Corrosion Propensity of Cold Deformed 5052 Aluminium Alloy in Seawater

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Abstract

Conventional 5052 aluminium alloys are known to exhibit characteristics response to deformation having a rebound effect on their corrosion propensity. This study investigates this phenomenon with a view to establishing the appropriate processing method that confers enhanced corrosion resistance to stem the incidence of facility failure in the food processing industry. Samples of the alloy were produced by casting after proper charge calculation. The cast samples were cold rolled in a two-high mill at ambient temperature to 20%, 40%, 60% and 80% size reduction. Corrosion test coupons were then prepared from the deformed samples on which electrochemical corrosion polarisation in seawater environment for 36 hours at an interval of 6 hours was carried out. Results of the corrosion campaigns show that corrosion rate increases as degree of deformation increases and this is attributed to high energy density in the deformed sample matrix which approximates initiation sites for corrosion.

Keywords: 5052 aluminium alloy; cold rolling; corrosion rate; seawater.
1. INTRODUCTION

Aluminium alloys are mostly used in sheet form in various applications. Both the hot and cold rolling that are used in sheet production often result in a high level of enhanced surface shear deformation. However, the hot rolling processing or the subsequent heat treatment in the case of cold rolling causes precipitation of fine intermetallic particles in the deformed layer. This often results in a higher dispersoid density and lower solute levels compared with the bulk of the material where the precipitation is sluggish in the absence of stress [1]. Thus, the deformed surface layer has different electrochemical properties and microstructural characteristics compared with the parent bulk microstructure that affects corrosion susceptibility [2]. Deformation has two effects on the electrochemical behaviour of aluminium alloys. One effect is to cause the precipitation of particles that act as local cathodes and pit initiation sites. The other effect is that the formation of precipitates depletes the adjacent matrix in solute, making it more susceptible to dissolution [3]. Filiform corrosion behaviour of aluminium alloys is generally controlled by the presence of this micro-deformed layer at the surface, which results in the precipitation of very fine intermetallic particles during subsequent heat treatment [4]. Preventing the formation of a deformed layer by a modified fabrication process or removal of the layer by etching or alternative surface treatment eliminates or significantly reduces the corrosion susceptibility [5].

Given that corrosion is the gradual destruction of a solid body through an unintentional chemical or electrochemical action with the environment, alteration in both the composition and physical integrity of the material are inevitable. In chemical corrosion, the material is dissolved by a corrosive liquid while in electrochemical corrosion; metal atoms are removed from the solid material as a result of an electric circuit that is produced. Corrosive environments include the atmosphere, aqueous solutions, soils, acids, bases, inorganic solvents, molten salts, liquid metals etc. On a tonnage basis, atmospheric corrosion accounts for the greatest losses [6].

The mechanism by which materials degrade due to corrosion must be well understood if an effective preventive procedure will be established. Generally, corrosion of metals is an electrochemical reaction which involves oxidation of the anode into a positive ion which is released from the solid metal according to equation (1).

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \text{(1)}$$

The oxidation also involves a reduction reaction. In the system (aluminium and water), the metal is the anode and the water is the electrolyte. Cathodic reactions common in the system are reduction of hydrogen ions to hydrogen according to equation (2), and reduction of oxygen to either hydroxide ion in alkaline or neutral medium according to equation (3) or water in acidic medium according to equation (4).

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \text{(2)}$$
$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad \text{(3)}$$
$$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad \text{(4)}$$

High purity aluminium (99.99%) has an excellent resistance to corrosion in neutral environments as a result of alumina (\(\text{Al}_2\text{O}_3\)) forming a passive film on the surface according to equation (5).

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6e^- \quad \text{(5)}$$

The alumina passive film is bonded strongly to its surface and, if damaged, re-forms immediately in most environments. Usually the film that develops in normal dry atmosphere grows to thicknesses much greater than 1mm making it highly resistant to dissolution in neutral environments, but soluble in both acidic and aqueous environments [7,8].

Commercial 5052 aluminium alloy generally contains 2.2 – 2.8 wt. % magnesium. In this alloy, and sometimes zinc and manganese are added as minor alloying elements. This range of elemental composition generally influences the type of microstructure which affects the physical and corrosion behaviour of the alloy subject to other processing procedures. The microstructure of hot and cold rolled aluminium alloys has been investigated during the past decade by several researchers. Hot rolled Al-Mg alloy was investigated and it was found that the heavily deformed micrograined layer at the surface of hot rolled aluminium alloy sheet can be attributed to a higher shear deformation at the surface. This produces fine intermetallic particles as a result of fragmentation of larger intermetallic exposed to deformation and an additional number of fine dispersoid particles nucleated during further annealing [9].
Most fabrication processes induce in metals and alloys severe plastic deformation resulting into distortions in microstructures. This condition invariably gives rise to increase in dislocation density which is a precursor for varied corrosion phenomenon in materials. Thus, certain studies carried out have shown corrosion responses of some non-ferrous alloys such as aluminium, magnesium, and titanium in various media consequent upon mechanical deformation. The outcomes of these studies have shown that plastically deformed iron-based alloys often exhibit lower corrosion resistance in aqueous solution compared to their non-ferrous counterpart. Generally, the corrosion propensities of most alloys are prone to increase on the account of the combined influence of deformation and peculiar chemical composition. However, certain elements may selectively influence the corrosion behaviour of these alloys due to their presence and prior plastic deformation carried out [10].

