

Protection of Tempered Aluminum Alloy in Contact with the Environment

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Abstract. In many service applications an increasing temperature or inadequate protections often give rise to localized forms of corrosion in an initially free and unprotected system. This research understudy the corrosion chemistry, the effect of chromium as the inhibitor, Vickers hardness test, and weight loss on tempered aluminium alloy 7075 in corrosive mediums. The tempers of the aluminium alloy used are T6 and T73 where obtained by solution heat treatment at 470°C and quenched before immersion test in acidic (pH3), and slightly alkaline (pH7.5) solutions. The results obtained were characterized by conventional weight loss process and morphology observation with a microscope. The surface morphology shows exfoliation form of corrosion and the weight loss analysis shows the as received sample experience more weight loss when compared with the other heat treated samples.

1. Introduction

Corrosion is known to be an electrochemical process in which a metal comes in contact with its environment to form an oxide or other compounds. As a result of this interaction, the resulting destructive attack of the material due to this corrosion process has become a problem of world-wide significance [1, 2]. In addition to the regular encounters with this form of degradation, which often leads to plants shut down, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over design, it also jeopardizes safety and inhibits technological progress [3-5]. The electrochemical process has three essential constituents: an anode, a cathode and an electrically conducting solution. The anode is the site at which the metal corrodes; the electrolyte solution is the corrosion medium; and the cathode forms the other electrode of the cell which is not consumed during the corrosion process [6].

At the anode the corroding metal passes into solution as positively-charged ions, releasing electrons which participate in the cathodic process. Thus the rate of corrosion is equivalent to the electron current flowing between anode and cathode of the corrosion cell. The distribution of anodic and cathodic areas is one of the most important factors determining the type of corrosion which occurs, but in the simplest case the corrosion cells are very small and numerous, and distributed in a random manner over the surface of the metal, and the effect is more or less uniform attack on the surface [7,



8]. The overall rate of the process under these circumstances may depend on a number of factors but the important criterion is the balance between rates of anodic and cathodic reactions required to maintain electro neutrality, and the overall rate of corrosion is controlled by the rate of whichever reaction occurs least readily. Although many metals display active corrosion behaviour when immersed in a corrosive solution, others including many engineering alloys carry a stable film of solid corrosion product, frequently an oxide. If this film has good cohesive strength and adhesion to the metal, and low ion conductivity, the rate of metal dissolution is limited to the rate at which metal ions can pass through the film [9-11]. This is the phenomenon of passivity, exhibited by stainless steels, nickel alloys, titanium and many similar materials and responsible for their utility as engineering materials in corrosive environments. This study aims to determine how effective the chromate inhibitor can be when the as received specimen, peak age and over age tempers are immersed in the solution with/without chromate and to also compare the hardness of the heat treated specimens with the as received sample.

2. Materials and methods

An aluminum alloy 7075 was purchased commercially for the sole purpose of this research. Specimens with dimensions of 25 mm x 30 mm x 15 mm were cut from the as received aluminum alloy 7075. The surface was ground and polished to mirror finish. This was accompanied by using 1200 grit abrasive papers and 0.5 μm alumina powders. Heat treatment process was initiated by solution heat treatment at 470 °C for 60 minutes and then quenched in water (at room temperature) for 60 seconds. The process was then followed by precipitation heat treatment for different durations of tempers for the aluminum alloy. The specimen in the T6 temper was subjected to solution heat treatment at 470 °C for 60 minutes, quenched for 60 seconds and followed by precipitation heat treatment or artificial ageing at 138 °C for 960 minutes. The specimen in the T73 was subjected to solution heat treatment at 470 °C for 60 minutes quenched for 60 seconds and followed by two precipitation heat treatments processes at 113 °C for 480 minutes and 182 °C for 720 minutes respectively. For the hardness test two heat treated and one as received specimens having dimensions of 20 mm x 20 mm x 10 mm were cut with diamond cutter from the aluminum alloy 7075. They were polished using 1200 grit abrasive papers and diamond paste to produce a mirror finish surface prior to the hardness test. The tests were conducted using a Vicker's hardness tester (model: FV-7) and measurements were carried out with a 10 kgF load.

