

Effect of Annealing Process on the Corrosion Resistance of Aluminium 7075-T6 Alloy

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Abstract - The material used in this study was a commercial 7075-T6 aluminum alloy rolled plate in the T6 temper with a thickness of 6mm and width 20mm purchased from SteelOFabrica, Pune. The chemical composition of the alloy was tested by optical emission spectroscopy (OES). The samples were annealed in an electrical type Carbolite furnace at temperatures of 400°C for 4, 8 and 12 h. The microstructure and hardness measurement were done before and after annealing. The corrosion behavior of alloy was investigated using electrochemical polarization techniques and immersion methods. The specimens were immersed in the test solution (3.5%NaCl) for the testing period of 28 days on interval of 7 days for static immersion test. The Electrochemical corrosion measurements were made using an electrochemical work station, CH600D-series, U.S. Model with CH instrument beta software potentiostat and test was carried out in 3.5wt% NaCl solution using the standard three electrode flat corrosion cell. Static immersion test indicated that the annealed samples (4, 8, & 12hr) have a corrosion rate greater than the base metal (BM) and rate decreased monotonically with increase in time duration due to the possible passivation of the aluminium alloy. The base metal showed better corrosion resistances as compared to annealed even after 28 days of immersion. The anodic polarization curves exhibited lower electrode potentials for specimens with more annealing time in 3.5% NaCl solution. The electrode potentials decreased with increasing annealing time. After polarization tests, the exposed surfaces were examined by SEM immediately to determine the type of attack which revealed intergranular corrosion. The SEM micrographs revealed that the most severe intergranular attack was observed on exposed surfaces of the 7075-T6 aluminum alloy specimens with larger annealing time. Annealing of the 7075-T6 aluminum alloy resulted in the lowering of its corrosion resistance.

Key Words: Al alloy 7075-T6, Chloride ion, Passivation, Electrochemical test, SEM.

1. INTRODUCTION

High-strength Aluminium alloys, such as 7075-T6, are commonly used in many applications such as in automobile and aerospace industries due to their light weight, good combination of high strength and ductility, and corrosion resistance properties [1-4]. However, these alloys are susceptible to various forms of localized corrosion in chloride ion environments, such as pitting, forming crevices, and intergranular corrosion [5-7]. The corrosion process of aluminum alloys is also influenced by several metallurgical factors such as heat treatment, chemical composition of the alloying element, material discontinuities such as presence of voids, inclusions, precipitates and grain boundaries [8,9]. Several environmental factors such as temperature, moisture content, pH, type of electrolytes and the time of exposure also influence the rate of corrosion either in some extent to larger extent depends on their presence in either individual parameters or combination of these [10,11]. Furthermore, high-strength aluminum alloys are often used in rolled or extruded conditions so that the microstructure is elongated and anisotropic to gain high strength. The corrosion kinetics will also be anisotropic in such a structure if the form of the attack is intergranular in nature.

Extensive investigations into the corrosion behavior of high strength aluminum alloys, especially the localized corrosion of aluminum alloys in aqueous chloride solutions have been conducted using different techniques [11]. It is well known that grain boundaries are often more susceptible to corrosion than are grain interiors because of microstructural heterogeneity. The severity of the exfoliation corrosion was related to the grain aspect ratio of the material in several studies [12]. Grain size and aspect ratio have been shown to be important factors in localized corrosion growth kinetics. Some researchers reported that the grain boundary region of a typical aluminum alloy can contain precipitates on the grain boundary and a precipitate-free zone (PFZ) next to the grain boundary, both of which have very different

electrochemical behaviors than the grain interior. They proposed that the intergranular corrosion in the 7075-T6 temper was caused by the anodic dissolution of $Mg(ZnCuAl)_2$ [12-13].

2. Methods

2.1 Material

The material used in this investigation is a commercial 7075-T6 aluminum alloy rolled plate in the T6 temper with a thickness of 6mm and width 20mm purchased from SteelOfabrica, Pune. The chemical composition of the alloy was obtained by using optical emission spectroscopy (OES) is listed in Table 1.