The effect of corrosion of materials on daily basis can be enormous in particular 5052AA that are used in many applications including pressure vessels that are subjected to service in seawater environment. Their fabrication processes often induced in the material severe plastic deformation resulting to distortions in its microstructures. This is known to have adverse impact on the corrosion behaviour which has been responsible for the colossal loss in revenue for ship owners. Corrosion also adversely affects the useful service lives of materials, a situation which has made a functional knowledge of corrosion behaviour of materials an imperative. This has become an essential aspect of material selection processes which has the potential to nip in the bud incidences of premature failure of materials in service. The focus of the present study is to establish a scientific relationship between degree of deformation and corrosion rate of 5052AA subjected to service in seawater environment with a view of proffering effective mitigation procedures.

2. METHODOLOGY

2.1 Materials

Five samples of 9 cm length and 16 mm diameter dimension were cast from the melt of appropriately sized ingot of 5052AA charged into an induction furnace. Four of these samples were plastically deformed by rolling in a two-high mill at ambient temperature to 20%, 40%, 60%, and 80% size reduction. The fifth sample was left undeformed to serve as control. The composition analysis of the cast samples was determined using an optical emission spectrometer QTD 226 model. The seawater that was used to simulate the corrosion medium was obtained from Lagos lagoon beach and analysed at the Chemistry laboratory, University of Lagos.

2.2 Corrosion Simulation

Fig. 1 illustrates the experimental corrosion campaign set-up. The initial weight of the test coupon sample was obtained on a digital pocket scale and connected as anode to the potentiostat through the voltmeter whereas zinc (Cathode) was connected to the potentiostat via the ammeter. Both the zinc and the test coupon were completely immersed in the seawater inside a beaker and the circuit was closed for 6 hours with current flow value of 6.1 mA. By adjusting the potentiostat, the current was kept constant throughout the experiment. After 6 hours interval, the test coupon was removed from the electrolyte (seawater), scrubbed with rubber stopper to remove the corroded part, dried and re-weighed to ascertain the mass loss. The experiment was repeated five more times at an interval of 6 hours and the corresponding mass loss was recorded.

Fig. 1. Corrosion cell set-up
The experiment was performed on each of the cold rolled samples identified as C, D$_{20}$, D$_{40}$, D$_{60}$, and D$_{80}$ and the mass loss in each case was recorded. The corrosion rate (R) in millimeters per year (mm/yr) was evaluated using the formula proposed by Krisher [11] according to equation (6).

$$ R = \frac{W \cdot T}{D \cdot A} $$

(6)

Where:

- W = Weight loss in milligrams
- A = Total surface area of sample in cm$^2$
- T = Total time sample was immersed in hours
- D = Density of the sample in g/cm$^3$
- R = Corrosion rate in millimeters per year

The samples used have cylindrical geometry and each has a total surface area according to equation (7).

$$ A = 2\pi (l + r) $$

(7)

Where:

- l = length of sample in cm
- r = radius of sample in cm

The area and density of the coupons used are 49.27 cm$^2$ and 2.68 g/cm$^3$ respectively. The corresponding corrosion rate (R) for each test coupon was determined and recorded.

2.3 Microstructure Examination

The test samples were prepared for microstructure analysis by sequential grinding using emery paper 60, 150, 220, 320, 400, 600 and 800 grits. Each of the samples was ground in one direction using 60grit first and turned to a right angle direction to eliminate all scratches from the previous grinding. The remaining varied emery papers grits were used in the same process but now with a light pressure. The fine scratches on the surface of the samples after grinding were removed using polishing machine. This was done by holding them against a rotating disc, which was kept moist with mixture of Alumina powder and water to obtain a mirror-like surface. The mirror-like surfaces obtained were etched in sodium hydroxide (NaOH) solution for 20 seconds and rinsed with water while the microstructural features were examined under an optical microscope (x200 magnification) and are presented in Figs. 3(a-e).

3. RESULTS AND DISCUSSION

3.1 Composition

The composition analysis of the cast samples is presented in Table 1 and the analysis of the seawater that was used to simulate the corrosion medium is presented in Table 2.

