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The Analysis of the Corrosion Susceptibility of Al-Zn Alloys in Tetraoxosulphate (VI) Acid Environments

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Abstract: A study of the susceptibility of Al-Zn alloys in molar concentrations of H_2SO_4 has been undertaken. Al-Zn alloys containing 1.0, 2.0, 2.5, 3.5 and 4.0% Zn were separately cast and machined to cylindrical test coupons of dimension range of about $17 \times 16.8 \times 15$ mm and average surface area of about 12.71 cm^2 . They were weighed and immersed into beakers containing 0.5 and 1.0 M tetraoxosulphate (vi) acid; allowed to stand for six days with intermittent withdrawal of a set of test samples daily for weight loss measurement and corrosion penetration rate analysis. The result showed normal corrosion rate profile for passivating metals with increased severity of attack as both the alloy and the media concentration increased. In comparative terms, the 2.5% Zn alloy was the most severely attacked, a situation that could be attributed to increased grain boundary concentrations consequent upon the maximum solid solubility phenomenon (solvus line) in the duplex Al-Zn alloy system.

Key words: Corrosion rate, passivation, solvus line, grain boundary, Al-Zn alloy

INTRODUCTION

Corrosion, which is defined as an unintentional attack and the destruction of a metal by chemicals, or electrochemical processes in its environment (Idenyi *et al.*, 2006 unpublished data), of which the driving force is the free energy of the system which is generally lowered by reaction of the metal to form a metal oxide of stable state (Ekuma and Idenyi, 2006). The corrosion process takes place at the metal-medium interface and therefore is a heterogeneous reaction in which the structure and condition of the metal surface have a significant role in determining the corrosion behaviour of metals and its alloys in any environment (Ijomah, 1991).

There are basically eight forms of corrosion: Uniform corrosion; Stress corrosion; Galvanic corrosion; Crevice corrosion; Intergranular corrosion; Pit corrosion; Selective leaching and Erosion corrosion (based on visual characteristics) (Fontana and Greene, 1978), but recent studies have expanded the corrosion categories redefining them by mechanism rather than by visual appearance (Ekuma, 2006).

Aluminium owes its excellent corrosion resistance and its usage as one of the primary metal of commerce to the barrier oxide film-alumina; coupled with its strong affinity for oxygen, which in environments harbouring aluminium and its alloys, assists in the formation of this passive film bonded strongly to its surface, such that it is stable in aqueous media between pH 4.0 and 8.5. If abraded, the film reforms immediately in most environments. This notwithstanding, aluminium alloys especially those containing zinc, magnesium, manganese etc., are known to manifest reduced corrosion resistances in alkaline and acidic environments (Ekuma *et al.*, 2006).

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The Corrosion Penetration Rate (CPR), which is, expressed in common units like mils/year or mm/year is an important corrosion-monitoring index that gives dependable information to corrosion experts on the degree of corrosion progress in a given material in service. The mathematical computation of CPR is based on the formula

$$CPR = \frac{kW}{\rho At} \quad (1)$$

where W is weight loss after exposure time t, ρ and A are density and exposed specimen area respectively and K is a constant whose magnitude depends on the system of units used. For instance, when $K = 87.6$, CPR is in mm/year and w, t, ρ and A are expressed in mg, h, $g\ cm^{-3}$ and cm^2 , respectively (Callister, 1997). For most engineering applications, a corrosion penetration rate of less than about 0.50 mm/year is acceptable (Ekuma and Idenyi, 2006).

The present study is aimed at evaluating the service performance of Al-Zn alloys in various molar concentrations of simulated tetraoxosulphate (vi) acidic environments. The outcome of this work is envisaged to be of paramount importance in material selection for designing of engineering systems and proper understanding of the corrosion behaviour of Al-Zn alloys when subjected to environments that are positively acidic.

MATERIALS AND METHODS

Materials/Equipment

The materials used for this work were virgin aluminium (99% pure Al) purchased from aluminum stockist and pure granulated zinc metal procured also from metal stockist. The other materials used were: acetone, tetraoxosulphate (vi) acid, distilled water, laboratory beakers, measuring cylinders, etc.

The equipments used were: lathe machine, drilling machine and a surface crucible furnace. The basic equipment used was analytic digital weighing machine X21-0014 KERN 770-15, 15402301 which measures to an accuracy of 0.0001 g and it is used to weigh the sample coupons before and after immersion to know the exact weight loss.

Sample Preparation

After the calculation of each of the Al-Zn alloy compositions have been carefully worked out and charged into a surface crucible furnace, the molten alloys were cast into rods after melt down, machined to sizeable dimensions and subsequently, cut into cylindrical sample coupons of dimension range of $17 \times 16.8 \times 15$ mm and initial surface area of about $12.71\ cm^2$. Each sample coupon was drilled with a 5 mm drill bit to provide hole for the suspension of the string. The surface of each of the coupon specimen was thoroughly polished with emery clothes according to ASTM standard G-I-72 as to expose its structure for immersion.

The samples for 1% Zn-99% Al alloy were coded A; 2% Zn-98% Al alloy were coded B; 2.5% Zn-97.5% Al alloy were coded C; 3.5% Zn-96.5% Al alloy were coded D and 4% Zn-96% Al alloy were coded E. The initial weight of each of the sample coupon was determined using a highly sensitive digital analytic chemical weighing machine, which measures to an accuracy of 0.0001 g.

