Optimization of Surface Treatment Parameters for Development of Lab Scale Pilot Plants

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Certificate

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Dedication

Our work is dedicated to our family, friends and the faculty at SCME.

Acknowledgement

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Abstract

The purpose of this project was to anodize and passivate the substrates, and to develop teflon and metaflex coatings at lab scale. The main parameters optimized were Voltage, Time, Concentration of Chemicals and Temperature of the baths. The scope of this project is to develop aerospace and marine coatings for multipurpose applications (corrosion resistant, non-stick applications etc.), following ASTM and Military and Industrial standards.

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Chapter 1: Introduction

Surface treatment is any process that is done on a surface to enhance its characteristics in any way. In today’s world it is all about how one surface of a certain material can be manipulated to enable it to develop or acquire an additional set of qualities. These qualities can be used to provide aesthetics, reflectivity, improved hardness etc. Surface treatments are being used by major industries like aerospace, marine, food industries etc. and all these uses them to ensure and enhance the quality for a lower cost. These surface treatments can be electrochemical reactions taking place on the surface or simply a physical deposition of the coating. These electrochemical reactions are depended on different variable like the voltage, the chemical concentrations being used, and the reaction time and where as physical deposition depends on morphology, composition of the coating, the pressure of the air gun being used if any. And all these parameters play a role in determining the quality of the surface treatment.

In order to optimize the different parameters that effect surface treatments and therefore the final result, it is necessary to first develop the setup of the coating being optimized. Once the setup is up, made by following international standards, and study of the thermodynamics has been carried away the most influential of the variable is studied while others being constant. This tells about which variable is the most effective and at which conditions the best result is produced. Hence the optimum parameter is reached.

To research this and optimize different surface treatments the use of commercial sized parts is not efficient, as it becomes relatively more time consuming and difficult to characterize. Therefore, a lab scale testing plant is needed where different materials can be treated and then studied upon to optimize, to link them with different coatings and make hybrids.

In the world today, a lot of research on similar terms is happening and to start that here in Pakistan the development of the said lab scale plants becomes necessary. And this is where this thesis plays its role. A field visit was done to see the applicability and it was seen that there was a deficiency of understanding of these coatings and how they worked and could be enhanced.

The aim of this research is to produce lab scale setups of 4 different surface treatments; Passivation, Anodizing, Teflon, and Metaflex, so reproducible and repeatable results can be achieved and therefore further studied upon. These material chosen for the coatings are stainless steels for passivation as it is a process that stainless steel due to its high chromium prefers, and for the other three the material chosen is aluminum due to its high number of applications in many industries and products.

Passivation and anodizing are electrochemical reactions whereas Teflon and metaflex and physical depositions. Passivation is reaction of the surface with its environment and in stainless steel it happens in air as well i.e. the development of the passive layer but that is a long process. Doing it in a bath with a specific concentration and temperature speeds up the process and makes the layer development in our control in the sense how quick it can develop since the process is not continuous.

Anodizing is an electrochemical oxidation process which is a continuous process and the voltage and time given to the process defines the oxide layer being developed. Teflon and Metaflex are deposited physically on the surface and that require expertise in the control of the air gun and pressure. If the morphology is enhanced in so much that it adheres to the surface better the coating is done better.

By defining the coating being developed in this thesis, their resulting properties define the scope of this project, which is to produce corrosion resistant, hydrophobic, insulated coatings that can be used in marine or aerospace applications. Other combinations of qualities can be achieved by making hybrids of the coatings or changing the parameters and all that control etc. is covered in this thesis.

This thesis includes a brief over view of the thermodynamics and how these coatings came into being. Furthermore, the details of the setup of the coatings are explained along with the international qualification standards as defined by the American Society for Testing and Materials (ASTM) and characterization.

Chapter 2: Literature Review

2.1. Passivation

Stainless steel was discovered by Harry Brearley in 1913, named so because of its property to not rust or stain under conditions where common wrought iron would corrode. Further in the development of stainless steel, various forms were developed and categorized by their microstructure[1] as mentioned below:

- Austenitic
- Ferritic
- Martensitic
- Duplex
- Precipitation hardening alloy

The difference among these types is due to variation in composition, with high amounts of chromium, which leads to different cooling properties and ultimately a different structure, upon which they are named[1]. Considering the region of concern for this thesis, austenitic and martensitic stainless steel has been discussed in detail below.

Austenitic Stainless Steel:

Austenitic stainless steels as the name suggest have an austenitic structure. With a maximum of 0.15% carbon and 16.1 to 25 % chromium, it is graded as 300 by ASTM standards. Nickel is added as an austenite stabilizer giving a FCC structure to it, therefore ensuring properties like non magnetism and low brittleness. In addition to these they are also weldable, as they are stable even at higher temperature[2]. Cold working can be performed to change the properties of the steel as needed.

Martensitic Stainless Steel:

Martensitic stainless steel as specified by ASTM is the 400-grade series. They are composed of carbon, nickel, chromium and molybdenum in a lower proportion that allows growth of martensite. 400 grades are not as corrosion resistant as others, since amount of chromium and other elements added are relatively lower. Due to martensite they have properties like high strength and toughness. And similar to other stainless steel they can be heat treated to change their properties as required by the application. But unlike austenite as nickel added is quite low they do show magnetic properties[3].

As it can be seen by the Time transformation diagram[4] martensite transformation at room temperature is possible considering the thermodynamics, if the needed driving force is provided by external forces providing sufficient shear. Therefore proper composition and temperature has to be provided to ensure our needed structure is obtained[5]. Therefore, martensitic and austenitic stainless-steel stability is dependent on their composition and cooling rates.

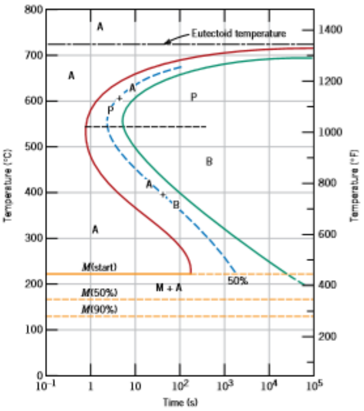


Figure 2.1 TTT diagram for Iron Carbon [1]

Stainless steel owes its name to the process of passivation. Passivation is an electrochemical reaction of the metal with its environment[6] forming a thin layer within the thickness range of few nanometers[7]. It is this thin passive layer that decreases the possibility of other chemical reactions from taking place, by acting as an impediment between the moisture and the surface. This corrosion resistance coupled with good mechanical properties is what makes stainless steel one the most commonly used materials[8].

Kier discovered metallic passivity in the 1790 when he observed that after a while of coming in contact with nitric acid the metal from being strongly corroded reached its passivation state and hence stopped corroding. And later explanations of this observation were provided by Michael Faraday in 1836[9]. Upon further research in 1960s it was discovered that this was due to the formation of an oxide layer on the metal surface[10]. Passivation since then has been studied with potential current curve in which the anode is made of different metals. The result of once such curve is shown in the figure below[11]. Later in research it was observed that as the pH of the solution was decreased the potential became more positive, therefore thermodynamically proving that it was the formation of a thin oxide layer that lead to the passivity of metals whose thickness increases with increase in anodic potential[12].

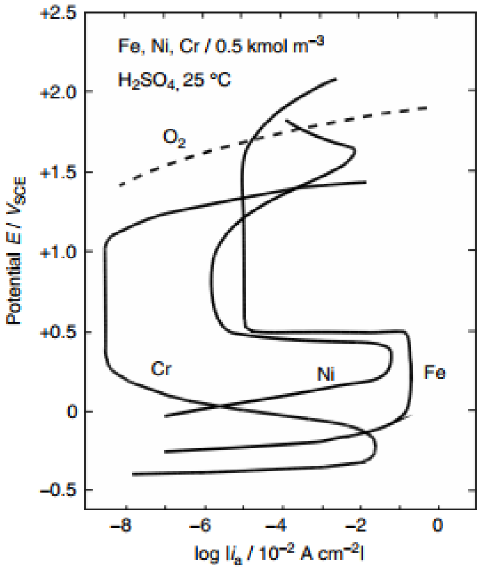


Figure 2 2 Potential Current Curve [11]

If an alloy is rich with an element that rapidly passivates, that element will contribute towards its resistance against corrosion. Chromium in stainless steel plays this role due to it having relatively higher affinity with oxygen[13] relative to other alloying elements added. Other elements also play a role like nickel, molybdenum but chromium as is in the maximum proportion it decreases the deoxidizing capability of other elements hence it is the main contributor and does not affect any other property of stainless steel negatively. The optimum amount of chromium has been agreed upon by researching the effect of chromium weight percent on the corrosion rate of the material surface[14] minimum 10% chromium is needed.