3.2 Corrosion Behaviour

Corrosion rate increases as degree of deformation increases with minimum corrosion rate of 4.462 x 10$^{-4}$ mm/yr on the control sample and maximum rate of 49.410 x 10$^{-4}$ mm/yr on the 80% deformed sample between 0 and 6 hours as shown in Fig. 2. Maximum corrosion rate was observed on the 80% deformed sample due to cold rolling which generates deformed layers at the surface with precipitation of fine intermetallic particles. The deformed layers have high electrochemical reactivity which often results into susceptibility to filiform corrosion [12]. Thus, a highly deformed sample is more susceptible to corrosion than the fairly deformed and undeformed samples.

| Table 1. Composition of 5052AA sample |
|--------------------------------------|
| Element | Al | Si | Fe | Cu | Mn | Mg | Zn | Cr | Ni | Ti | Zr |
| Wt.%    | 95.709 | 0.250 | 0.391 | 0.001 | 0.100 | 2.399 | 0.100 | 0.300 | 0.200 | 0.050 | 0.500 |

| Table 2. Seawater analysis |
|-----------------------------|
| PH | 8.67 |
| Temperature | 29.5°C |
| Conductivity | 50,650 µS/cm |
| Total dissolved solids | 36,000 mg/L |
| Salinity | 25,750 mg/L |
| Chloride | 14,238.21 mg/L |
| Acidity | 56 mg/L |
| Iron | 0.45 mg/L |
No corrosion was observed on all the five categories of samples between 6 and 12 hours probably due to a temporary passivation which protects the samples from sea water attack [7]. The passive film is often assumed to be a simple inert layer covering the underlying sample and blocking access of the environment to the sample. This film can have a range of thickness, structure, composition, and protectiveness depending on alloy composition, environment, potential and exposure. However, corrosion simulation between 12 and 18 h oval indicates that corrosion rate was observed only on the 20% deformed sample. This might be as a result of the coherence of the intermetallic particles and the Mg2Si precipitates developed in the microstructure of the 20% deformed sample. Such highly stratified colonies within the alloy matrix are known to be potential sites for corrosion initiation [12]. However, corrosion rate increases with increase in the degree of deformation as the fractions of the intermetallic particles increase forming more nucleation sites. This eventually often develops into pits within the grains [13]. Between 30 and 36 hours, there was an initial uniform corrosion rate of the deformed samples (20-60%). This is due to the accumulation of cations within the pit which led to super-saturation of the salty sea water solution, and thus precipitation of a salt film which plays an important role in the stability of the corrosion rate [14,15]. Dissolution of the salt film led to increased corrosion rate as seen in the 80% deformed sample [88]. Corrosion rate increase in the deformed sample is not only time dependent, but also markedly influenced by the applied potential and the chloride concentration of the sea water [16].

3.3 Microstructure

Figs. 3(b-e) show the micrographs of the 5052AA samples that were plastically deformed by cold rolling to a varied size reduction. As shown in Table 1, the 5052AA under investigation contains 2.399 wt. % of Magnesium (Mg) and 0.25 wt. % of Silicon (Si). The presence of silicon enhances precipitation of Mg in the form of intermetallic particles (Mg2Si). It has been established that one parameter that impacts significantly on the microstructure and texture is the type of intermetallic particles based on their chemistry, size and inter-particle spacing [1]. Further, deformation aids the precipitation of Mg2Si at a low temperature with higher level of deformation leading to significant increase in the rate of precipitation. However, the undeformed sample contains evenly distributed fine grains of Mg2Si precipitate in the α-aluminium matrix (Fig. 3a) which agrees well with Merchant et al. [17]. Deforming the sample at ambient temperature by 20% caused a relatively large fraction of the Mg2Si to be precipitated out of the matrix (Fig. 3b) which exhibits visible grain boundaries. Further re-precipitation of fine Mg2Si crystals occurred at the 40% size reduction. In Fig. 3c, it appears the precipitates are not as apparent as in the 20% cold-work. However, it is clearly seen in Fig. 3d (60% cold deformation) that higher volume fractions of Mg2Si crystals developed in the deformed samples compared to the undeformed sample resulting to clustering. At 80% cold work, there is an increase in the volume fraction of the Mg2Si precipitates as well as increase in fineness of the precipitates as shown in Fig. 3e. This development has a huge potential of impacting the alloy surface
Fig. 3. Micrographs of AA5052 samples (a) Control (b) D20 (c) D40 (d) D60 (e) D80

topography and its ability to develop tenacious passive film. Scamans, et al. [18] made similar submission sequel to certain experimental outcomes with regard to aluminium science and technology.

4. CONCLUSION

Conventional 5052 aluminium alloys are known to exhibit characteristics response to deformation having a rebound effect on their corrosion propensity. The corrosion data obtained from this work and their analyses indicate that the deformed 5052AA is highly susceptible to corrosion attacks in seawater environment. It is observed that the inducement of high density of strained fields within the matrix as degree of deformation increases developed into veritable corrosion initiation sites. There is an increase in the volume fraction of the Mg2Si precipitates which results into clustering as well as increase in fineness of the precipitates as deformation increases. Corrosion rate increase in the deformed sample is not only time dependent, but also markedly influenced by the applied potential and the chloride concentration of the sea water. The highest corrosion rate of 49.4 mm/yr was exhibited by the 80% cold deformed sample compared with 4.46 mm/yr of the as-cast sample suggesting that 5052AA is best employed in seawater environment in its as-cast state. In the event that cold deformation is inevitable, it is advisable that cold deformation should not exceed 40% size reduction to avoid catastrophic failure in service.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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