Variation of Surface Roughness of Chromated and Non-Chromated Al Electroplated Mild Steel

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Abstract - *On specimens of mild steel, aluminium was electrodeposited from aluminium chloride (AlCl$_3$) bath at current density 0.6-0.8 A/dm^2, electroplating voltage 2V for 30 minutes at room temperature. The concentration of aluminium chloride bath was changed from 15% v/v to 20% v/v and the differences in depositions were observed. One specimen was chromated with potassium dichromate. The surface roughness of the deposition was measured before and after chromating. The specimens were analysed under metallurgical microscope. It was observed that chromating smoothens the surface significantly. Also, H$_2$O$_2$ was added to the electrolyte to examine the changes in deposition for both conditions.*

Key Words: Surface Roughness, Electroplating, Chromating

1. INTRODUCTION

Mild steel is one of the most commonly used metals. Among the various options for its corrosion resistance, Aluminium coating is a very good option. [1] For any coating material, surface roughness plays a great role to its adhesion. [2] Also the prime cause of surface defects, crack initiation and premature failure in many metal-made components is poor surface integrity.[3] Improving corrosion properties of mild steel by surface deposition is studied by various researchers among the world. Surface depositions with Al and Al based alloys are also very popular choices to the researchers. [1][4][5] But taking surface roughness to be a factor of consideration, there are plenty of scope to study the result of different coating materials and coating techniques on mild steel. During surface modification, the surface is modified over a relatively shallow depth, using an appropriate method.

Many works of Al coatings on mild steel were carried out by the method of arc spraying, hot dipping etc. [6][7]We have chosen a cheaper alternate of all the available methods and that is electroplating. It is a well-known surface modification method where metallic coating is produced by the action of an electric current on a conductive material immersed in a solution containing a salt of the metal to be deposited.

When steel substrates are exposed to chloride containing atmosphere, Al and Al-rich coatings become active and gives very good cathodic protection (>100 mg Cl$^-$ m^{-2} d^{-1}). [8] On the other hand, chromating usually works like a coat of paint, protecting the surface from corrosion, depending on thickness of the coat. Darker coatings of chromate provide higher corrosion resistance, thus enhancing the lifespan.

Chromating solutions vary in composition, based on the metals to be coated. Any steel specimen coated with aluminium or Al-rich alloy is difficult to chromate without using any additives. A proper additive in a chromating solution aids in wetting, activating and sealing the surface and helps form a dense chromate layer over the it. [5]

In this experiment, we expected benefits like less surface roughness along with corrosion resistance after chromating of the electrodeposited Al. Results show improvement in the smoothness of the Al coating. Also,

2. EXPERIMENTAL

Chemicals used here for the electrodeposition of Al, aluminium chloride (AlCl$_3$) of analytical grade was used. For cleaning purpose, the chemicals sodium hydroxide (NaOH), sodium carbonate (Na$_2$CO$_3$), ethanol were also of analytical grade. Potassium dichromate (K$_2$Cr$_2$O$_7$) and sulphuric acid (H$_2$SO$_4$) were used in golden chromating. These were also of analytical grade.

Commercially available aluminium plates were used as anodes here. They were suitably gritted with sand papers to further ensure that no foreign bodies are on the outer surfaces.

Mild steel specimens were also commercially available ones. 2 × 1 inch^2 pieces were cut out to be used as cathodes.

The electroplating was done in two group of mild steel cathodes. Firstly with 15% AlCl$_3$ solution (500ml) bath. The voltage was used 2 volt (constant) and current density was used 0.81 A/dm^2. The pH and temperature of the bath were measured with pH meter and thermometer and were recorded 3.9 and 27°C respectively at the beginning. For the second set of specimens the bath was changed to 20% AlCl$_3$ solution (500ml). The voltage was used 2 volt (constant) and current density was used 0.61 A/dm^2. The pH and temperature of the bath were recorded 3.5 and 29°C initially. Both sets of the electroplating were allowed for 30 minutes.

The effect of hydrogen peroxide (H$_2$O$_2$) to the process was analysed by adding 50 ml H$_2$O$_2$ to 400ml solution of 15% AlCl$_3$. Input voltage and current density were kept the same. This time the pH of the bath was 3.2 at the beginning at 30°C.

2.1 Preparing the Surface of the Cathode

The specimen surfaces were polished using emery papers of grits P180, P320, P800, P1200 and P1500. To focus the results of surface roughness the polishing was done quite carefully. After that, NaOH and Na_2CO_3 solution were used for cleaning. Degreasing was done by ethanol. Finally, specimens were electrolytic cleaned and rinsed thoroughly.[9]

2.2 Chromating of Al Coated Mild Steel

After electroplating was done the specimens were rinsed well with distilled water. Then they were immersed in 10% nitric acid (HNO_3) solution for a few seconds. Again, rinsing with distilled water they were transferred to the chromating solution and dipped instantly.