2.1. Immersion Test

Two heat treated specimens and one as received specimen were immersed in different solutions for a period of time. Two different pH environments were used which is an acidic environment with pH3, and a slightly alkaline medium of pH7.5.

2.2. Acidic Medium (pH3)

The peak aged T6, and over aged T73 with as received AR (Al-alloy 7075) were used in the acidic medium containing 4 M sodium chloride, 0.5 M potassium nitrate and 0.1M nitric acid diluted to make one litre with deionised water for 6 days according to exfoliation test of aluminum and aluminum alloy ASTM G112-92 (2003) and ASTM G34-01 for visual and optical observations. The dimension of these specimens are 51 mm X 17 mm X 6 mm, they were polished with 1200 grit abrasive papers and 0.5 μm diamond paste to produce a mirror finish surface. Keller's reagent was used to clean the furnace of the specimens prior to the immersion test.

2.3. Alkaline Medium (pH7.5)

The dimensions of specimens used are 51 mm X 17 mm X 6 mm respectively they were polished with 1200 grit abrasive papers and 0.5 μm diamond paste to produce a mirror finish surface. Keller's reagent was used to clean the furnace of the specimens prior to the immersion test. Two separate solutions were prepared for the alkaline medium the first solution contains 3.56 wt% of sodium

chloride diluted with deionised water to make one litre without any inhibitor according to ASTM standards G31 72 (2004) while the second solution contains 3.56 wt% of sodium chloride, and 0.2 wt% of sodium chromate as an inhibitor and diluted with deionized water to make one litre.

3. Results and discussion

Solution heat treatment involves heating to a high temperature very close to the solidus temperature and above the solvus line. It is vital and important to stick to the specific temperatures because if the temperature is too low, the resulting mechanical properties will be low, whereas too high temperature will over heat the product (formation of hot spots), leading to irreversible damage on the aluminum alloy. This is due to partial fusion of complex eutectics and elements precipitated at the grain boundaries [12]. Peak aged T6 specimen produced by solution heat treatment has the highest mechanical strength shown in Table 1 while the Over aged specimen produced also have high strength but lower in value to the peak age strength. The solution heat treatment strongly increased the volta potential difference between the intermetallics and the surrounding matrix [13].

Table 1. Heat treatment and hardness value.

Temper Designation	Solution Heat treatment	Precipitation Heat treatment	Hardness Value
T6	470°C/60 min	138°C/960 min	193 HV
T73	470°C/60 min	113°C/480 min 182°C/720 min	188 HV
AR	-	-	183HV

3.1. Hardness Test

The Hardness test measures the resistance of the aluminum alloy 7075 to an applied load or indentation. The Vickers hardness testing machine that was used for the test on the as received sample with an applied load of 10 KgF indentation on the polished surface of the aluminum alloy gives a value of 183 HV based on the index number which is determined by the depth or penetration level of the indentation. Solution heat treatment and subsequent quenching of AA 7075 causes dissolution of MgZn₂ strengthening particles, which are formed during aging to the T6 temper and provide high-strength to the alloy [14].

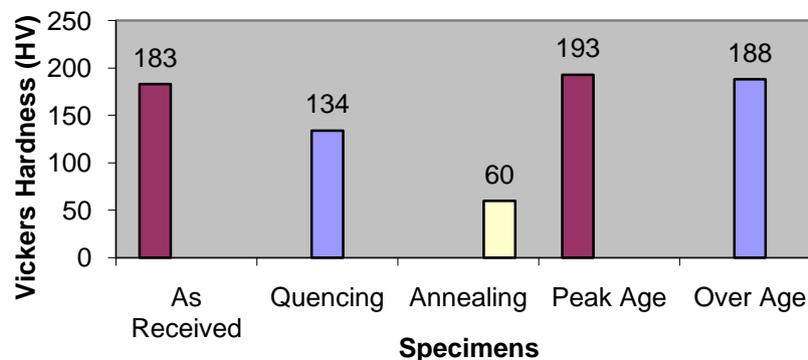


Figure 1. Vickers hardness test.

