Enhancement of Corrosion Resistance of AA7075 By Using Surface Coating Method

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Abstract- *Mention In our modern technology, everyone tends to move towards lightest materials which cheap cost without negotiating in quality and performance in general. For this, alloys play a major role which leads to ultimate innovation. However alloying helps in improving a particular property but it lags behind in some other properties which must be compensated with some special processes.*

Alloy 7075 is cold aluminium with the highest strength of all grades of aluminium alloys and has good fatigue strength and average machinability, but has less resistance to corrosion than many other Al alloys. In order to improve this corrosion resistance property we selected anodizing and Plasma Electrolytic Oxidation (PEO) coating process.

We have taken two samples of AA7075 for coating and the samples are being tested for knowing the corrosion resistance property with the help of Scanning Electron Microscope (SEM) and corrosion test. By means of analyzing the test results we are going to select the coating method which provides us with better performance in general.

Keywords- Aluminium alloys, Corrosion, plasma electrolytic oxidation

I. INTRODUCTION

Alloy 7075 is a cold Aluminium with the highest strength of all grades of aluminium alloys. **7075** is an aluminium alloy with zinc as the primary alloying element. It is strong, with a strength comparable to many steels, and has good fatigue strength and average machinability, but has less resistance to corrosion than many other Al alloys.

Due to its high strength, low density, thermal properties and its ability to be highly polished, 7075 is widely used in mold tool manufacture. Introduced of Alcoa in 1943, alloy 7075 has been the standard workhorse 7XXX series alloy within the aerospace industry ever since.

It was the first successful Al-Zn-Mg-Cu high strength alloy using the beneficial effects of the alloying addition of chromium to develop good stress-corrosion cracking resistance in sheet products. Although other 7XXX alloys have since been developed with improved specific properties, alloy 7075 remains the baseline with a good balance of properties required for aerospace applications. Alloy 7075 is available in bare and AL clad sheet and plate produce forms in the annealed state as well as several tempers of the T6, T73 and T76 types.

Aluminium alloys have been the main airframe materials since they started replacing wood in the late 1920s. Even though the role of aluminium in future aircraft will probably be somewhat diminished by the increasing use of composite materials, high-strength aluminium alloys are, and will remain, important airframe materials.

The attractiveness of aluminium is that it is a relatively low cost, lightweight metal that can be heat treated to fairly high-strength levels; and it is one of the most easily fabricated of the high-performance materials, which usually correlates directly with lower costs. Disadvantages of aluminium alloys include a low modulus of elasticity, rather low elevated-temperature capability (130 °C), and in high-strength alloys the susceptibility to corrosion.

Dramatic improvements in aluminium alloys have occurred since they were first introduced in the 1920s. These improvements are a result of increasing understanding of chemical composition, impurity control and the effects of processing and heat treatment.

II. SAMPLES AND FACTORS FOR COATING

Considerations For Choosing A Coating Finish:

Many manufacturers do not realize that there is a better fit coating on the market to increase the quality of their products than the standardized coating they are currently using. Better yet, some manufacturers are not choosing the correct coating finish. Here are five considerations to keep in mind while choosing a custom coating finish for your project:

Substrate:

One of the first items to determine revolves around a simple question: *What material are you applying the paint to?* Manufacturers should think about the substrate of their product materials and everything that comes along with it. You probably already know if you need acrylic, epoxy, Urethane, etc., but consider thinking through questions like:

➢ Will surface change from time to time?
➢ Are there multiple surfaces that will need to be considered?

These types of questions help to drive the decision of what type of coating needs to be specified from the start of a project. One of the greatest revenue losses for manufacturers involves the rework and scrap from matching the incorrect coating finish with a given substrate. This type of problem could always be avoided from the beginning.

Temperature:

It's important to think about what temperature the coating will be applied, and furthermore, the temperature of the surface. Then, think about the lifetime of the product. What are the service parameters that the coated product will see after it leaves your facility? Are you manufacturing snowboards for the snowy slopes or beach umbrellas for hot temperatures? Consider the temperature that the material will be subjected to during the life of the part that is being coated.