Samples were prepared by sectioning the Al alloy plate by use of wire cut-off wheel machine for polarization studies, weight loss measurements, mechanical testing and metallographic practice. The research material was supplied in T-6 plate form. It is worth mentioning that during the aging process of T6 temper, GP (Guinier-Prestone) zone and a small fraction of η' phase are formed in the microstructure of 7075. The formation of the η' phase indicates over-aging and results in decreased strength properties.

Table 1: Composition of Aluminium 7075-T6 obtained by OES

Elements	Composition (%)
Al	90.3
Zn	5.3
Mg	2.4
Cu	1.7
Cr	0.23
Si	0.4
Fe	0.5
Mn	0.3
Ti	0.2

2.2 Sample Preparation

The samples were obtained in the size of 10x10 mm, 25x25 mm and 25x30mm using electric discharge machining (EDM) from larger flat plate of size 20*6 mm of 3m length flat bar. The specimens were polished up to 1200 grade in the water proof silicon carbide (SiC) abrasive paper and washed with acetone before each experiment. The samples were polished till the scratches formed during previous paper polishing completely removed. After completion of polishing on lower grit size,

higher grit paper polishing were done at a 90° angle to the previously polishing direction i.e. in a perpendicular direction to the previous polishing. A rotary polishing grinder with the provision of water tap is used for the polishing, in cloth polishing 1 μ m Diamond paste and 0.5 μ m diamond paste along with extender are used for very fine surface finish. The morphologies of base and annealed specimens were observed by optical microscopy after metallographic etching in Keller's reagent made up of 1 ml HF, 1.5 ml HCl, 2.5 ml HNO₃ and 95 ml H₂O with the etching time of 30 s. The obtained microstructures were then examined using an optical microscope under a magnification of 250X.

2.3 Heat treatment

The samples of size 10x10 mm, 25x25 mm and 25x30mm were machined using electric discharge machining (EDM). These samples were then annealed by using an electrical type Carbolite furnace at temperatures of 400°C for 4, 8 and 12 h. The samples were named as S₁, S₂, S₃, and S₄. The S₁ sample is the base metal (BM). Fig.1 shows Carbolite furnace performing annealing heat treatment of aluminium 7075-T6 alloy at 400°C.



Fig.1: Carbolite furnace at 400°C for annealing heat treatment at NIFFT Ranchi.

2.4 Hardness test

The hardness test were conducted on HTM-7510 Vicker tester. The surface of the specimens were prepared smooth, clean and dry, polishing from 400 grit to 1000 grit SiC emery paper. A Vickers hardness testing machine was employed to determine hardness by applying a load of 10 kgf for 15s. Hardness measurements were made along the mid-thickness of polished sections cut along the rolling direction. Five measurements were made for each specimen (ASTM-E384).

2.5 Corrosion testing

2.5.1 Immersion test

Corrosion rates for the samples i.e. Base metal, S₂, S₃ and S₄ were determined by weight loss method in the 3.5% NaCl solution having pH 6.9.



Fig.2: Specimens exposed to 3.5% NaCl solution for a period of 28 days.

To expose sample in aqueous solution of the above pH value, the solution was prepared in a 1000 cc beaker by adding 35 g NaCl to 1000 ltr. of distilled H₂O. Samples of 10x10 mm were polished to 800 grit and cleaned with ethanol prior to weighting. The samples for immersion test were prepared in accordance to the procedure recommended by ASTM G31-72. The specimens were then weighted and then immersed in the test solution for the testing period of 28 days on interval of 7 days. After exposure period, the samples were taken out and brush-cleaned with water to remove the corrosion product and rinsed with ethanol and dried before reweighing. Fig.2 shows specimens exposed to 3.5% NaCl solution for a period of 28 days. The corrosion rates were determined using the relation (1).

$$\text{Corrosion rate, } CR = \frac{87.6 \times W}{DAT} \text{ mm/y} \quad (1)$$

Where W = Weight loss in the sample in milligram

D = Density of the material in g/cm³

A = Area of cross-section in inch²

T = Time in hours

2.5.2 Electrochemical test

The Electrochemical corrosion measurements were made using an electrochemical work station, CH600D-series, U.S. Model with CH instrument beta software potentiostat interfaced to a Pentium-3 compatible computer.