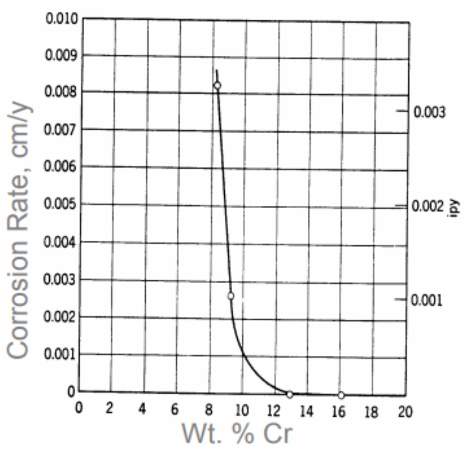


Figure 2.3 Change in corrosion rate with Cr of Fe-Cr alloys in water spray [14]

Chromium goes through the following reactions to form the passive layer, which makes the surface to appear more cleaner and smoother[15].

$$2Cr + 3H2O \rightarrow Cr2O3 + 6H^{+}(aq) + 6e^{-}(M) \qquad (2.1)$$

In stainless steel this thin surface layer of oxide has two parts; one which is rich in chromium and iron oxide and the other with chromium hydroxides depending on the environment conditions[16]. It is not so that a thicker layer will provide maximum resistance but the one with least defects. As defects cause the underlying alloying elements leak out and cause surface damage[17].

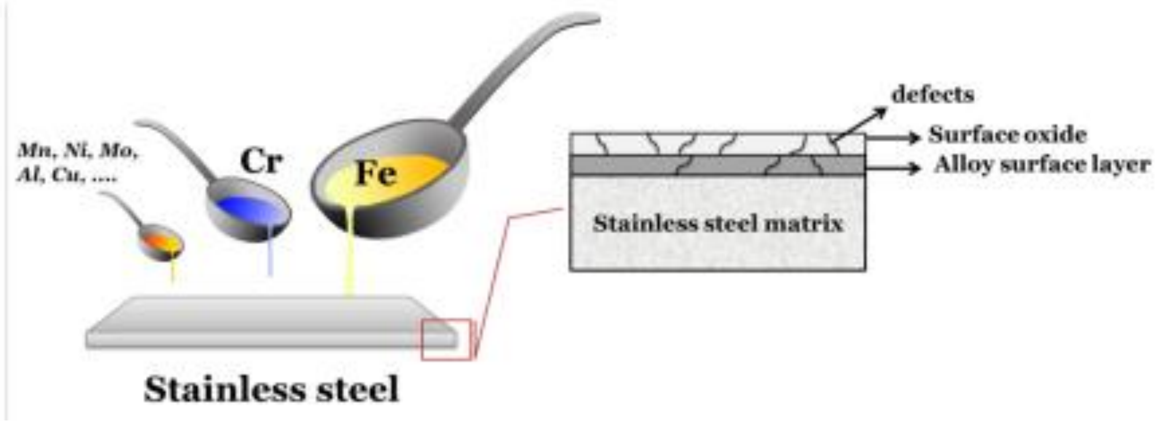


Figure 2.4 Illustration of stainless steel surface layers[17] .

The passive film formation is entirely depended on its environment, any strong ions, like chlorides or heavy weight halides in case of stainless steels[18] can cause the film to deteriorate. This leads to further defects and breaking of the film that can either initiate repassivation (as it is a spontaneous process) or pitting corrosion[6].Pitting corrosion is defined as the corrosion that starts from a small point and eats the material through if the corroding environment is not removed. Materials without a protective layer are more likely to go through uniform corrosion[19].

Stainless steel has been industrialized over the years due to its high corrosion resistance coupled with good mechanical properties. Different organizations like ASTM (American Society of Testing and Materials), NACE (National Association of Engineers), have therefore researched on to perfect the chemical passivation process and have now standardized it in the ASTM standard A038.

The process has been designed for different grades of stainless steel. The core of this process is to not only form a passive layer but to ensure no unalloyed iron remains on the surface as that can be a cause of corrosion, imperfect coating and can lead towards wrong material identification.

A common problem that arises when the material is exposed to an acid, a hydrogen environment, during this standardized process is hydrogen embrittlement. Hydrogen embrittlement is the diffusion of atomic hydrogen into the material, which causes a decrease in mechanical property by increasing brittleness. Therefore, baking is followed after the material has been passivated. [20] Baking is a process by which the material is heated high enough so that the hydrogen can diffuse out and the mechanical properties of the steel are not corrupted[21].

2.2. Anodizing

Aluminum has been heavily used since its discovery in the 19th century, during the roman era It is famous[22] for its properties of high strength, light weight, corrosion resistance, ductility, and more such mechanical properties. These properties are the reason that aluminum has such diverse applications and has replaced many commonly used materials in the industry, with its most common use being in the aerospace industry[23]

Aluminum anodic treatment has been under study since the 20th century, in order to enhance the surface of aluminum. Not only this study has led to a development of a protective, decorative surface layer, but the porosity of the film has also been used to develop membranes, nanowires, nanotubes and more such advanced applications[24].Anodizing of aluminum is an electrochemical oxidation process in which a cathode is fixed in the tank and your target metal, in this case aluminum, acts as anode .Oxygen needed for the formation of the oxide film is provided by the electrolyte being used which is a strong acid. These oxygen atoms make bonds with the aluminum on the surface leading to development of a barrier film with a honey comb structure on the naked surface[25].This structured porosity of the film allows different coloring of the aluminum surface and can also be sealed. Many patents have been produced for coloring of aluminum with anodizing, in the 1950s and since then it has been frequently used[26]

Other than coloring and sealing for better corrosion resistance, anodizing is used to make the surface more adhesive for better coating, along with improved lubricity. It also enables to detect surface flaws (if chromic anodizing solution used) and insulates the surface.

With time, more techniques have developed, that lead to a better understanding of every process, electron microscopy is one example, with which the structure of aluminum oxide was discovered, in 1953 by Keller[27]. Over the next 40 years further characterization was done by the scientists. And since then many organizations have worked to further work into this discovering new and better applications by improving the porous structure of the alumina.

Aluminum oxide develops spontaneously in air due its really low change in Gibbs free energy[28]. The following two reactions can take place:

$$2Al(s) + \frac{3}{2}O_2\,(g) \rightarrow \alpha Al_2O_3(s) \qquad \Delta G^\circ = -1582\text{kJ/mol} \tag{2.2}$$

$$2Al(s) + 3H_2O(l) \rightarrow \alpha Al_2O_3 + 3H_2(g) \quad \Delta G^\circ = -871\text{kJ/mol} \tag{2.3}$$

In electrochemical anodization this oxide grows on the anode leading to evolution of hydrogen gas. In order to form the porous layer both the chemical and electrical formation of oxide needs to occur simultaneously in the tank [28, 29];

$$Me + xH_2O \rightarrow MeO_x + 2xH^+ + 2xe^- \quad \Delta G^\circ{}_{el} \tag{2.4}$$

$$MeO_x + 2xH^+ + nE^- \rightarrow [MeE_n]^{n-2x} + xH_2O \;\; \Delta G^\circ{}_{ch} \tag{2.5}$$

These two reactions define the entire thermodynamics of the porous film formation during anodizing. It is required that the ΔG° el is lower than that of ΔG° ch, so that a stable oxide is also developed, since the latter is responsible for the breakdown of the oxide as can be seen by the equations above[29]. The following graphs;

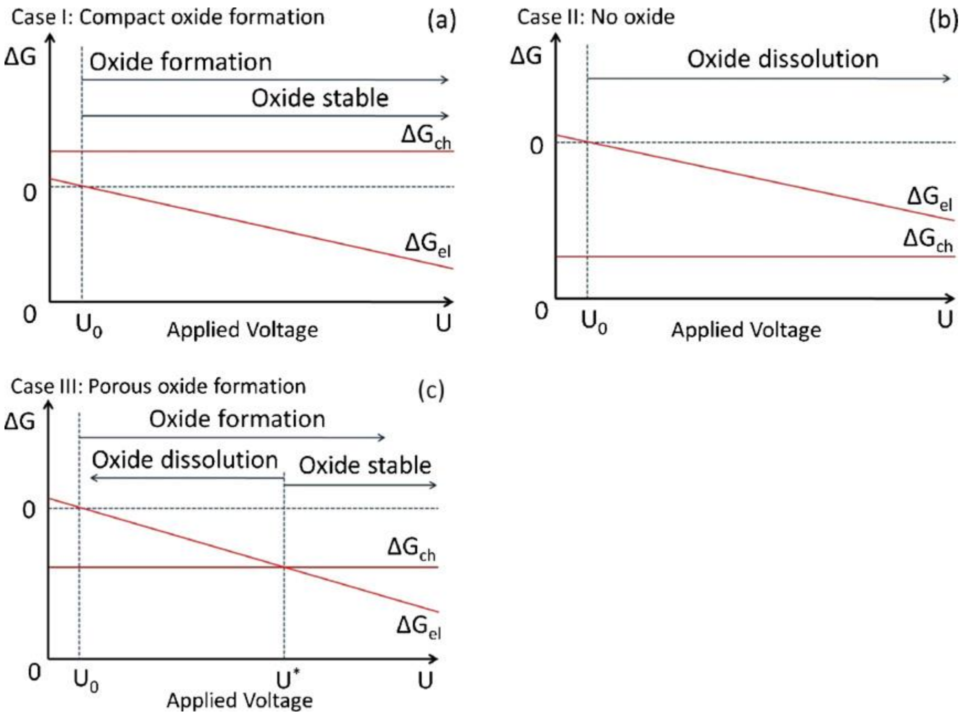


Figure 2. 5 Porous film formation as related with Gibbs free energy [29]