Drying Conditions:

A common mistake manufacturers make is when the coating seems dried and they package the products for shipping, but film cure is not thorough. In this case, durability suffers and the paint peels away, fails by erosion or exhibits another form of coating or product disappointment. Asking questions about temperature up front helps match up the proper coating with the drying conditions and overall climate conditions.

➢ What are the drying conditions of the paint after application?
➢ Will the coating be force dried?
➢ Will the coating be cured under ambient conditions?
➢ Will heat be applied during the drying process?

Determine the drying conditions during the beginning stages of your project. When manufacturers package products that are not truly cured, parts will stick together in package, strip coating, and create waste or rework.

Performance:

Think about the performance requirements of the paint and make sure specifications made to the coating are all a necessity; this is similar to paying for an option that you may not need, or want. The performance characteristics can be anything from:

➢ Smoothness of film
➢ Gloss
➢ Color quality
➢ Adhesion
➢ Abrasion or Mar resistance
➢ Corrosion resistance
➢ Color retention
➢ Many others

Economics:

Price is always an object. However, we look to create coating finishes of quality and spec. Try selecting paints that meet your need to keep your customers coming back for more and the end users of products happy with their purchases.

Rectangular samples **(Shown in Figure 2.1)** of AA7075-T6 with dimensions of 20 mm $\times$ 18 mm $\times$ 3 mm were used in this present study. Prior to PEO treatment, samples were abraded with 400, 800, 1000 and 1200 grit SiC abrasive papers successively and subsequently cleaned by ultrasonicating in acetone and double distilled water for 5 min. Samples were prepared to setup in anodizing and plasma electrolytic oxidation.

(Fig 2.1) Prepared Sample

Emery Paper:

Emery paper is a type of abrasive paper or sandpaper, that can be used to abrade surfaces or mechanically finish a surface. Operations include deburring, polishing, paint removal, corrosion removal, sizing, etc. This is accomplished by moving the abrasive-coated paper, with some pressure, against the object being processed. Abrasion may be

performed by hand, electrically powered, or air powered equipment. Emery is a naturally occurring rock of impure crystalline aluminum oxide or corundum. The emery is milled and sieved into different mesh sizes. Emery of a certain size range is then bonded to a paper backing to produce emery paper.**(Shown in the Figure 2.2).** The larger the mesh size, the smaller the abrasive particles. Smaller particles abrade smaller amounts of material and are used to produce a finer finish.

(Fig 2.2) Different Emery Grade Sheets

Ultrasonic Bath Sonicator:

Ultrasonic Bath Sonicator is a surface cleaning process in order to clean the test specimen prior to coating by means of using distilled water. The cleaning usually last for 3 to 6 minutes but can also last upto 20 minutes depending upon the size of the specimen in general **(Shown in the Fig 2.3)**


(Fig 2.3) Ultrasonic Bath Sonicator
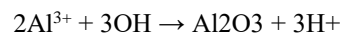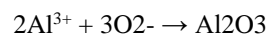
Anodizing Process:

Anodizing is a process for producing decorative and protective films on articles made from aluminium and its alloys. It is essentially a process where a thick film of aluminium oxide is built up on the surface of the aluminium

through the use of a direct current electrical supply. In the majority of anodising plants in New Zealand it is carried out in an electrolyte bath containing sulphuric acid with aluminium sheet cathodes and the work to be anodized attached to the anode When the current is flowing in the cell the following sequence of events is believed to occur. Sulphuric acid begins to , the hydrogen ions moving to the cathode where they are reduced to hydrogen gas:

$$2H+ + 2e \rightarrow H_2(g)$$
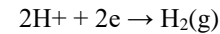
Simultaneously, negatively charged anions, i.e. hydroxide, sulphate and maybe oxide ions move to the anode. The electrical charge in the circuit causes positively charged aluminium ions (Al_3+) to be generated in the anode and in turn move toward the cathode. At the anode surface they react with the oxide/hydroxide ions to form aluminium oxide (in the case of the hydroxide ion, hydrogen ions are released into the solution)
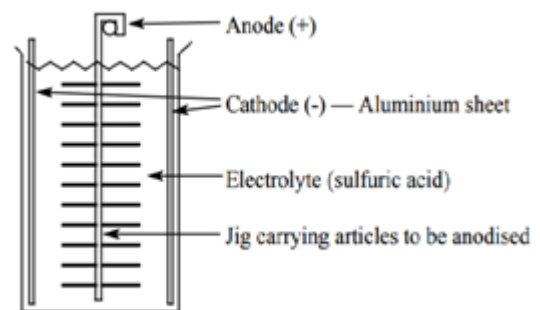
Equations of the anode reactions