2.3 Using the Chromate Solution

The chromate solution contained potassium dichromate of 125 – 150 gm/L along with sulphuric acid of 2.0 – 2.5 gm/L. Bath pH was around 1.25. The specimens were dipped for 1 minute 30 seconds.

2.4 Measuring Surface Roughness

The measurement of surface roughness was carried out before and after chromating using a probe profilometer. At least three readings were taken for each specimen and the average values are reported.

To ensure accuracy, measurements were done on horizontal and apparently flat surface every time. Roughness is reported in μm.

3. RESULTS AND DISCUSSION

Surface roughness measurement of the specimens clearly show that chromating has smoothened the Al coated surface significantly. The values of difference between the readings before and after chromating is calculated to be 32 ~ 37%.

Moreover, the effect of change of bath concentration on surface roughness is not so significant. Chart 2 shows that the smoothening of the surfaces is nearly the same for both sets of $AlCl_3$ concentrations.

**Table -1:** Surface Roughness Readings of the Specimens

Samples 15% $AlCl_3$		
	Non-chromated	Chromated
1.	6.866 μm	4.380 μm
2.	6.520 μm	4.165 μm
3.	6.581 μm	4.292 μm
Samples 20% $AlCl_3$		
	Non-chromated	Chromated
1.	7.006 μm	4.410 μm
2.	6.907 μm	4.674 μm
3.	7.618 μm	5.092 μm

The process of chromate coating involves an oxidation and reduction reaction between the hexavalent chromium (Cr^{6+}) and the metal to be chromated. According to a work of J. H. Osborne, the suggested reaction can be the following for aluminium,[10]

$$Cr^{6+} + Al \rightarrow Cr^{3+} + Al^{3+}$$
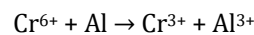
After that, hydroxides are formed within the electrolyte.

$$Cr^{3+} + 3HO^- \rightarrow Cr(OH)_3$$

$$Al^{3+} + 3HO^- \rightarrow Al(OH)_3$$
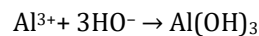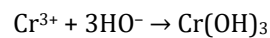
Under proper conditions, these hydroxides get accumulated on the surface of the metal. Elimination of water leads to deposition of a colloidal sol of very small particles as a hydrogel on the metal's surface. The skeleton of the gel consists of a three-dimensional arrangement of oxides and hydroxides. This skeleton encloses a liquid phase along with nanoscale elements and voids to form the gel. It can be also assumed that the structure of the gel is dependent on metal ion concentration, pH, and other ingredients of the solution, such as chelating agents and counter ions.[10]

This is how chromate coating yields a smoother, decorative and corrosion resistant surface.
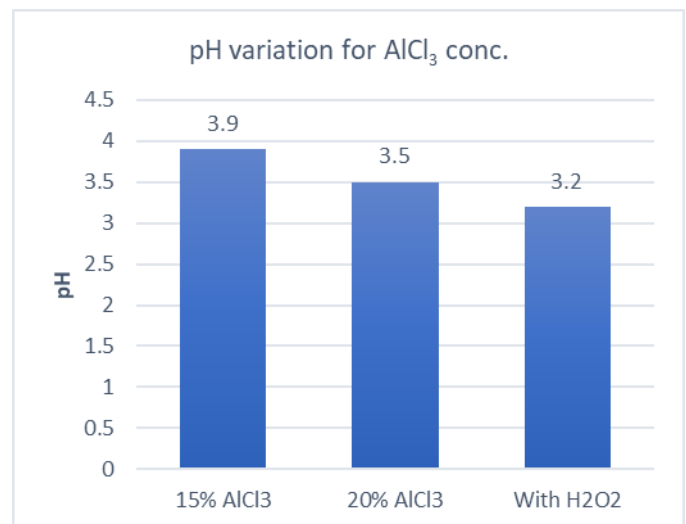

Chart -1: Bar chart for a graphical representation of pH change for change in $AlCl_3$ concentration.
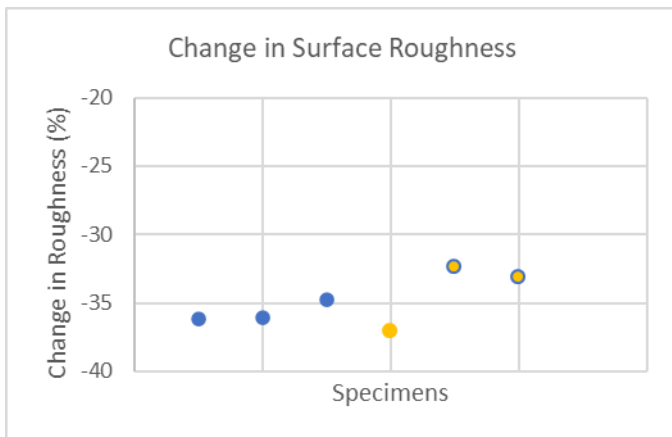
Chart -2: Representation of change in surface roughness for different specimens. The blue dots are for 15% $AlCl_3$ and the yellow ones are for 20% $AlCl_3$.