In the process at the cathode there is an evolution of hydrogen gas, which is reduced from its ionic condition and formation of alumina at the anode, the oxidation part of the reaction. Therefore, aluminum anodizing is like any other redox reaction. To calculate the Gibbs free energy for the electrochemical reaction taking place Nernst equation is used which uses gas constant, temperature(Kelvin) and faradays constant[30];

$$E = E_{\circ} - \left(\frac{RT}{zF}\right) \ln(\frac{[red]}{[ox]}) \qquad (2.6)$$

Placing all the constants in the equation above we get the final equation for anode potential:

$$E = -1.55 - 0.0591pH \qquad (2.7)$$

Now considering the thermodynamics there are two types of films that can be made, a barrier film and a porous film[31]. The barrier film is dense, compact and non-porous. It is the active layer of the two and quite thin. This thinness of the film, coupled with defect, causes conduction through the film even with no pores. Depending on the process conditions and parameters like time electrolyte, temperature etc, the film thickness and its properties can be affected. The pores are formed, as mentioned above, when the formation of the oxide happens at a rate slower than the rate at which it is dissolved by the solvent. Again, the porous film properties can be varied with changes in the mentioned parameters. For example, if the acid used is more concentrated it will produce a more porous film than the one with lower concentration. Therefore, upon the end application acid baths, temperatures and other parameters are decided.

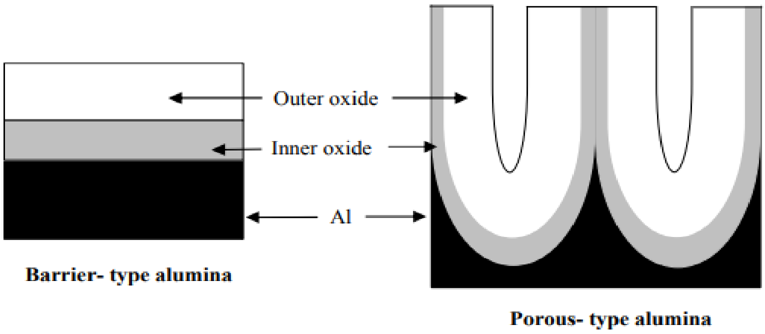


Figure 2.6 Schematic diagram for barrier and porous film [31]

Considering the thermodynamics and kinetics discussed above, it can be seen that anodizing is a continuous process. Therefore, the parameters can be controlled so that the required properties can be achieved which are determined by the film strength and thickness. Both of which can be determined by using the Pilling-Bedworth ratio, in short the P-B ratio[32].It is the ratio between volumes of the elementary cell of the metal oxide to that of the metal employed. For aluminum the ratio found is 1.28. It can be described the following equation;

$$R_{PB} = \frac{V\ oxide}{V\ metal} = \frac{Moxide\ .\rho metal}{n.Mmetal\ .\rho oxide} \qquad (2.8)$$

If the R_{PB} is less than 1, then the coat is too thin and can be broken easily hence it will not be that effective. If it is greater than 2, the coating can chip off and hence again are of no use. Therefore, it is ideal to keep it between 1 and 2 as that will provide maximum protection and the coat will not break easily [32, 33]

Once the thermodynamics and kinetics of the process were well understood the standardization of the process was followed by further research in the 20th century[33]. Two acids have been standardized and used since then, which are chromic acid and sulfuric acid. Films produced by the two have a set of different properties and therefore depending on the end application the decision is taken. Chromic acid is used mostly when a ductile film is needed. Other than this it is quite useful to detect defects as it produces colored stains. Whereas sulfuric acid is used when a harder or a colorless film is needed[34] . There are chances some of the acid getting trapped inside the film, in this case the use of chromic acid is more beneficial as it will not cause any corrosion on the metal surface.

Recent research has been concentrated on the use of oxalic acid relative to that of sulfuric acid since its disposal, storage is more feasible. Results obtained with the use of oxalic acid together with sulfuric acid have been seen and the most observed result is an increase in hardness of the film obtained[35]. In addition to this oxalic acid is been found to be able to develop greater pore sizes, thicker and more durable films. The optimum properties achieved so far has been with a bath of sulfuric acid coupled with oxalic acid.

2.3. Metaflex

Metaflex coating, developed by the efforts of AkzoNobel Aerospace Coatings has the brand name Metaflex FCR Primer. It is a wash primer that works on the principle of mechanical anchoring in which the chromate conversion coating acts as an alternative to pretreatment required during chemical conversion coatings.

A filiform coating that provided not only resistance to corrosion and better adhesion of different organic primers like epoxy primer but is also used for the reactivation of the anodized parts that are aged or sealed, including the reactivation of the aged chromate alloys. It is also designed for strip ability that can be used with alkaline paint removers. It has been developed as an equivalent to Alodine 1200, a coating that can be sprayed. [36]

The wash primer according to the Akzonobel consists of different components [37]:

Name	**Percentage**
Propan2-ol	50-75
Potassium hydroxyoctaoxodizincatedichromate(1-)	10-25
Phenolic resin	2.5-10
Toluene	1-2.5
Isobutyl acetate	1-2.5
Talc , not containing asbestiform fibres	1-2.5
Butan-1-ol	1-2.5
Barium chromate	0-1

Table 2.1 Composition of FCR primer

According to Akzonobel the FCR Hardener consists of different components [38]:

Name	**Percentage**
Propan2-ol	50-75
Phosphoric Acid	<10
Toluene	20-25
Butan-1-ol	20-25

Table 2.2 Composition of FCR hardener

When the FCR primer is to be coated on the substrate it is mixed with FCR Hardener and thinner in a fixed ratio, and that mixture is applied over the object. The major industries using this product are the Airbus, FFV and Boeing.

Coming towards the coating and how they develop, the mentioned composition makes the Metaflex FCR primer a wash primer, that when coated on the metal substrate forms both organic and inorganic films. These wash primers are fast drying, having a low odor and can be recoated unlimited time. The soluble constituents react with the metals and first form the inorganic film. The inorganic part is later on deposited over the inorganic film as the solvent starts to evaporate. And the inorganic forms as a protective action. Following this the inhibitive chromate film develops when the coating is penetrated by water, present in the environment.

The formation of the inhibitive chromate film is due to the high surface activity of the coating applied, that leads to a chromate conversion reaction. Phosphoric acid is present in the compositions as it is a strong oxidizing agent, causing a redox reaction to take place converting the hexavalent chromium to be reduced to the trivalent chromium along with the oxidation of aluminium to trivalent aluminium [39]. The reactions are:

$$Al \rightarrow Al^{3+} + 3e- \qquad (2.8)$$

$$HCrO_4^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_20 \qquad (2.9)$$

These trivalent bodies in the coating are responsible for the protection against corrosion. This is due to the fact that an insoluble hydrated oxide of trivalent chromium has formed, and the hexavalent chromium provides protection against any future attacks as a reaction with the oxidizing species will develop a trivalent chromium following corrosion. [40]

Even though such chemical reactions and conversions take place once the metaflex has been applied but the adhesion process of the coating is mechanical anchoring. This means that the coating is mechanically bounded to the surface of the substrate on which the coating is being sprayed, given that it contains roughness, pores, holes etc. something to bound with. The coating penetrates these undercuts and pores, curing there and forming a hard mass, resulting in mechanical anchoring. The schematic is as follows:

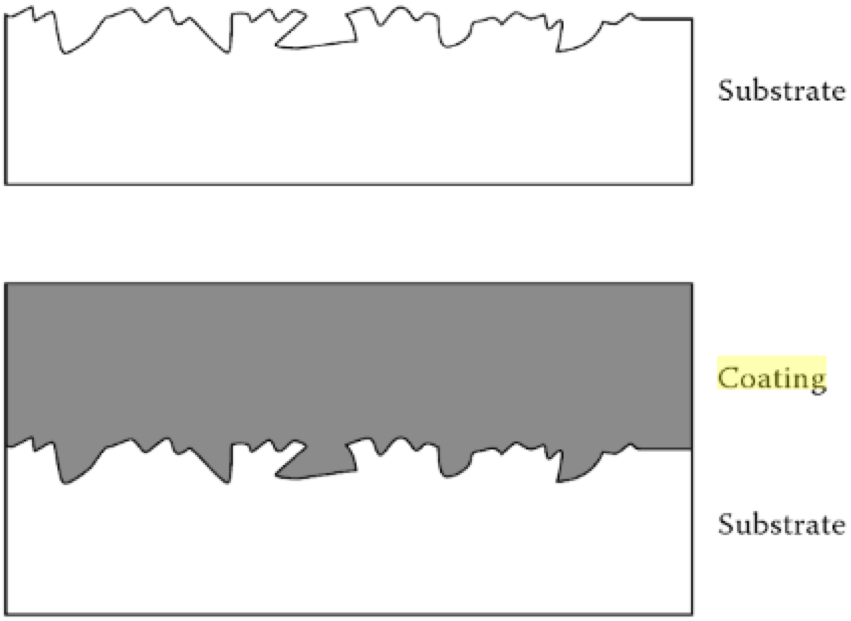


Figure 2.7 Way of mechanical anchoring [41]