$Al \rightarrow Al^{3+} + 3e$
$2Al^{3+} + 3O2- \rightarrow Al2O3$
$2Al^{3+} + 3OH \rightarrow Al2O3 + 3H+$
For which the overall process is:
$2Al + 3H2O \rightarrow Al2O3 + 6H+ + 6e$

The sulphate ions also play some part as the oxide coating contains 12 - 15% sulphate ions. It is suggested that the sulphate ions facilitate the movement of hydrogen ions reducing the cell voltages required.

(Figure 2.4) Schematic Representation Of Anodizing Process
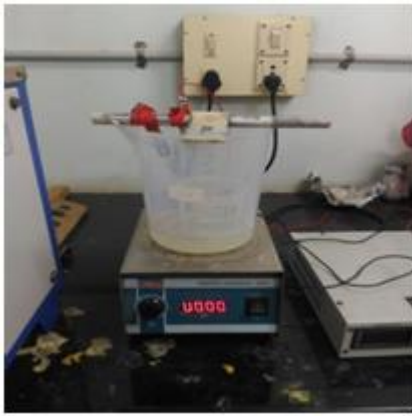
(Fig 2.5)Experimental Set Up Of Anodising

III. RESULTS AND DISCUSSIONS

The Development Of The Aluminium Oxide Layer:

Fresh aluminium reacts readily with oxygen to produce aluminium oxide. Once formed the oxide remains firmly bonded to the surface forming an impenetrable layer. Consequently, further reaction ceases. The film is very thin (0.01!m), and despite its tenacity it can be removed by abrasion and chemical corrosion. In such instances the aluminium is subject to wear or the surface will mark or become pitted at the site of corrosion.

Anodizing produces much thicker coatings (12 - 25 !m) which, if properly sealed, can extend the life of the surface appreciably. Recent research in New Zealand has shown that pitting of the surface can be reduced by up to 90% with a 12 !m coating, and by up to 93% with a 25 !m coating. In the initial stages (i.e. first 60 s) of anodising the oxide layer formed is dense and of even consistency. It provides the greatest resistance to wear and corrosion and consequently is called the barrier layer.

The growth of this layer ceases when the high electrical resistance of the oxide reduces the potential of the applied voltage in the electrolytic cell. The depth of the coating at this stage is about 0.08!m. Subsequent growth is very slow and competes with the acid reaction:

$$Al2O3 + 6H+ \_ 2Al3+(aq) + 3H2O$$
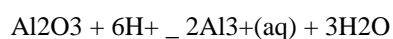
which releases Al3+ ions into the solution. Note that the H+ can be at high concentration near the oxide layer due to one of the anode reactions above. See equation (5). At low applied voltages only the barrier layer forms. However, the gradual production of Al3+ ions tends to smooth out the underlying metal surface and give a brightening effect to the article. Objects such as wheel trims and bumper bars are general treated in this way.

At higher voltages the growth of the layer continues beyond the barrier layer. Unlike the initial barrier layer this secondary layer, although constitutionally the same, has an open pore-like structure; a consequence of the competing anodising and acid solution processes.

Electron photomicrographs reveal the structure of these anodised surfaces. The conditions required to produce coatings vary according to the concentration and nature of the electrolyte, the voltage - current density applied, the alloy being anodised and the temperature of the bath. In the majority of electrolytic plants articles are anodised at a potential of 15 - 20 V and a current density around 1.6 A d-1 m -2; the electrolyte is 3.5 mol L-1 sulphuric acid maintained at temperatures between 20 and 23o C. Under these conditions the quality of the coating is satisfactory for most applications. At higher electrolyte concentrations and temperatures, and at lower voltages or current densities, the acid solution process occurs earlier in the development producing thin, open oxide coatings. Conversely, hard dense coatings are produced at low temperatures and high current densities. The conditions established in each plant are determined by the type of application.