To study the localized corrosion and to get an idea about the corrosion behavior of base metal and annealed S₂, S₃

and S₄ samples, potentiodynamic polarization test were done. The test specimens were metallographically polished from 120 grit to 1000 grit SiC emery paper and with alumina powder; specimens were cleaned with ethanol before starting the test. Potentiodynamic Polarization test was carried out in alkaline media namely 3.5wt% NaCl solutions. The test was carried out in the standard three electrode flat corrosion cell using platinum as the counter electrode and silver-silver chloride electrode as the reference shown in Figure 3. The polished Aluminium 7075-T6 BM and annealed specimens were mounted in the corrosion testing cell to expose a surface area of 1 cm² to the test solution. The corrosion cell was electrically connected to Versa STAT Multichannel Potentiostat.



Fig.3: Setup of three electrode flat corrosion cell.

The sample was cathodically cleaned by applying a potential of -30 mV vs. OCP. The experiment was carried out at the scan rate of 50 mV/s. The potentiodynamic polarization plot was generated between voltage and the log of current density for the sample. The plot thus generated was used for comparing corrosion behavior of the aluminium alloys. E_{corr} and I_{corr} were evaluated by drawing anodic and cathodic Tafel slope. All measurements were made at room temperature. Corrosion rate is determined from the following equation (2):-

$$CR(\text{mm/yr}) = \frac{3270 \times M \times i_{corr}}{\rho \times Z} \quad (2)$$

Where 3270 is a constant that defines the unit of corrosion rate, i_{corr} is the corrosion current density in A/cm², ρ is the density of the corroding material (g/cm³), M is the atomic mass of the metal, and Z is the number of electrons transferred per atom.

2.6 Scanning Electron Microscopy (SEM)

The surface morphology is examined by JEOL JSM-6390LV scanning electron microscope (SEM). The scanning electron microscope images were recorded to establish the interaction of alkaline medium (3.5% NaCl) with the metal surface using JEOL JSM-6390LV scanning electron microscope (SEM). The surface morphology of 7075-T6 aluminium alloy immersed in 3.5% NaCl medium for a period of 28 days was compared with that of annealed metal samples.

3. RESULTS & DISCUSSIONS

3.1 Microstructure

Optical micrographs of the surfaces of as-received 7075-T6 aluminium alloy specimens is shown in Fig. Coarse and dense intermetallic particles are evident on the surface of the as-received specimen (Fig.4). It is seen that the grains are elongated and flattened and the matrix contains precipitates stretched along the rolling direction.

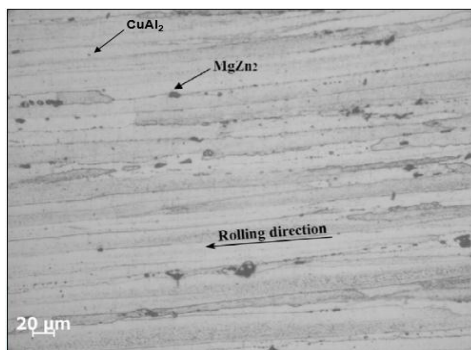


Fig.4: Optical micrographs of as received 7075-T6 aluminum alloy.

Generally, in Al-Zn-Mg-Cu alloys (7xxx Al alloys) two different strengthening precipitates will form and they are: (i) MgZn₂ and (ii) CuAl₂. The black particles seen in BM are strengthening precipitates but there is an appreciable difference in size of the precipitates. Fine precipitates generally belong to CuAl₂ and coarse precipitates belong to MgZn₂, because the maximum available copper for the precipitation reaction is 1.7% only in this alloy but the available magnesium and zinc for the precipitation is plenty.

3.2 Hardness test

The hardness values were measured at various points on the polished specimens of alloy.

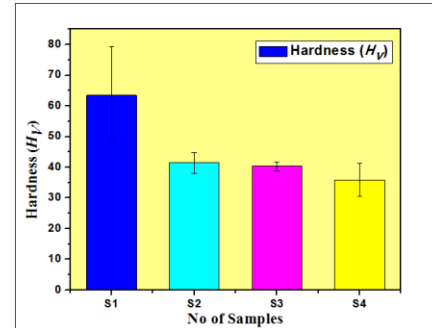


Fig.5: Vickers hardness of the 7075-T6 aluminum alloy as a function of annealed and base metal samples.