For the adhesion to be strong proper penetration of the mixture is needed so that there is maximum interface between the coating and the surface of the substrate otherwise air can be trapped and this accumulation of the air bubbles lead to delamination or simple removal of the coating. The mechanism is shown below[41]:

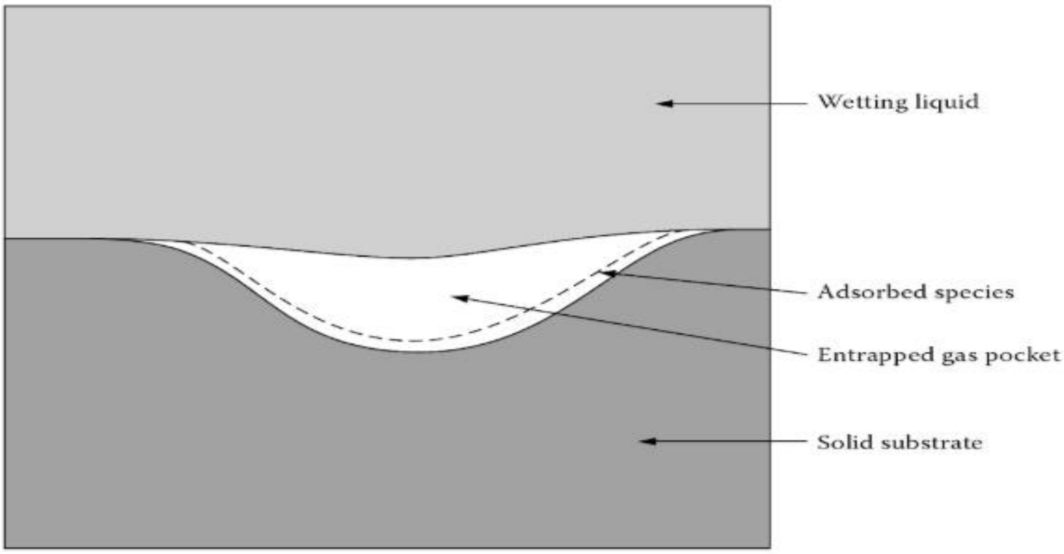


Figure 2 8 Incomplete wetting resulting in entrapped air in a depression [41]

Therefore, to avoid this and achieve optimum results the spray equipment being used, the surrounding temperature, the humidity and the air flow (ventilation) in the area where the coating is being done should all be considered and ensured to meet the standard conditions. The visible indication of an improper coating is that the desired color and appearance of the coating is not achieved.

2.4. Teflon

Teflon was discovered in 1938 by Roy Plunkett while he was attempting to make refrigerants of chlorofluorocarbon. He discovered that the tetrafluoroethylene gas flowing in the pressure bottle had stopped and the weight measure of the bottle signaled to the point of it being empty. Upon cutting the bottle apart he discovered a slippery waxy white material that had made a coat on the interior of the bottle. After analyzing he found that tetrafluoroethylene had polymerized due to the high pressure and the iron container acting as a catalyst, and hence Teflon was discovered [42]. Teflon is the registered trademark of the DuPont Company for the fluoropolymer resin that it owns [43]. Teflon is a synthetic polymer also known as polytetrafluoroethylene.

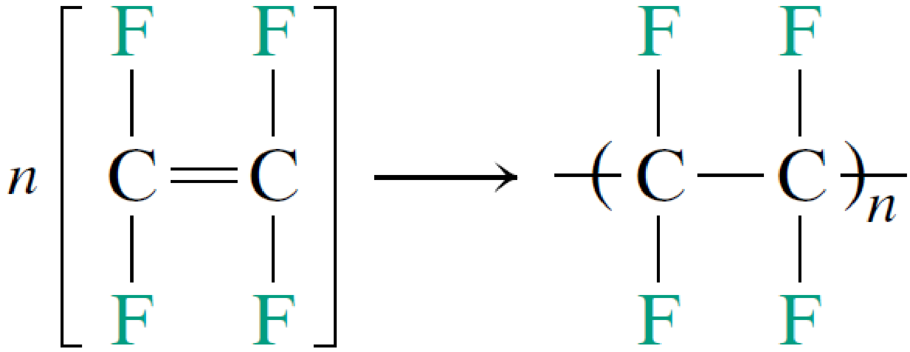


Figure 2.9 Structure of tetrafluoroethylene (left) polymerized to Polytetrafluoroethylene (right) [4]

Teflon consists of only carbon and fluorine but its high molecular weight makes it a solid and is white in color. It is famous for its nonstick property and hydrophobic nature due to the high electronegativity of the fluorine and can be categorized as a thermoplastic. Since it is non-stick it has a very low coefficient of friction and is used in cookware for the same reason. It is non-reactive due to the strong bond present between its chains of C and F and can’t be crosslinked. The fact the Teflon is chemically resistant it hence offers protection from corrosive reagents as well. Other than this it is nonflammable, non-adhesive, non-soluble, has low dielectric constant, shows flexibility at low temperatures and stability at high temperatures.[43]

A lot of work is being done on Teflon and DuPont has made different types of teflon coatings: [44]

2.4.1. Teflon PTFE

This is the Teflon type used for this thesis. It is a two-coat system consisting of a primer and a topcoat, which have high operating temperatures up to 260 degrees Celsius and low temperature applications till 240 degrees Celsius. Other than this the two coats have a low coefficient of friction and show good chemical resistance. The commercial name for this type is DuPont Teflon PTFE DISP 30 which is milky white and an aqueous dispersion of the Teflon which is stabilized by a non-ionic surfactant. The components present are [45]:

Components	Concentration
Polytetrafluoroethylene	55 - 65 %
Polyoxyethylene alkylether	1 - 5 %
Water	35 - 40 %

Table 2.3 Components of DISP 30

2.4.2. Teflon FEP

Fluorinated ethylene propylene copolymer (FEP) provides a non-porous coating as it melts and flows back and forth during the baking process. This is available in both liquid and powder form. It shows excellent properties and can be used up to 204 degrees Celsius.

2.4.3. Teflon one coat

It is a solvent based liquid coating, with different blends of fluoroplastics and resins to achieve enhanced properties. It offers high toughness and resistance to abrasion.

2.4.4. Teflon PFA

It is the same as FEP, the only difference being that it offers high temperature applications up to 260 degrees Celsius and film thickness of up to 40 mils hence overall better properties than FEP.

Research is being done on Teflon to achieve the optimized properties, like Coefficient of friction at low sliding speed which was found to be around 0.05-0.08 which is very low and provides great non-stick applications. Furthermore, a phase transition occurs for Teflon at around 20 degrees Celsius due to which at higher temperatures Teflon shows increase in friction. Hence research is being conducted to improve the properties of Teflon and explore what more it has to offer. [46]

These properties define the effect it has on the surface it is coated upon. The coating itself follows a mechanical anchoring method as discussed in **Section 2.3**. Along with mechanical anchoring Teflon follows a melt flow process, as it goes from liquid to adhered coat. That melt flow process allows Teflon to adhere well to the surface and therefore there is a need for the surface to be roughened by sand blasting to ensure the presence of grooves and valleys leading to better adhesion of the coating. Other than this roughness is also needed since Teflon itself is nonstick it needs it to be able to adhere on to the surface. [41].

In order to get the best adhesion and best properties the surface has to be pretreated accordingly, and that is the base of this thesis as well.

Chapter 3: Experimental

3.1. Passivation

3.1.1. Sample Background and Preparation

To carry out the experiment for passivation three different grades of Stainless Steel; 304, 316, 420 were taken. Different grades give the capability to see the extent of the process therefore providing the capability to broaden the study. The composition of these grades is displayed in the table below[47].