Simulation of Environment

The environments for this work were acidic environments with two different concentrations made from tetraoxosulphate (vi) acid using normal procedure. The concentrations were 0.5 and 1.0 M of the acidic solutions.

Experimentation

In each beaker containing the various concentrations of H_2SO_4 were suspended 6 samples each of the polished and preweighed specimens for a constant time of six days. A set of coupon was withdrawn 24 h, washed with distilled water, cleaned with acetone and dried in an open air for corrosion rate characterization. The weight loss of each of the test coupon was measured using the digital analytic weighing balance; and the corrosion rate in millimeter per year (mm/year) was calculated using the weight loss measurements.

RESULTS AND DISCUSSION

The corrosion penetration rate was calculated using the measured weight loss values and Eq. 1. Figure 1-2 represent the corrosion rate profile obtained when the graph of CPR was plotted against exposure time for the alloys in the different media concentrations.

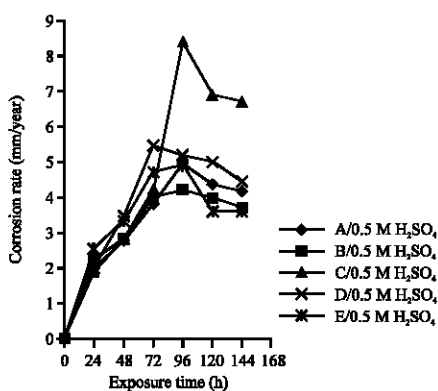


Fig. 1: Corrosion rate (mm/year) against exposure time (ho) for samples A, B, C, D and E in 0.5 M media concentration of H_2SO_4

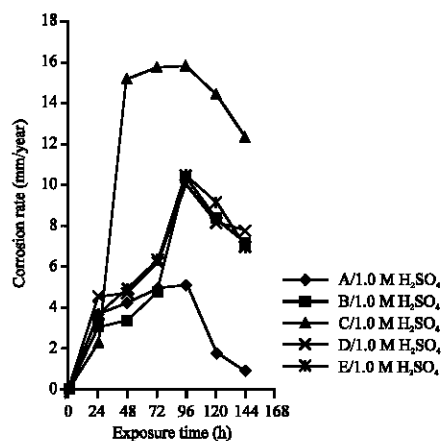


Fig. 2: Corrosion rate (mm/year) against exposure time (h) for samples A, B, C, D and E in 1.0 M media concentration of H_2SO_4

The corrosion rate profile will be discussed in the light of two out of the many important parameters determining the rate of material degradation in simulated acidic environments.

It can be seen from the figures that the corrosion penetration rate varied albeit parabolically with exposure time. The CPR initially increased, but then decreased as duration of exposure time increased. This observation is in agreement with previous observations for passivating metals which aluminium is known to belong to, suggesting that the initial increase in corrosion rate corresponds to the active region and the decrease representing the passive region. Pasivation is generally characterized by decreasing the concentration of the corrosion inducing species (Idenyi *et al.*, 2006; Ekuma, 2006). Comparatively, the 1.0 M H_2SO_4 has the greatest attack on the alloy system due to increased solubility, a consequence of high presence of oxygen.

Impurity atoms (alloying elements) are known to provide favourable sites for corrosion attacks, generally along the grain boundaries. The more soluble the atom, the greater the concentration of grain boundaries. A cursory look at Fig. 1 and 2 shows that this theory has been satisfied by this present study. The 2.5% Zn alloy was the most severely attacked in both media and hence the more vulnerable the alloy is to corrosion attacks (Ekuma, 2006). It is believed that at this weight percentage of Zn, maximum solid solubility has occurred, resulting in maximum grain boundary concentrations. Beyond this percentage of zinc composition range, new phases may have been formed due to supersaturation which obviously presented the increased resistance to the incidence of corrosion observed. It can be explained from this result that such changes are most probably due to the presence of significant amount of aluminium in the alloy matrix since a stable aluminium oxide layer forms on the surface of sample in H_2SO_4 environments, which delays the dissolution of the aluminium-rich alloy systems.

CONCLUSIONS

The analyses have shown that though pure aluminium has high corrosion resistant in diverse environments (pH 4.0 to 8.5) due to the phenomenon of passivation, the presence of alloying elements (in this case zinc), which acts as impurity and varying molar concentration can and indeed do reduce the degree to which it resists corrosion in acidic environments. In our case, it is supposed that the presence of zinc in aluminium renders it susceptible to corrosion attack due to the formation of a zinc-rich phase which is a eutectic compound. This causes cracks and hence development of micro-galvanic cells within the matrix on the alloy surface. Also, pits and invisible inter-or trans-granular cracking occasioned by bimetallic corrosion develops which is a well known problem in aqueous media habouring binary alloy systems. Here, it is concluded that passivation phenomenon is a consequence of both alloy impurity atom concentration and media concentration. In this particular study, the observed severity of attack on the 2.5% Zn alloy is attributed to possible attainment of the solvus line of Al-Zn alloy within this range.

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