Selection parameter for Anodizing coating platinum over AA 7075 were given in the **table-3.1**

Table 3.1 Factor and parameter used for anodizing coating

SI NO	FACTOR	PARAMETER
1	Current	0.4Amps
2	Electrolyte	0.1molar H2SO4 soln
3	Cathode	Platinum
4	Anode	Aluminium 7075
5	Time	60mins

Plasma Electrolytic Oxidation Coating:

Plasma electrolytic oxidation (PEO) is also known as micro-arc oxidation and spark anodizing is often regarded as a version of anodizing of valve metals (Mg, Al, Ti, and several others) and their alloys. Indeed, the essence of both anodizing and PEO is the production of oxide layers on a metal surface by the action of electricity in a convenient electrolyte (Shown in Fig 3.1)

An oxide layer has a complex composition and includes various oxides of a base metal, alloy additives and

species coming from the electrolyte. For both anodizing and PEO, an oxide layer forms due to electrochemical oxidation of the metal constituents and inclusion of some components of the electrolyte with possible further interactions in the vicinity of the electrode.

However, some features of PEO are clearly different than those of the anodizing. Normally, low-voltage direct currents are used for anodizing and the formation of the oxide layer occurs under a quiescent regime. The produced layer has relatively homogeneous structure with more or less evenly distributed blind pores. The thickness of an oxide layer is limited by ~ 20-50 μm for most cases, because the electrical conductivity of the oxide layer is low and the formation of the layer effectively breaks the electric circuit in the cell.
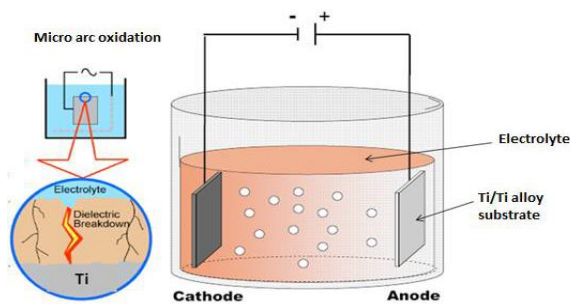

Fig 3.1 Schematic diagram showing the major components of an PEO/MAO set up and dielectric breakdown process on anode surface

For PEO, significantly higher voltages and (normally) alternating currents cause intense sparking due to micro-arc discharges that break down the oxide layer. Extreme temperatures and pressures develop in the discharge channels and cause complex phase-transformation processes that result in the production of a compact, thick hard layer, which often has attractive abrasion and corrosion resistances. Although PEO layers have a relatively high porosity, they can effectively protect the base metal against corrosion because the pores formed by a discharge can subsequently "heal" by molten oxides due to high local temperatures in the vicinity of plasma discharge channels and are therefore impermeable to corrosion media. The improved corrosion stability of PEO-treated metals as compared to bare metals has been reported for aluminum and magnesium alloys (see, for instance Both

direct and alternating current can be used for PEO. However, AC regime is preferable, because pores formed during a cathodic breakdown "heal" by molten oxides during the next anodic pulse, the electrolyte in the metal vicinity is refreshed and the produced oxide layers are more uniform. Industrial 50–60 Hz sine-wave AC voltages of 100–600V are most frequently used for the PEO processing. Due to the partial rectifying effect of the valve metal oxide, complex sew-like waves are observed in practiced

The most frequently used electrolytes for the PEO processing of aluminum and aluminum alloys are

- ➢ Sodium metasilicate (Na2Sio3)
- ➢ Potassium hydroxide (KOH) with water solution compose

(Table 3.2) Electrolytic Composition

SL. NO.	Electrolytic Composition	Grams/1.5 litreofwater
1	Sodium metasilicate (Na2Sio3)	4.5
2	Potassium hydroxide (KOH)	3

And the electrolytic solution is tested for conductivity and PH values by using its respective testing equipments.