SS	**C**	**Mn**	**P max**	**S**	**Si**	**Cr**	**Ni**	**N**	**Mo**	**Others**
420	0.15 min	1.00	0.040	0.030	1.00	12.0-14.0	0.75	…	0.50 max	…
304	< 0.07	<2.00	0.045	<0.15 to 0.35	<1.00	17.00 - 19.00	8.00-10.00	<0.11	…	Cu < 1.00
316	< 0.07	< 2.00	0.045	< 0.015	<1.00	16.50-18.50	10.00-13.00	<0.11	2.00 – 2.50	…

Table 3.1.1 SS Compositions [47]

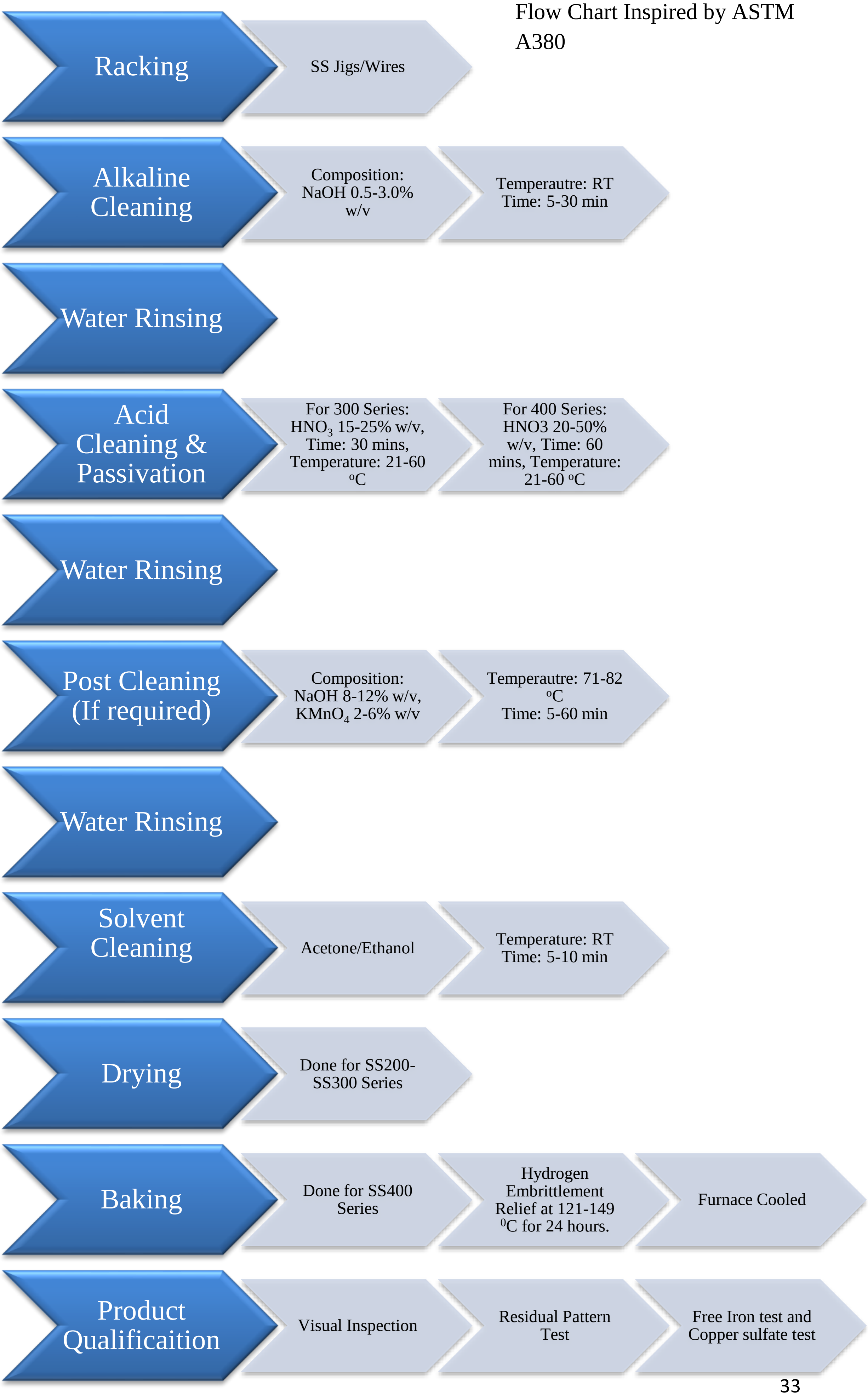
400 series of Stainless steel are martensitic in nature and 300 series are austenitic[1, 2].

3.1.2. Experimental Setup

The samples of the above-mentioned grades; 304,316, and 420, were cut into pieces of diameter 1cm and length 1cm so characterization to be followed could be carried out easily.

Following the ASTM standard, A380 samples were provided with the required conditions to be passivated. The cleaning before and after the oxide layer has developed is not a part of the passivation process[20].The following flow chart demonstrates the steps leading to the oxide layer formation and the qualitative techniques followed after to determine the success of the process.

Flow Chart Inspired by ASTM A380



Racking	SS Jigs/Wires		
Alkaline Cleaning	Composition: NaOH 0.5-3.0% w/v	Temperautre: RT Time: 5-30 min	
Water Rinsing			
Acid Cleaning & Passivation	For 300 Series: HNO_3 15-25% w/v, Time: 30 mins, Temperature: 21-60 ^{o}C	For 400 Series: HNO3 20-50% w/v, Time: 60 mins, Temperature: 21-60 ^{o}C	
Water Rinsing			
Post Cleaning (If required)	Composition: NaOH 8-12% w/v, $KMnO_4$ 2-6% w/v	Temperautre: 71-82 ^{o}C Time: 5-60 min	
Water Rinsing			
Solvent Cleaning	Acetone/Ethanol	Temperature: RT Time: 5-10 min	
Drying	Done for SS200-SS300 Series		
Baking	Done for SS400 Series	Hydrogen Embrittlement Relief at 121-149 ^{0}C for 24 hours.	Furnace Cooled
Product Qualificaition	Visual Inspection	Residual Pattern Test	Free Iron test and Copper sulfate test

Prior to following the chart, it was crucial to ensure that the sample is free of any rust, smut, heat tints etc. as these cannot be removed by the standard cleaning processes to be followed. This could have been done chemically by employing pickling or mechanically by grinding, sand blasting and other similar processes[48]. The samples as they were cut did not need to be cleaned by either of the mentioned methods.

After this the following steps were performed step by step as shown in the flowchart above:

3.1.2.1. Alkaline Cleaning

Following the complete mechanical cleaning of the surface (if needed) alkaline cleaning was performed. Here Sodium Hydroxide solution was used due to it being a strong base which ensured removal of polar bodies like fats by either emulsification or conversion of the fat to glycerol and soap, if it was originated from anything other than petrol like vegetables[49]. Once sufficient time had passed the samples were rinsed in water to ensure that no unwanted chemical reactions took place.

3.1.2.2. Acid Cleaning and Passivation

Nitric acid was used as it is a strong oxidizer allowing proper cleaning of scale and passivation. Hydrofluoric acid was used in combination with HNO3 as a reducing agent descaling the surface by reducing the unwanted oxides[50]. A combination of the two acids ensures good cleaning and oxidizing of the surface.

HF was not used for 400 series of stainless steel in accordance with the code F of the ASTM A380 standard[20]. This is done due to the composition of the 420 grade being used; low Ni, low Mn, and low Cr hence the stainless steel will corrode under the influence of HF[8]. Again, the samples were rinsed before shifting to the other bath.

3.1.2.3. Post Cleaning

At times some formation of smut on the samples was seen and in this case the sample was placed in a post cleaning solution of Noah and KMnO4[51]. This specific solution was used as sodium hydroxide removes excess acid and KMnO4 is an oxidizer which ensures no damage comes to the oxide layer. Water rinsing was followed.

3.1.2.4. Drying:

To ensure complete removal of water the surface was dried and cleaned with acetone as well.

3.1.2.5. Baking:

Since the samples were placed in an acidic environment, exposing the sample to free hydrogen which is the cause of hydrogen embrittlement in stainless steel. Therefore to prevent the severe consequences of hydrogen embrittlement the samples were baked at 132 °C for 24 hours[20, 51]. Following the standard 420 was baked and not 300 series as the 420-grade due to the low alloy composition is more prone to hydrogen embrittlement.

The concentrations of the baths used during these different steps are demonstrated in the table below. Neither the acid nor the base was added first in the bath, this prevented any severe reactions from taking place. Small amount of water was added prior to the addition of other constituents, unless mentioned otherwise.

Bath (400 ml)	Concentration	Temperature (°C)	Time (minutes)
Alkaline Cleaning	NaOH 2g/100ml	Ambient	30
300 Passivation	HNO3 23ml/100ml HF 1ml/100ml	35	30
400 Passivation	HNO3	35	60
Post Cleaning	NaOH 10g/100ml KMnO4 4g/100ml	75	10

Table 3.1.2 Passivation Baths[47, 51]

Shifting from one bath to another the samples were rinsed in distilled water, and all aqueous solutions were made in distilled water as well. Distilled water was used to ensure that no chlorides came in the solutions, as they are a cause of corrosion[52]. The temperatures were achieved by using a heating plate or heating rod and a thermometer to cross check the temperature displayed.

3.1.3. Qualification Tests

After the sample had gone through all the above defined processes certain qualification tests were done to ensure the success of the recipe used. Various tests are defined in the standards out of which the following were performed; visible test, residual pattern testing, free iron test and copper sulfate test.

3.1.3.1. Visible test

As soon as the sample was passivated it was seen that the sample was cleaner and monotone, relative to the initial sample surface, indicating the formation of a passive layer[53].

3.1.3.2. Residual Pattern Test

The sample was heated in an oven at 60°C for 20 minutes. This provided sufficient time to show the presence of any foreign body. Upon heating no water spots or scarring was seen. If upon heating the opposite was observed, presence of water spots, or any scars that would have meant that the coat was not adhered properly and was therefore contaminated[54].