The dissolution of the MgZn₂ strengthening particles causes enrichment of the matrix in solute atoms like Zn, Mg and Cu resulting in the presence of a supersaturated solid solution when the alloy is

fast quenched from the solution heat treatment temperature to room temperature this microstructure changes occurring in the alloys causes a reduction in the alloy strength. Characterization of the specimen strength by Vickers hardness testing machine gives the value 134 HV showing a reduction in strength which can be attributed to the dissolution of the strengthening intermetallics $MgZn_2$ in the microstructure [14]. Peak age (T6) in Figure 1 shows the increased strength which is attributed to a high density metastable precipitation distributed homogeneously in the Al matrix while the T73 (Figure 1) strength is attributed to lower density of thicker precipitates more stable in nature which accounts for the inferior strength to the peak aged specimen but it should be noted that there is no change in the microstructure [15].

Both specimens produced by the heat treatment have mechanical strength higher than the as received sample. The hardness test result shown in Figure 1 as a tendency for it to increase this can be attributed to the fact that being a high strength alloys it continually undergo natural ageing.

3.2. Heat treated specimen at pH3

Figures 2 (a), (b), & (c) shows exfoliation corrosion which is one of the localized corrosion on the specimens after immersion into the solution by optical observation. Exfoliation is a form of intergranular corrosion that can occur in wrought high strength aluminum alloys, the attack takes several forms ranging from pitting, powdering or flaking of the surface to the development of blisters several millimetres in diameter. It was observed that overageing has beneficial effects on the susceptibility to exfoliation corrosion by reducing the rate of intergranular corrosion one difference between these two tempers' microstructures is that the η - $MgZn_2$ hardening phase is lined up in beads along the grain boundary in the T6 temper with small spacing, whereas in the T73 temper the η - $MgZn_2$ -particles spacing are larger [14]. Large sheets of the surface had loosened from the substrate in all immersed specimen, the flakes had loosened, which floated in the testing solution or lay near the sample at the bottom.

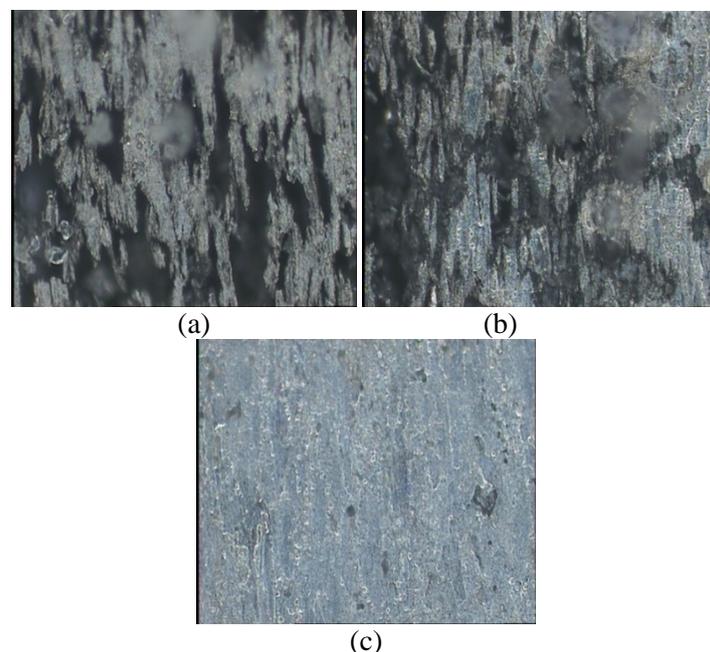


Figure 2. (a) AR Exfoliation test observed from an optical microscope at 10X, (b) T6 Exfoliation test observed from an optical microscope at 10X, and (c) T73 Exfoliation test from an optical microscope at 10X.