SL. NO	FACTORS	PARAMETERS
1	Conductivity	10m²
2	PH Level	12.22 PH

Surface Morphology And Chemical Composition Of The Coatings:

The surface SEM micrograph of the PEO coated sample shows pores, cracks and pancake-like features which are typical PEO characteristics. Pancake structures spread over the sample surface indicates the spread over of the ejected molten metal oxide through the discharge channels which appear as small holes at the centre of pancake structures during the coating formation. Most of the discharge channels in are filled with ejected compounds which suggest that the higher number of fine discharges occur at high frequency (1000 Hz). In other words, the 1000 Hz frequency condition increases the spatial density of the micro-discharges and subsequently decreases its intensity as a result sealed pancake morphological features are observed. A similar observation was reported by Bala Srinivasan et al, Effect of pulse frequency on the microstructure, phase composition and corrosion performance of a phosphate-based plasma electrolytic oxidation coated AM50 magnesium alloy, Appl.

Surf. Sci. 256 (2010) 3928–3935) in the PEO treatment of AM50 magnesium alloy at 1000 Hz frequency. Micro-cracks can be observed on the surface, which could have been produced by thermal stress due to the rapid solidification of the molten metal oxide ejected through the discharge channels during the formation of coating. Fabrication of duplex coatings on biodegradable AZ31 magnesium alloy by integrating cerium conversion (CC) and plasma electrolytic oxidation (PEO) processes, J. Alloys Comp.,722 (2017) 698-715).
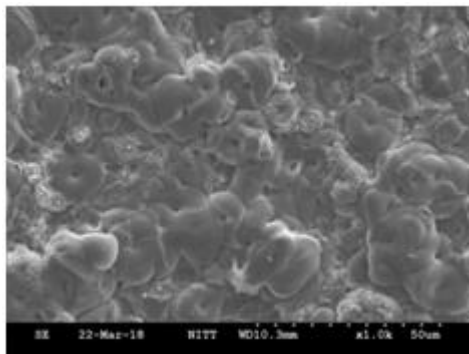
Fig 3.2. SEM Surface micrographs of the PEO coating

Surface morphology of Anodized coated sample

From SEM images of Anodized samples, we can see that the coating is uniformly formed and resemble like a dry mud with lots of cracks and some pores which denotes the rough surface formed, and small pancake like structures. The cracks may be due to evolution of water molecules during drying process.
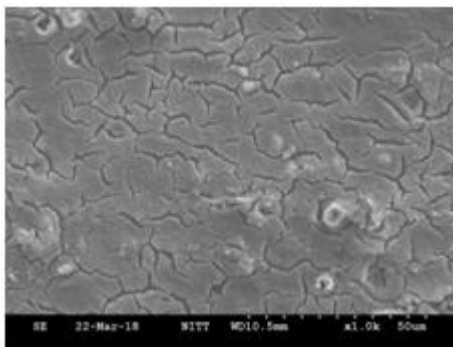

Fig 3.3 SEM Surface micrographs of the Anodized coating

Energy Dispersive Spectroscopy:

The surface composition of PEO coated sample by EDS is reported in the below **table 3.3**. The EDS analysis indicates that the Al, O and Si are major elements in the coatings. During the coating process, H+ ions are produced and react with SiO_3^{2-} from the electrolyte and forms

amorphous silica phase which appears as a granular structure on the coating surface.

Table 3.3 Surface composition of the Substrate, Anodized and PEO coated samples measured by EDS in wt.%.

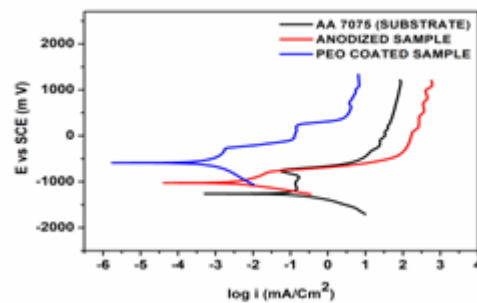| Substrate								
Element	Ti	Fe	Mg	Al	Cr	Cu	Zn	Total
Weight %	0.19	1.34	1.36	87.9	0.41	1.42	7.38	100
Anodizing								
Element	O	Na	Mg	Al	Si	Cu	Zn	K	Total
Weight %	49.61	0.15	0.49	46.88	0.12	0.19	2.54	0.02	100
PEO Coated Sample								
Weight %	45.6	0.41	1.28	4.75	44.42	0.56	2.23	0.75	100

