thousandth of an inch), K = a constant, T = time of exposure in hours, A = area in cm^2, W = mass loss in gm, and D = density in gm/cm^3

The surfaces of all test specimens for the potentiodynamic polarization experiments were polished following standard metallographic techniques. A hole of 1 mm diameter was drilled near one edge of each specimen and a piece of copper wire was passed through this hole to develop electrical contact. Each specimen was then lacquered, so as to leave only the polished surface exposed to the electrolyte during the electrochemical tests. The point of contact between the specimen surface and the copper wire was also lacquered so as to avoid galvanic corrosion between the dissimilar materials. The polarization studies were carried out using a platinum electrode as the counter electrode and saturated calomel electrode as a reference electrode. A salt bridge was used to connect the reaction chamber having the working electrode with the other containing the calomel electrode. Prior to each run the working electrode was immersed in the respective electrolyte (300 ml) and allowed to stabilize for about 20 min. Subsequently, each specimen was potentiodynamically polarized in the potential range between −2000 to −700 mV (from cathodic to anodic) over the respective open circuit potential at a scan rate of 1 mV/s using a computer controlled Meinsberg Potentiostat Galvanostat PS 6 for producing polarization curves instantaneously. All potentials were measured against the saturated calomel electrode. The polarization curves obtained for all the alloys were similar and that for the unmodified alloy as shown in Fig. 1.

The instantaneous corrosion rate was also determined from the potentiodynamic polarization tests using the following equation:

$$\text{Corrosion rate (in mpy)} = (129aI_{\text{corr}})/nD,$$

where a = atomic weight of the metal, I_{corr} = corrosion current density (A/cm^2), n = number of electrons lost (valence charge), and D = density (g/cm^3).

It is observed that the corrosion rates measured using the two different methods are considerably different (Fig. 2). Corrosion being a complex mechanism, there are many important factors in determining the reproducibility of the experimental results. These factors may be divided into two categories, viz. (1) those involving the metal surface and (2) those involving the environment. For the immersion corrosion tests, the samples had been subjected to rough polishing,

TABLE I Corrosion parameters as determined from potentiodynamic polarization tests

Alloy designation	O.C.P (mV)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Corrosion rate (mpy)
ZA1	−1010	−1009	0.006289	4.44
ZNi1	−1031	−1030	0.015814	11.17
ZNi3	−1014	−1014	0.040208	28.39
ZNi4	−1027	−1025	0.043681	30.85

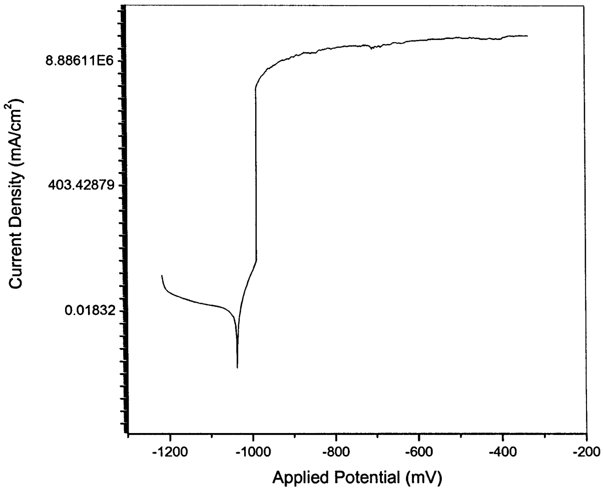

Figure 1 Potentiodynamic polarization curve of ZA1 (unmodified ZA27).