The hardness of 7075-T6 aluminum alloy as a function of annealed and base metal samples is shown in Fig.5. As shown in this figure, the annealing treatment applied to coarsen the grain size showed a significant decrease in hardness for the base metal and annealed samples. The average value of base metal hardness is 63.4 H_v. The average hardness values of annealed samples S₂, S₃ and S₄ are 41.4, 38.1 and 40.1 H_v, respectively. The dissolution of strengthening precipitates (MgZn₂ and CuAl₂) in HAZ may be attributed to the reduction in hardness. It was reported that grain refinement strengthening was not the main contributor that enhanced the strength and hardness of the Al-Zn-Mg-Cu alloy because the dislocation networks and tangles within grains and near grain or sub-grain boundaries make dislocation glide more difficult.

3.3 Corrosion test

3.3.1 Immersion test

Immersion test was done for the various samples of aluminium alloys in 3.5% NaCl solution for a period of 28 days.

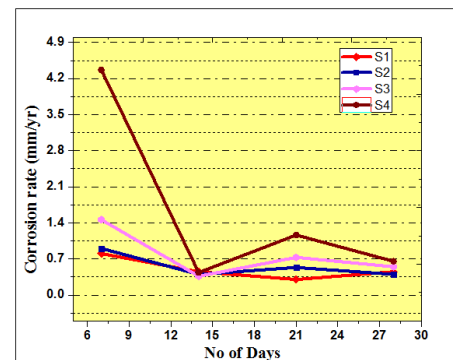


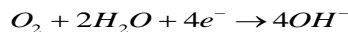
Fig.6: Corrosion rate variations with time for base metal and annealed samples of Aluminium 7075-T6 alloys in 3.5% NaCl solution.

Fig. 6 illustrates the relationships between corrosion rate (mpy) and immersion time by weight loss measurements. In comparison to base metal and annealed alloys showed high difference in weight loss up to initially 7 days of exposure. Thereafter, their steep decrease of weight loss was measured, as there is elimination of the possibility of hydrogen bubbles clinging on to the surface of the specimen and forming a permanent layer affecting the corrosion process. The phenomenon of gradually decreasing corrosion rate indicates the possible passivation of the aluminium alloy. De Salazar [9] explained that the protective black film consists of hydrogen hydroxy chloride, which retards the forward reaction. Castle et.al [10] pointed out that the black film consists of aluminium hydroxide compound. This layer protects further corrosion in alkaline media.

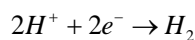
The corrosion rate (mm/yr) derived as per Eq. (1), is plotted against time (Fig. 6). From the trend one can see that the corrosion rate of S₄ occurs comparatively much high than BM alloy till initial 7 days of immersion. After this, there was a steep fall in their corrosion rate of S₄ (from 4.3681 to 0.4368 mm/yr) was measured, whereas BM alloy showed even less than two mpy corrosion rate after 7 days of immersion. The increase in corrosion rate of S₃ and S₄ alloy was further continued with fast rate (4.4555 and 7.10073) till 21 days of immersion. After this period, a decline in their corrosion rate was measured. A steep increase of corrosion rate after 14 days of immersion of annealed alloy evidences the occurrence of fast corrosion reaction that increases with exposure period possibly due to start of intergranular corrosion. Moreover, intensity of the intergranular corrosion appears to be quite high for S₄ annealed alloy. This phenomenon implies that preferential corrosion of the grain boundary region could have occurred, which is due to the fact that the grain boundary region was made more anodic by the segregation of Zn and Mg atoms in solid solution.

The reaction involve in the formation of Al(OH)₃ can be expressed as per following

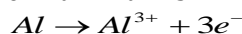
Oxygen reduction reaction as



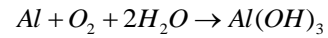
or hydrogen reduction in acidified solution such as in a pit environment as a result of aluminium ion hydrolysis:



Oxidation reaction of Aluminium is



The overall reactions could be given as per following reaction.