The galvanic interaction between grain boundary precipitates and adjacent solute depleted zones cause the intergranular corrosion [16]. The corrosion products have a larger volume than the original aluminum alloy and the expansion causes stresses that lift the surface grains, exposing the underlying material as shown in the visual observation of the specimens Figures 3 (a), (b), & (c). The grain shape, the degree of cold deformation and the heat treatment condition are key factors influencing the exfoliation corrosion [17].

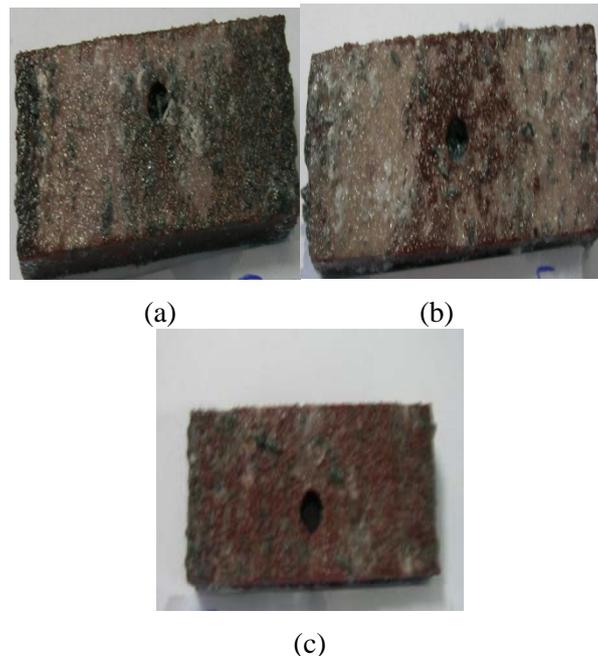


Figure 3. (a) T73 exfoliation corrosion by visual observation, (b) AR exfoliation corrosion by visual observation, and (c) T6 Exfoliation Corrosion by Visual Observation.

Table 2 shows the weight losses and corrosion rate observed for AR, T6, and T73 immersed in a test solution at pH3 for 6 days. The weight loss obtained for the three different specimens in the acidic solution is 0.8242 g, 0.7968 g and 0.7734 g which are all high. These show that regardless of the heat treatment solution if the material is unprotected, the deterioration and weight loss becomes rapid that can lead to material failure when in an acidic environment.

Table 2. Weight losses and corrosion rate test result at pH3.

Specimen	Initial Weight (g)	Duration (days)	Final Weight (g)	Weight loss (g)	Solution	Corrosion Rate (mm/yr)
AR	17.2143	6	16.3901	0.8242	NaCl KNO ₃ HNO ₃	20.65
T73	18.3232	6	17.5498	0.7734	NaCl KNO ₃ HNO ₃	19.38
T6	15.7532	6	14.9564	0.7968	NaCl KNO ₃ HNO ₃	19.97

3.3. Heat treated specimen at pH7.5

Table 3 and 4 shows two and four weeks immersion test of the different specimens showing its weight losses and corrosion rate in a slightly alkaline environment. AR has the highest susceptibility to corrosion. This susceptibility is partially decreased by the precipitation of the MgZn₂ particles at the grain boundaries when the alloy is aged to the T6 temper. However, the susceptibility to intergranular corrosion remains rather high for the T6 temper since the grain boundaries present an almost continuous precipitation of particles. Aging to the T73 temper strongly improves the resistance to intergranular corrosion because the size of the MgZn₂ particles at the grain boundaries and their interparticle distance increases during overaging [16].

The Table 4 shows the corrosion rate result after 4 weeks of immersion, it is observed that the corrosion rate decreases with time. This is most likely due to the ability of the alloy to undergo a form of passive film repair which further decreases or slows down the rate of electrochemical reaction taking place in the solution.

Table 3. Weight losses and corrosion rate for 2 weeks test result at pH7.5.

Specimen	Initial weight (g)	Duration (days)	Final weight (g)	Weight loss (g)	Solution	Corrosion rate (mm/yr)
AR	9.3804	14	9.2842	0.0962	NaCl	1.03
T6	9.1950	14	9.1079	0.0871	NaCl	0.94
T73	10.0513	14	9.9796	0.0717	NaCl	0.77

Table 4. Weight losses and corrosion rate for 4 weeks test result at pH7.5.