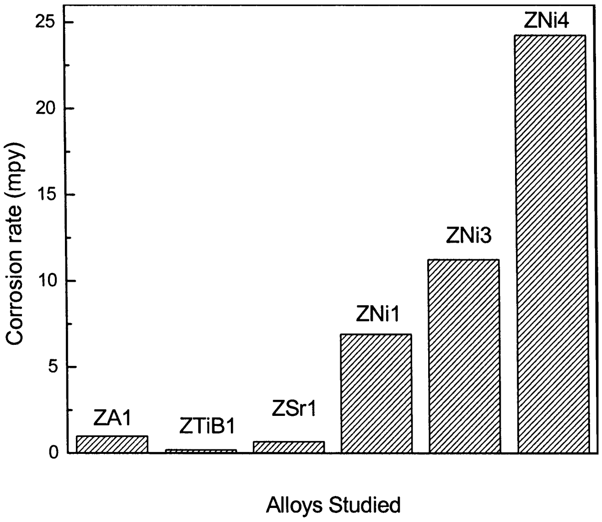

Figure 2 Relative immersion corrosion rates of the alloys studied. (ZA1: unmodified, ZTiB1: 0.1% Ti, ZSr1: 0.1% Sr, ZNi1: 0.3% Ni, ZNi3: 0.9% Ni and ZNi4: 2.0% Ni containing ZA27 based alloys).

whereas, for the polarization tests the samples were subjected to diamond polishing to obtain mirror finish prior to the tests. With regard to the environment, conditions had been kept the same for both immersion corrosion as well as polarization tests.

Secondly, immersion corrosion, even though a simple method, may give rise to error due to incomplete removal of corrosion product and/or loss of uncorroded metal along with the corrosion products. A large number of specimens are generally required for better reproducibility [6]. Taking into account of all these factors, the results obtained from the polarization tests can be considered to be more accurate as compared to those obtained from the immersion tests.

The ZA27 based alloys fall in the hypereutectoid range of the Zn–Al phase diagram [7]. The unmodified alloy, ZA1, comprises of primary α dendrites surrounded by the eutectoid (αAl) + (Zn). In addition to the above, the Ni-containing alloys consist of Ni-based intermetallic particles whose morphology changes from blocky to rod-shape with increasing Ni content. The optical microstructures of all the as-cast alloys are given elsewhere [8]. The addition of Ti results in rosette-shaped dendrites whereas that of Sr results in dendrites with increased curvature. In the unmodified alloy, the zinc-rich matrix is anodic (more positive potential) with respect to the aluminium-rich dendrites. Thus, the anodic and cathodic sites are not distinctly separated in this alloy. In the fully immersed situation, zinc undergoes dissolution as Zn^{+2} ions, which subsequently reacts with water in the dilute aqueous aerated Cl^- solutions to form $Zn(OH)_2$ according to the reaction $Zn^{+2} + 2H_2O \rightarrow Zn(OH)_2 + 2H^+$ [3]. Subsequently, the hydroxide provides protection to the metal surface. The interdendritic regions are the Zn-rich areas, and hence, undergo greater dissolution than the dendritic regions (Al-rich). The Ni-based intermetallic particles are cathodic (noble) with respect to the Zn-rich matrix. This leads to the formation of galvanic cells at the interfacial regions between the particles and the matrix. Intermetallic particles have a more positive potential relative to the matrix. However, only the area adjacent to the anode may be effective as a cathode [3]. Hence, in the present case, only the interfacial area between the intermetallic particle and the Zn-rich matrix will be effective as the cathode. The formation of galvanic cells leads to a flow of electrical current between the anodic and cathodic sites. This results in a rapid dissolution of zinc (anodic site) as Zn^{+2} in the regions adjacent to the intermetallic particles (cathodic sites). The corrosion product is formed by the same reaction as that in ZA1. Subsequently, the hydroxide forms a protective layer on the surface of the metals and is expected to prevent or reduce further dissolution in the later stages.

In the alloys ZTiB1 and ZSr1, the mechanism of corrosion and the corrosion product remain the same as in the other alloys.

For heavy castings, corrosion rate upto 50 mpy is considered to be good in terms of corrosion resistance of the material [9]. Hence, the results of the present investigation shows that cast components of modified ZA27 alloy containing Ni can be successfully used in marine environment. Elsewhere [8, 10], it has been shown that the addition of Ni results in improved wear behavior of ZA27 alloy. Hence, the modified alloy can be used as machine parts in submarines.

Financial support received from the Defence Research and Development Organization, Department of Defence Research and Development, Government of India to carry out this research is gratefully acknowledged.

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Received 28 July 2003
and accepted 20 May 2004