3.3.2 Electrochemical test

The effect of alkaline medium (3.5% NaCl) on the corrosion rate of base metal and annealed samples of 7075-T6 aluminium alloy was studied using Tafel polarization technique. Fig.7 represent the potentiodynamic polarization curves of 7075-T6 aluminium alloy (BM and annealed) in same concentration of 3.5% NaCl solution. The sample was cathodically cleaned by applying a potential of -30 mV vs. OCP. The experiment was carried out at the scan rate of 50 mV/s.

Corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic slope (b_a) and cathodic slope (b_c) are obtained from the Tafel polarization curves. Results of Tafel polarization studies of base metal and annealed (4, 8 & 12 hr) samples of 7075-T6 aluminium alloy in 3.5%NaCl are tabulated in Table 2. The corrosion rate was calculated using Eq. (2).

$$CR(mm/yr) = \frac{3270 \times M \times i_{corr}}{\rho \times Z} \quad (2)$$

where 3270 is a constant that defines the unit of corrosion rate, i_{corr} is the corrosion current density in A/cm², ρ is the density of the corroding material (g/cm³), M is the atomic mass of the metal, and Z is the number of electrons transferred per atom (Fontana, 1987).

The results of Tafel polarization measurements are reported in Table 2 respectively.

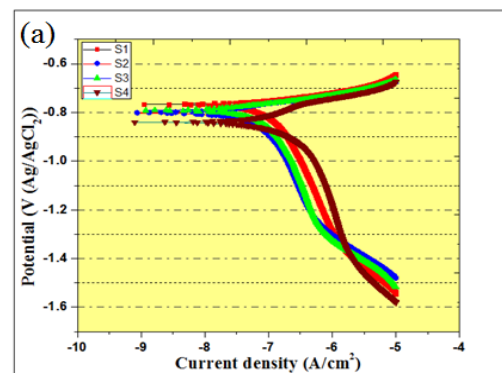


Fig.7: Tafel polarization curves for 7075-T6 aluminium alloy of (a) base metal and annealed samples.

Table 2: Tafel polarization of base metal and annealed (4, 8 & 12 hr) samples of 7075-T6 aluminium alloy

Samples	E_{corr} (V vs. SCE)	i_{corr} ($\times 10^{-4}$ A/cm ²)	b_a (V dec ⁻¹)	$-b_c$ (V dec ⁻¹)	CR(mm/yr)
Base metal	-0.7569	4.7813	3.2945	3.41	5.39697
S ₂	-0.7934	5.58072	6.78	3.192	6.29929
S ₃	-0.8123	7.1875	4.9309	3.85	8.11296
S ₄	-0.8593	7.7088	2.9167	3.168	8.70141

The results indicate the increase in the corrosion rate with an increase in the annealing time (S₂, S₃, & S₄) immersed in 3.5% NaCl medium. The positive shift in the corrosion potential (E_{corr}) with the increase in annealing time indicates that the anodic process is much more affected than the cathodic process (El-Sayed, 1997). This observation is in accordance with Muralidharan (Muralidharan and Rajagopalan, 1979), who proposed dependence of E_{corr} and i_{corr} on solution parameters. Tafel slopes remained almost unchanged indicating that alkaline medium does not change the mechanism of the corrosion process. It is evident from data of Table 2 that corrosion rate is more in case of 12 hr annealed compared to as received sample.

Moreover, the electrode potentials of the specimens with large annealing time are significantly lower than those of the as-received specimen, which indicates that the specimens with large annealing time are more susceptible to localized corrosion in chloride solution (Table 2). The lowering of the electrode potentials recorded for the specimens with large annealing time can be explained by a decrease in the precipitate content in the aluminum matrix due to the annealing treatment.

The severity of IGC appears higher on the surfaces of specimens with large annealing time, as more precipitates accumulate at the grain boundaries of aluminum alloy specimens with large annealing time.

3.4 Scanning Electron Microscopic study

The surface morphology examined by SEM on the surfaces of as-received and annealed 7075-T6 aluminum alloy specimens before corrosion testing are shown in Fig. 8. Coarse and dense intermetallic particles are evident on the surface of the as-received specimen (Fig. 8a). In contrast, the intermetallic particles observed on the surfaces of large annealed specimens are finer and decreased with increasing annealing time. No precipitates are evident on specimen S₄ (fig. 8d), indicates that the precipitates are segregated at the grain boundaries of the alloy, leaving the adjacent region free of precipitates. This process is due to

the slow cooling of the aluminum alloy from the annealing temperature, which results in the diffusion of the alloying elements in a solid solution to concentrate at the grain boundaries.