3.1.3.3. Free Iron Test

A simple test that makes it easy to determine the presence of any free iron on the sample. Free iron as the name determines is the iron that has not been alloyed. It is often the result of different fabrication techniques, and if not properly cleaned can remain on the surface.

The test was carried out by wrapping the sample or wiping the surface with a wet cotton cloth [50]. If any iron was present on the surface it would have reacted with the water and would have had formed oxides which appear as rust, giving a visible indication where the passive layer had failed [53]. No rusting meant no free iron as present.

3.1.3.4. Copper Sulfate Test

Looking at the electrochemical series[55, 56] it can be seen that the redox reaction between iron and copper allows aqueous copper to solidify as it is replaced by iron.

$$Cu^{+2} + 2e^{-} \rightarrow Cu(s) \qquad \text{E= 0.337V} \qquad (3.1)$$

$$Fe(s) \rightarrow Fe^{+2} + 2e^{-} \qquad \text{E= 0.440V} \qquad (3.2)$$

$$Fe(s) + Cu^{+2} \rightarrow Fe^{+2}(aq) + Cu(s) \text{ E= 0.777V} \quad (3.3)$$

This redox reaction was used to test our surface for the presence of any free iron. If any amount of free iron was present due to the above reaction the copper would deposit on the surface and a shade of orange would have been seen on the surface of the sample. This is also referred to as copper plating[57].

The test was performed using a copper sulfate solution; for an aqueous 400ml solution 6.4g copper sulfate and 1ml sulfuric acid is used [47]. H2SO4 enhances the colorimetric behavior[58].

Since 400 grades of stainless steel are low alloyed and have a lot of iron, this grade always shows coloring under this test as copper plating occurs. Therefore, does not hold accountability.

3.1.3.5. Continuity Test

It was performed in a similar way as in Section 3.2.3 and since passivation coating is conductive. The samples cleared the test and were completely conductive.

All these tests are simple go or no go tests which indicated that our baths were performed under the right conditions

3.1.4. Characterization techniques

Once the process was performed it was characterized to ensure whether the results obtained so far were because of chromium oxide layer or not. To determine the formation of chromium oxide passive layer, the characterization techniques chosen were Scanning Electron Microscope with EDX (Energy Dispersive X-Ray Spectroscopy) and XRF (X-ray Fluorescence). The techniques were chosen among others because of their capability to give elemental analysis of conductive and insulating bodies.

3.1.4.1. EDX

Refer to Section **3.2.4.1.**

3.1.4.2. XRF

XRF is a technique for elemental analysis, in which fluorescence is used. The basic working principle of the technique is that the when atoms of any element are given energy, they get excited. Under the influence of this excited state, there is an emission of X-ray photons which are characteristic to that element therefore allowing the identification of elements and their quantity[59].

Similar to SEM an electron beam is used, which when strikes the surface produces photons and photoelectron. Theses photoelectrons are produced from the shells near to nucleus (K shells) as defined by Bohr model) and the gap between these shells and the outermost shell is compensated by their kinetic energy, the difference between the binding energy and the incident energy.

Since an electron has left the atom a hole is produced, and to fill this space an electron migrates. This migration of the electron leads to the production of fluorescence[60].

The energy of the ray emitted is equal to the difference between the excited state energy and relaxed state energy of the electron i.e. the initial and the final state. Now this photoelectric absorption can also cause production of Auger electron, as that is another way the atom can move to the relaxed state. A spectroscopic data is formed to determine the probability of getting the photons produced instead, determined by the fluorescence yield. And that is on what the XRF machine is built [59].

3.1.4.3. XRD

An analytical technique that is used to identify phases of crystalline material and provides the unit cell dimension or d-spacing is known as X-ray powder diffraction (XRD). The working principle behind XRD is that the crystalline substances diffract the incoming x-ray wavelengths in three dimensions similar to inter planner spacing in a crystal lattice. In XRD, monochromatic X-rays are used that are generated from a cathode ray tube in the direction of the sample.

When the condition suffices the Bragg’s law i.e. constructive interference takes place due to the interaction of the sample and the incident rays and the diffracted rays are then detected and processed. The scanning is done through a range of 2 theta angles. The diffraction peaks are converted to d-spacing which allows the identification of the sample because each mineral has a unique set of d-spacing. This is possible due to the comparison with the standard reference patterns. Generally, CuKα radiation = 1.5418Å are used for XRD. A graph of 2-theta and counts per second is plotted after XRD is done. This is how XRD works.[61]

3.1.4.4. Tribometry

Refer to Section **3.3.4.1.**

3.2. Anodizing

3.2.1. Sample Background

To study the process of anodizing we chose the Al 2219 T6 as our substrate. Al 2219 was chosen because of it being the most commonly used commercial grade of Aluminum in the market. Al 2219 T6 composition is as mentioned in the table below: [62]

Component	Weight %	Component	Weight %	Component	Weight %
Al	91.5-93.8	**Mn**	0.2-0.4	**Ti**	0.02-0.1
Cu	5.8-6.8	**Other each**	Max 0.05	**V**	0.05-0.15
Fe	Max 0.3	**Other, total**	Max 0.15	**Zn**	Max 0.1
Mg	Max 0.02	**Si**	Max 0.2	**Zr**	0.1-0.25

Table 3.2.1 Composition of Al 2219 T6

3.2.2. Experimental Setup

The samples of Al 2219 were cut into pieces of various sizes, with punches made for the samples to be able to be jigged. It is common practice to make the punches in the area of least significance. The samples were engraved with an ID, using a scriber, to ensure easy recognition once the process was completed. All the pieces were pre-cleaned once they had been visually inspected for scratches, nicks etc. Since our pieces were supplied fresh they had no imperfections on the surface. After which they were solvent cleaned using non-inflammable chlorinated hydrocarbon solvent, Trichloroethylene, to remove all grease, solid particles that could be on the surface. After solvent cleaning the sample is prepared for anodizing.

The steps mentioned in the flowchart (refer to next page) were followed as mentioned in the order. Once the pre-cleaning was done the following steps were performed.

3.2.2.1. Jigging and Racking

Since the experiment was being done on a lab scale the jigging was done using aluminum wires, that were tightly wrapped around the punches to avoid any lose connections that can burn the sample.

3.2.2.2. Pre-Cleaning

In this step the sample was chemically cleaned and alkaline etched with rinsing in-between. For chemical cleaning following the ASTM standard B117 the equivalent to the military standard mentioned above, the composition of the chemical cleaning bath was;

Component	Quantity
Sodium Carbonate	5-15 g/l
Trisodium Phosphate	4- 6 g/l
Alkalinity	pH 9 – pH11

Table 3.2 2 Pre-cleaning

The sample was placed in the cleaning bath for 3-10 minutes at ambient conditions. After this the sample was rinsed and the alkaline etched to remove any oxides on the surface. Alkaline etching left behind a black smut which is why after rinsing de-smutting was done using Nitric Acid 25-50% volume ratio. After which the samples was rinsed once more to ensure no excess acids remained on the surface of the sample. [63]

3.2.2.3. Water Break Test

To see whether the surface was clean or not from all the oil and grease the sample was tested in distilled water, in a water break test. It is a quick, simple nondestructive test that tells about the cleanliness of the surface. Once the sample has been pre-cleaned it is then placed in the distilled water. Now if the sample surface is clean then either a clear well-defined line will appear or there will be no line. But if there are water spots on the surface or even patches that means the surface is contaminated. The samples cleared the test.[64]

The following flowchart shows the steps carried out and the order which is made by following the military standard **MIL–A–8625F**.

3.2.2.4. Anodizing

The anodizing bath is prepared using sulfuric acid 15 wt% which acts as the electrolyte for our electrochemical reaction. According to the standard the operating conditions are kept within the optimum range of 12-22 DC Volts where using 18V provided the best results under room temperature conditions, for 40 minutes. The voltage was controlled using a rectifier. The bath self-heated due to the reaction being exothermic.[65]

During the process it was seen that there was vigorous agitation in the bath, as bubbles of hydrogen gas were being produced over the lead cathode. The chemical reactions taking place in the anodizing bath are mentioned in the literature review chapter.

3.2.2.5. Sealing

The samples were removed and rinsed in distilled water before they were placed in the sealing baths and are visually inspected for a clean smooth surface. Then the samples were placed in the water sealing bath and potassium dichromate bath, at boiling point and 97 degrees. The dichromate bath is of 48 –52- g/l, which is responsible for leaving behind an anodic coating of a yellowish color.

3.2.2.6. Drying, Removal and Storage

The samples were removed from the jigs and dried under ambient conditions and stored in desiccators.

The anodizing bath solution and the chemical cleaning solutions were made in plastic jugs with the water being added first followed by the addition of the chemicals.

3.2.3. Qualification Tests

Once the samples were obtained they were sent for product qualification testing. According to the military standard being followed the qualification, which is mentioned below.