3.1 Effect of H_2O_2

The addition for H_2O_2 to the electrolyte led to a change in colour of the bath. It turned yellowish golden. After 30 minutes of electrodeposition, darker coating of the same colour was found on the surface of the mild steel specimen. This suggests the formation of iron oxides. As, H_2O_2 has the speciality of being both oxidizing and reducing agents depending on pH, the phenomenon that took place here
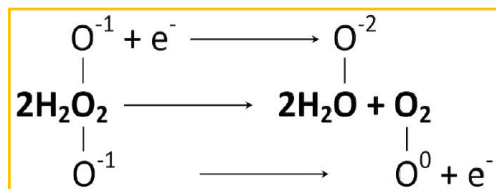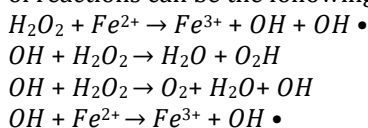

Fig -1: Disproportionation reaction of H_2O_2. Source: [11]

demands further explanation. When active catalytic surface of a catalyst is available, hydrogen peroxide can decompose and oxide easily. [11]

Fenton's reaction is a very likely phenomenon for the decomposition of H_2O_2. But it happens readily with the presence of organic compound which is not a factor in this experiment. So, the availability of Al might have contributed as a catalyst here. It is possible that H_2O_2 can decompose into H_2O and O^{2-} during the electrolysis process and this O^{2-} can oxidize Fe present in the mild steel specimen. A probable set of reactions can be the following here. [11]

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH \bullet$

$OH + H_2O_2 \rightarrow H_2O + O_2H$

$OH + H_2O_2 \rightarrow O_2 + H_2O + OH$

$OH + Fe^{2+} \rightarrow Fe^{3+} + OH \bullet$

3.2 Change in pH During Electrodeposition

For both of the electrolyte concentrations the change of bath pH was recorded. Slight increase in pH values is observed.

Chart 3 shows climbing lines of pH values. These changes have trivial significance and do not provide any special interpretation. Both the lines followed quite a similar pattern throughout the 30 minutes span.

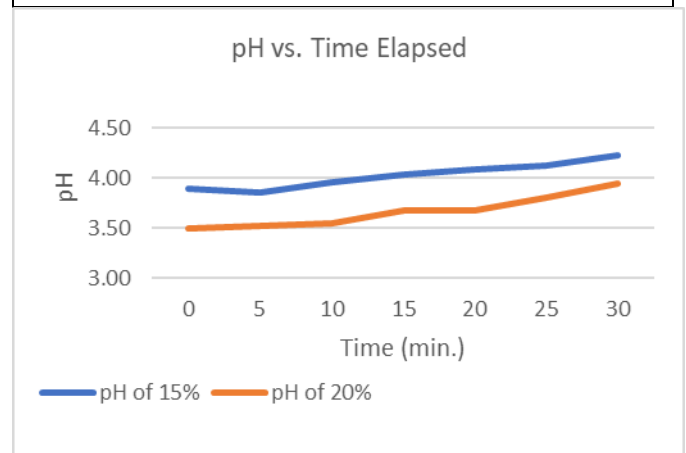| Time (min)	pH of 15%	pH of 20%
0	3.90	3.5
5	3.85	3.52
10	3.96	3.55
15	4.03	3.68
20	4.09	3.68
25	4.13	3.8
30	4.22	3.95

Chart -3: Change in pH value reading throughout the electrodeposition process.

4. CONCLUSION

In this work, aluminium was deposited from aluminium chloride ($AlCl_3$) bath on mild steel specimens. The concentration of aluminium chloride bath was changed from 15% v/v to 20% v/v and the differences in depositions were observed. When the concentration of electrolyte was increased, better deposition was found. Values of pH varied very slightly throughout the experiment. Increasing $AlCl_3$ concentration decreased the pH value. The most profound outcome of this experiment is – the surface roughness of reduced significantly after chromating. Chromating with potassium dichromate smoothened the aluminium coating from 32 to 37%. Addition of hydrogen peroxide didn't yield any jubilant result. After H_2O_2 was added with $AlCl_3$ solution, it gave dark yellowish golden deposition on mild steel and this suggests a premature oxidation. Hence it was not considered to be a good additive to the electrolyte.

The experiment has further scope of work for the future. Doing an SEM and EDS study of the colourful deposition on the specimen when was H_2O_2 added, would have given a broader explanation of what really happened. Moreover, finding the effect of different additives, temperature change etc. on the chromate solution is a scope of future works. Wear resistance and adhesion of the coating may show

differences when various experimental parameters will be changed. These are some of the other things to be explored in the future.

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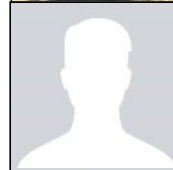
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