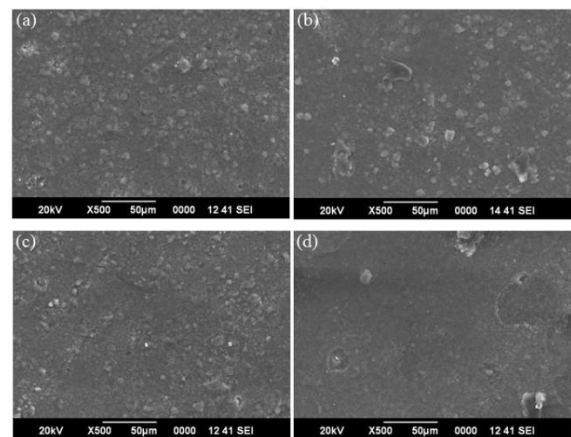


Fig.8: SEM micrographs of the 7075-T6 aluminum alloy at 500X showing the precipitate phases in the as received specimen (a) and the annealed specimens (b) (c) & (d) for 4, 8 & 12 hr annealing time.

The surface morphology was examined by SEM immediately after corrosion tests in 3.5% NaCl medium. The SEM image of corroded sample given in Fig. 9 shows the degradation of alloy, which revealed the intergranular attack was initiated on the surfaces of the as-received specimens and the specimens with large annealing time. In contrast, the initiated intergranular cracks (IGCs) formed on the surface of the large annealing time specimens were denser and longer (Fig. 9d), which clearly demonstrates that the intergranular corrosion rate increases with annealing time (Fig. 9b–d). The higher current density (Table 2) observed during polarization of the samples with large annealing time indicates a more severe IGC attack because the current or, more precisely, the charge passed is directly proportional to the amount of metal dissolved by intergranular corrosion. The IGC growth can be attributed to the segregation of more grain boundary precipitate phases such as MgZn₂ and CuAl₂, which are

more active than the matrix. Moreover, it is believed that the high-grain boundary angle associated with large grain size provides an easy path for the IGC.

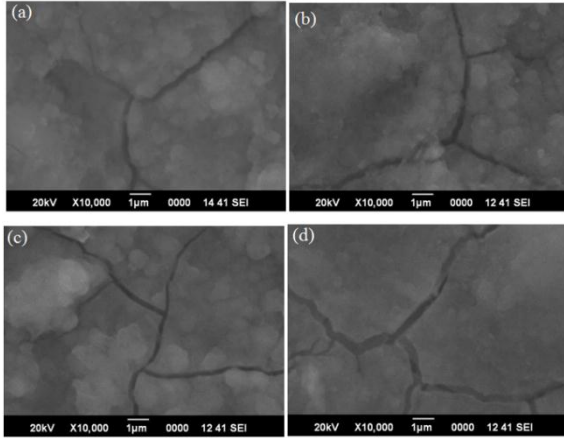


Fig.9: SEM micrographs of the surfaces of 7075-T6 aluminum alloy specimens at 10,000X immersed in 3.5% NaCl solution for 28 days (a) as-received specimen and (b), (c) and (d) are annealed samples for 4hr, 8hr and 12hr respectively.

4.0 CONCLUSIONS

- The optical micrographs of the as received sample showed coarse & fine precipitates on the surface of sample which increased strength & hardness of the 7075-T6 Al alloy.
- Annealing heat treatment applied to coarsen the grains showed a decrease in hardness profile for annealed samples
- Annealed samples of the 7075-T6 aluminum alloy results in decreasing electrode potentials (E_{corr}) in 3.5% NaCl solution.
- The most severe corrosion attack was observed on exposed surfaces of the 7075-T6 aluminum alloy specimens with 12hr annealing time. Moreover, the severity of attack increased with annealing time.
- The SEM micrographs revealed that the most severe intergranular attack was observed on exposed surfaces of the 7075-T6 aluminum alloy specimens with larger annealing time.
- Consequently, annealing of the 7075-T6 aluminum alloy resulted in the lowering of its corrosion resistance.

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