Specimen	Initial Weight (g)	Duration (days)	Final Weight (g)	Weight loss (g)	Solution	Corrosion Rate (mm/yr)
AR	11.7512	30	11.5803	0.1709	NaCl	0.87
T6	9.7110	30	9.5504	0.1606	NaCl	0.80
T73	9.2586	30	9.1266	0.1320	NaCl	0.66

3.4. Heat treated specimen at pH7.5 with chromate inhibitor

The unique chemical and electronic properties of the oxo-compounds of chromium, Cr (valence electronic structure 3d⁵ 4s¹), gives them a seemingly unique ability to inhibit corrosion in ferrous and nonferrous materials. The electronic properties of Cr allow for very different behaviours for the oxo- and hydroxo- compounds of Cr⁶⁺ and Cr³⁺. The tetrahedral, d⁰, hexavalent oxoanion compounds of chromium (chromate, dichromate, bichromate, and chromic acid) dissolve as stable complexes in water, transport easily, and adsorb on oxide surfaces.

Chromate used as inhibitor in aluminum alloy 7075 effectively protects it against localized corrosion attack because chromate is a powerful cathodic inhibitor even at high chloride, chromate ratios are excellent inhibitors of oxygen reduction in near neutral and alkaline solutions [13, 16]. In these environments, they can stifle corrosion by suppressing this cathodic partial reaction. The inhibition appears to involve reduction of Cr⁶⁺ to Cr³⁺ at a metal surface and formation of an irreversible adsorbed Cr³⁺ hydroxide surface layer of near monolayer thickness.

The Table 5 shows the low rate of weight loss and corrosion rate of the AA 7075 protected by chromate inhibitor because the treatment of AA 7075 with chromate in the sodium chloride solution causes a significant reduction of cathodic activity. This was attributed to rapid formation of a thin chromium oxide film on the α -Al (Cu, Fe,) particles resulting in significant cathodic passivation of the phase, inhibition of the oxygen reduction reaction at cathodic intermetallic particles.

Table 5 Weight losses and corrosion rate for 4 weeks in chromate inhibited solution.

Spe.cimen	Initial weight (g)	Duration (days)	Final weight (g)	Weight loss (g)	Solution	Corrosion rate (mm/yr)
AR	7.6583	30	7.6539	0.0044	NaCl Na ₂ CrO ₄	0.022
T73	6.4742	30	6.4709	0.0033	NaCl Na ₂ CrO ₄	0.017
T6	6.7052	30	6.7021	0.0031	NaCl Na ₂ CrO ₄	0.016

The performance of the chromate inhibitor has been attributed to several factors providing barrier protection of the aluminum matrix and providing stability over a wide pH range [13].

4. Conclusions

The corrosion behaviour of tempered aluminium alloy in two corrosive mediums were studied. The hardness test shows increase in strength during the solution heat treatment which is higher for both T6 and T73 when compared with the as-received material. For T6 and T73 the increased strength is due to high density metastable precipitation distributed homogenously and in the case of T73 it is due to low density of thicker precipitate more stable in nature. The corrosion test shows T6 and T73 experience marginal weight loss and the introduction of the chromate inhibitor further reduces the weight losses and the corrosion rate per year. The AR specimen the surface is with only a thin oxide layer on it, thus corrosive attack initiates rather fast because this oxide layer can be dissolved easily by the aggressive test solution and the resulting hydrogen evolution which leads to severe embrittlement of the material. While the oxide layer of the T6 and T73 are much thicker because of the heat treatment at elevated temperatures – including solution heat treatment and different artificial ageing processes which might significantly delay the onset of corrosion.

5. References

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Acknowledgements

I would like to express my gratitude to Universiti Malaysia Perlis (UniMAP) and Center of Excellence Geopolymer and Green Materials (CEGeoGTech) for giving me the opportunity to be involved in this project.