3.2.3.1. Visual Inspection

Visual inspection was carried out by inspecting the sample surface for a uniform, smooth and permanent color of sealing. Permanent coloring is seen by sliding a finger across the sealing and if it sticks then the sealing is permanent. There should be no burning on the samples due to contact points. One sample did burn due to the lose connections, which was indicated by black spots near the punches. Along with burning shade variations are observed as well and it was seen that there were no variations in our final samples that were sealed at the optimum condition mentioned.[66]

3.2.3.2. Coating Thickness Test

Digital coating thickness meter was used to measure the coating thickness in microns. The standard thickness to qualify should be between 1.8µm~25.4µm, for the coating to qualify. Our coating achieved a thickness of 6.2um.[60]

3.2.3.3. Continuity Test

This test was performed using a simple multimeter in which the contact lead was moved on the surface and if the multimeter at any point gave a value other than 0 meant current was flowing and hence the coating was not done right, since Aluminum oxide layer is nonconductive. The samples cleared the test and were completely nonconductive. [67]

3.2.3.4. Salt Spray Test

The salt spray test was carried out to test the corrosion resistance of the coated sample. For the coating to qualify the standard ASTM B117, the sample was sprinkled with 5% NaCl solution and this was performed at room temperature and pressure for 15 days. [65]

3.2.4. Characterization Test

3.2.4.1. SEM and EDX

In SEM an electron gun is used to generate electrons which are directed by different electromagnetic fields and lenses in order to focus the electrons on the sample surface. Like any electron gun to avoid unnecessary interactions a vacuum environment is created. When the electrons hit the surface, they cause an emission of electrons and photons of different types like back scattered electrons (BSE), secondary electrons (SE), X-Rays etc. For this to happen it is necessary that surface is a conductor otherwise an argon coating is needed for the said interaction to take place. BSE and SE provide with information regarding the composition of the surface and the topography, respectively[68] in an image. Any loss of electrons will decrease the image's resolution, making it difficult to analyze the data[69].

Along with BSE and SE, X-Rays are also generated. These X-Rays help determine the elements present, as the wavelength of the x-ray emitted is characteristic to that element. This lays down the foundation of EDX. Using EDX the electron beam can be placed over different spots of the surface to give an elemental analysis of the surface as an average[70].

The samples were characterized using SEM and EDX both, before and after the passivation process, to ensure that the correct grade was processed- the right way- and the passive layer had formed. This was made certain by analyzing the difference between the results of two elemental analyses taken.

3.2.5. Optimization by Voltage

It is known that the voltage controls the thickness. This theory was put to test as the samples were prepared and each sample was placed at a higher voltage keeping all the other conditions constant. This was done to optimize the coating using voltage so it is knowing which voltage will produce which thickness of coating.

3.3. Metaflex

3.3.1. Sample Background

Metaflex coating was carried out on the sample of Al-2219 T6 (Solution heat treated and artificially aged). The composition of the sample is given below: [62]

Weight%	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Others	V	Zn
2219	Bal	0.20 max	0.30 max	5.80-6.80	0.20-0.40	0.02 max	0.10 max	0.02-0.10	0.050 each 0.15 total	0.05-0.15	0.10-0.25

Table 3.3.1 Al-2219 T6 Composition

3.3.2. Experimental Setup

Al-2219 was cut into different pieces of size 3 inches by 3 inches by 0.12 inches and then prepared for metaflex coating. Following the Akzonobel standards, the sample were prepared according to the requirements to achieve optimum coating. [36]

The samples were prepared according to the flow chart (refer to next page):

3.3.2.1. Solvent Cleaning

Solvent Cleaning was done with trichloroethylene to ensure that before the application of the FCR primer coating the sample was free of any grease and surface contaminants. [49]

Rinsing: And then the sample was rinsed with distilled water properly.

3.3.2.2. Alkaline Cleaning

Trisodium phosphate of 5g/L was used as an alkaline cleaning solution and the sample was dipped in this solution bath for 10 mins and at 60°C. This was done to ensure that the sample was free from all traces of oil and grease, solid dust particles or other markings. [49]

Rinsing: The sample was then rinsed thoroughly with distilled water.

3.3.2.3. Etching

The sample was etched in caustic soda (NaOH) solution of concentration 7% at temperature of 65°C for 5 minutes. On weld beads residual blackish smut may be present after etching. [49]

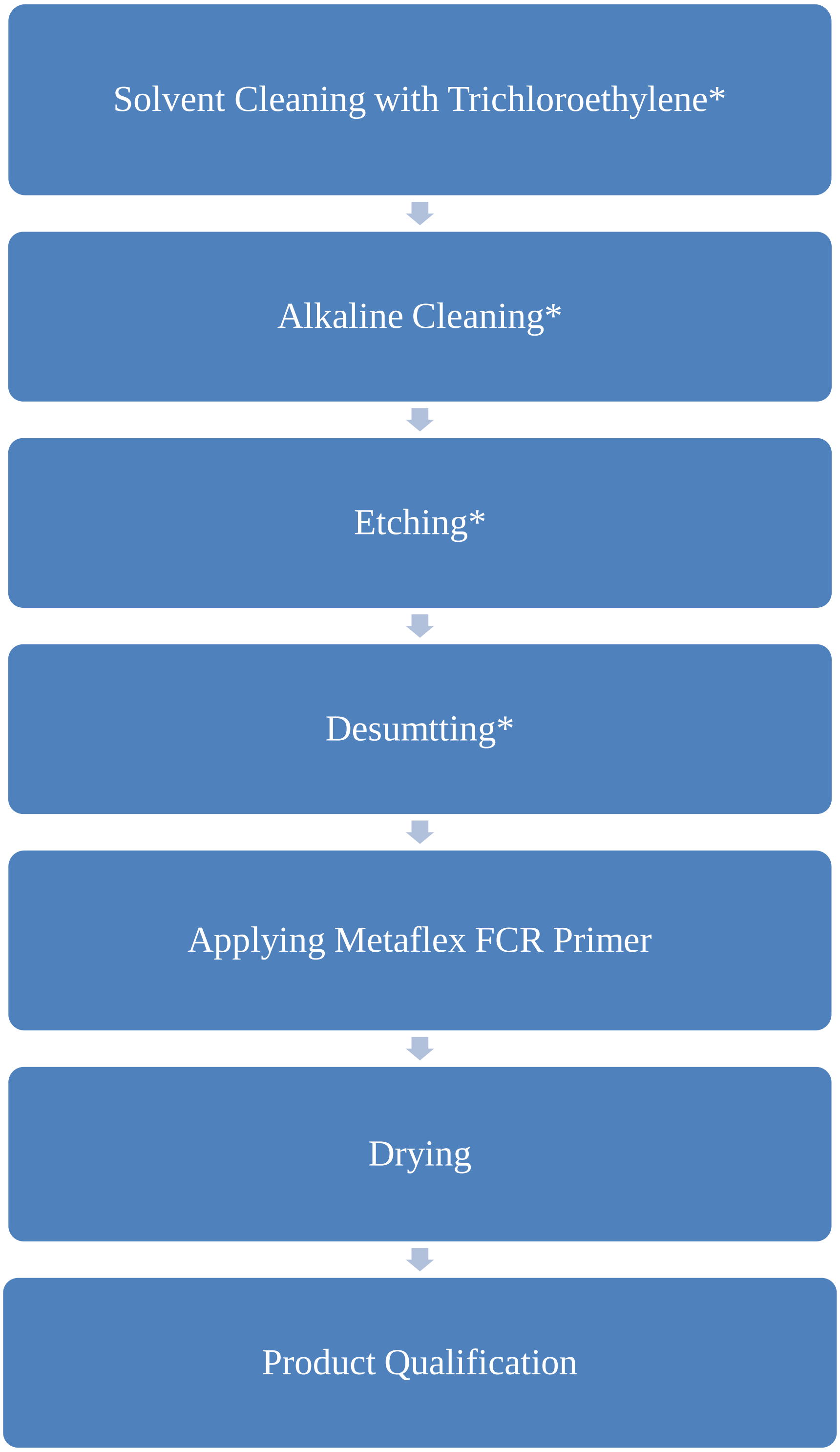
Rinsing: After etching the sample was rinsed with distilled water thoroughly.

3.3.2.4. Desumtting

The sample that showed smut was then dipped in a dilute nitric acid bath of 35% by volume at room temperature for 5 minutes and the black smut was removed completely and a uniform matt surface was obtained. [49]

Rinsing: Then the sample was rinsed again.

Flowchart showing the process of metaflex coating performed on Al-2219 substrate according to **AkzoNobel standards [36]:**



***Water Rinsing**

3.3.2.5. Application of Metaflex FCR Primer

By using spray deposition method, the premix Metaflex compound was applied over the sample surface at room temperature. This was done properly by following the standard practice for manual spray deposition technique i.e. the spray gun to be held perpendicular to the sample and whipping the gun in an arc for proper deposition of the coating.