Fig:3.4 Potentiodynamic potential curves of uncoated AA7075, anodized and PEO treated samples in 3.5% NaCl solution
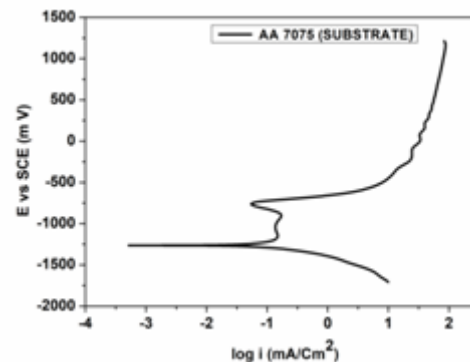

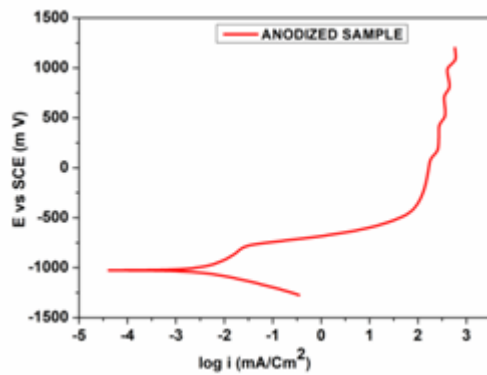**Fig: 3.5** Potentiodynamic potential curves of uncoated AA7075

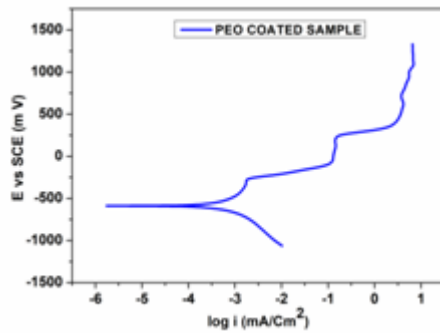**Fig: 3.6** Potentiodynamic potential curves anodized samples.

Fig: 3.7 Potentiodynamic potential curves of PEO treated samples.

The testing's are done with the following equipments:

1.Scanning Electron Microscope
2.Corrosion Measuring Cell
3. X-Ray Diffraction Spectrometer

X-Ray Diffraction

Phase analysis

The below figure depicts the XRD patterns of Aluminium substrate, anodised Aluminium and PEO coated Aluminium specimens as indicated. It can be seen that alumina peaks have formed in both anodised and peo coated specimens. From the graphs of peo and anodised aluminium, it can be observed that the peaks of alumina are evident in the peo coated sample, indicating the fact that peo gives a better alumina coating. The lesser amount of peaks in anodised sample may be attributed to the lesser coating thickness. It can also be seen that the alumina peaks in the peo coated pattern are broadened. This can be attributed to the smaller particle size of the alumina coating.
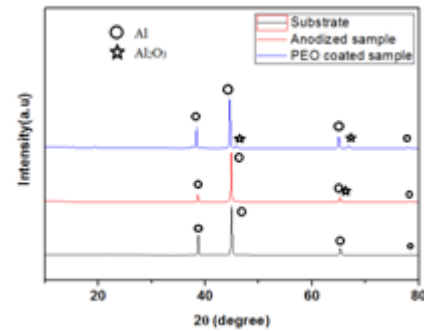

Fig 3.8 XRD patterns of the Substrate, Anodized and PEO coated samples

IV. CONCLUSION

In our project the ultimate motive is to select the best coating method for coating AA7075 which is used in aerospace industry in order to contribute a miniscule amount of work towards DRDO project..The AA7075 is successfully coated by using   anodizing and PEO processes, surface topology and corrosion test was conducted and analyzed thoroughly. From the SEM test we came to the conclusion that PEO has an upper hand because anodizing producing more micro-cracks and pores. When analyzing the corrosion test we came to the conclusion that icorr value of the PEO sample is very less when compared to that of the anodized sample. Basically for a good corrosion resistance sample the current density point value that is the icorr value should be low and hence PEO has an upper hand here also. Thus we came to the ultimate conclusion that PEO has better coating ptocess for AA7075 and hence it has been selected for coating as a whole.

V. ACKNOWLEDGEMENT

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