The mixing ratio by volume of the metaflex components used according to AkzoNobel was as follows:[36]

Mixing Compounds	Ratio
Metaflex FCR Primer	1
Metaflex FCR Hardner	2
Thinner C 25/90S or equivalent	1/4

Table 3.3.2 Metaflex mixing ratio

Metaflex premix was prepared using the following method:

- All three components to be mixed were acclimatized at room temperature.
- The FCR Primer was stirred till all the pigment were uniformly dispersed.
- The metaflex FCR hardener was added to the primer and the mixture was stirred properly.
- The thinner was added in ¼ ratio maximize the spraying viscosity and the mixture was stirred to gain a homogenous mixture.

3.3.2.6. Drying

The sample after the coating was applied was left to air cool for 15 minutes.

3.3.3. Qualification Tests

After the sample was prepared according to the AkzoNobel standards, the sample went through certain qualification tests to check whether it was up to the standards or not. Various tests that performed were: Visible Inspection, Film thickness, Post boiling water fingernail test, and crosshatch test.

3.3.3.1. Visible Inspection

Metaflex coated sample is visually inspected to see for any powdery or loose coating, voids, scratches, flaws, and any other defects which might reduce the serviceability of the parts and also the color of the coating is noted that whether the color is yellowish or not and that the coating is smooth. [36]

3.3.3.2. Film Thickness

Digital Coating thickness meter (Model No. CM-8826FN) was used for measuring the thickness of the sample in microns and thickness should be in microns. It uses the principle of eddy current to measure the thickness. [71]

3.3.3.3. Adhesion Strength

Adhesion test was performed on the metaflex sample to find out the adhesion strength of the coating according to ASTM D4541. The test performed was by using Elcometer 510 Model S UK origin, with a dolly size of 20 mm and a pull rate of 0.7 Mpa per second according to the standard. [72]

3.3.3.4. Salt Spray Test

The salt spray test was carried out to test the corrosion resistance of the coated sample. For the coating to qualify the standard ASTM B117, the sample was sprinkled with 5% NaCl solution and this was performed at room temperature and pressure for 7 days. [65]

3.3.3.5. Continuity Test

It was performed in a similar way as in Section **3.2.3** and since metaflex coating is nonconductive. The samples cleared the test and were completely nonconductive. [67]

3.3.4. Characterization Techniques:

After the metaflex process was performed, it was characterized to ensure that whether the coating was giving the required properties. The technique performed was tribometry. This technique was chosen because it was necessary for the testing of the wear resistance and coefficient of friction of the coating.

3.3.4.1. Tribometry

A tribometer is an instrument that measures the tribological (science of interacting surfaces in a relative motion with each other) quantities, for example, the frictional force, the coefficient of friction, the wear volume etc. between the two interacting surfaces. Pin on disk tribometer was used to test the sample to find out its coefficient of friction and the wear rate.

A pin on disk tribometer consist of a rotating disk with a stationary pin above it. The pin used to simulate the specific contact geometry was spherical. The coefficient of friction found in this is by taking the ratio of the frictional force/loading force on the pin. This was done according to ASTM standard G 99. [73]

The indenter of the pin on disk tribometer was made up of 100Cr6 Steel ball of 6mm diameter. Other specifications were:

Radius	**10mm**
Speed	40cm/s
Normal Load	10N
Total Distance	250m

Table 3.3.3 Parameters of Tribometer

3.3.4.2. SEM and EDX

Refer to Section **3.2.4.1.**

3.4. Teflon

3.4.1. Sample Background

Teflon coating was carried out on a sand blasted sample of Al-2219 T6. The composition of the sample is similar to as given in Section **3.3.1**. [62]

3.4.2. Experimental Setup

Al-2219 was cut into different pieces of size 3 inches by 3 inches by 0.12 inches and then prepared for teflon coating. Following the Dupont standards, the sample were prepared according to the requirements to achieve optimum coating. [74]

The samples were prepared according to the flow char (refer to next page):

3.4.2.1. Sample Preparation

In case of some samples that were already Teflon coated, the coating was removed by sandblasting. The job was inspected for smooth, crack free surface. In case of rough surface or presence of scratches, the surface was made smooth and clean.

3.4.2.2. Prebaking

Before prebaking of job, the furnace needs to be cleaned and inspected. The temperature controller and indicator were checked for calibration. The sample was then heated to 345°C and held at this temperature for 25 minutes. The sample was air cooled afterwards. Prebaking was done to ensure that all organic surface contamination has been removed and was done at a slightly above the final cure temperature that prevents the formation of blisters, discoloring or removes any remaining surface contamination from volatizing that might happen during the curing step.

3.4.2.3. Sandblasting

Most of the teflon coated substrate require the surface to be roughened by sand blasting to ensure that good adhesion is there. The blasting medium needs to be free of any contaminants and for that reason sand was used. Compressor was first cleaned and inspected for smooth operation. For ferrous non-ferrous sample i.e. Al-2219, fine sand was used of 20 mesh count and the pressure used was of 6 bars obtain optimum coating. The pressure of compressor was adjusted according to the surface roughness of sample required. The job was later cleaned with emery paper. Sand blasting roughens the surface of the sample and allows better adhesion. This was done according to ASTM D1730. [75]

3.4.2.4. Solvent Cleaning

Solvent Cleaning was done with trichloroethylene to ensure that before the application of the prime coating the sample was free of any grease and surface contaminants. [49]

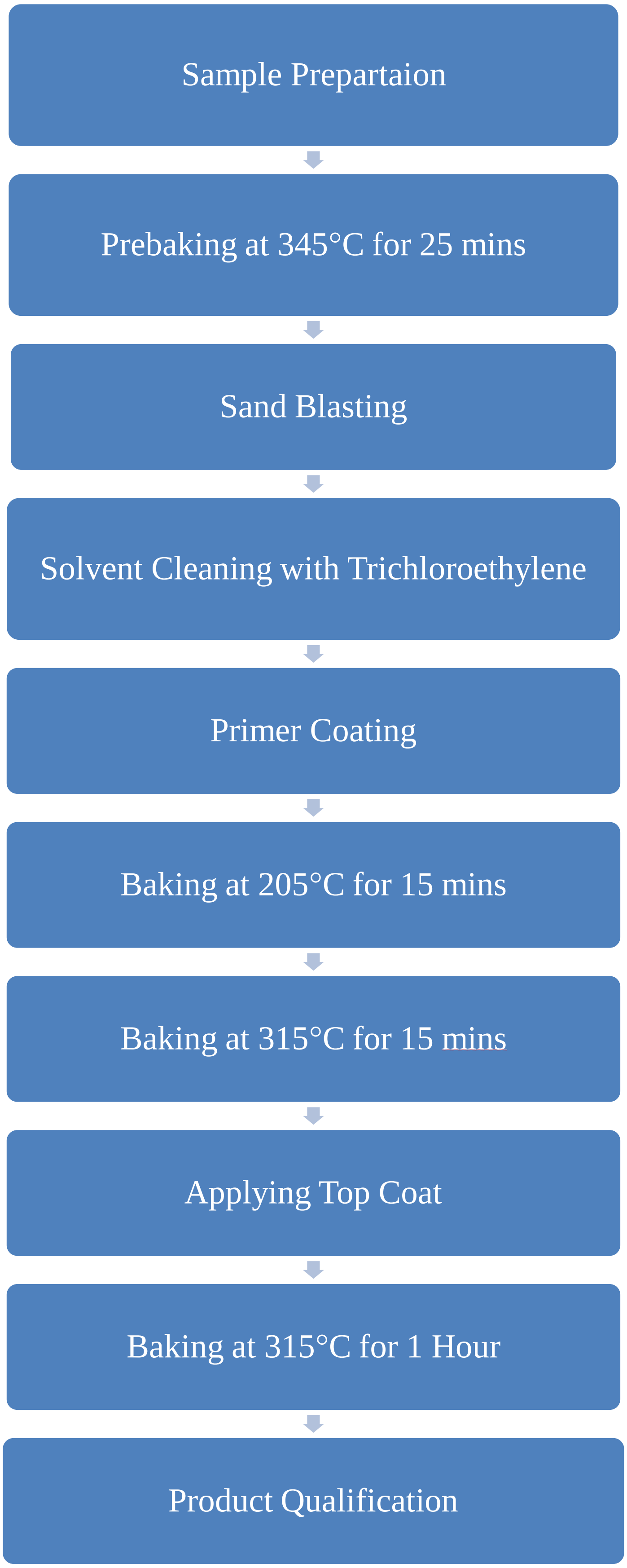
3.4.2.5. Prime Coating

The sample was cleaned again to ensure that it was free of any surface contamination. Then by using spray deposition technique the prime coating was applied over the surface of the sample. And this was done properly by following the standard practice for manual spray deposition technique i.e. the spray gun to be held perpendicular to the sample and whipping the gun in an arc for proper deposition of the coating and maintaining a distance of 4-12 inches from the sample. The black surface of sample after prime coating was checked. The sample was then heated to 205°C and held there for 15 minutes and heat to 315°C. The sample was left for air cooling. This was done for the curing of the prime coating and changing it from soft coating to hard coating. And the prime coating acts as a base for the final coating and for better adhesion between the final coating and the surface of the sample.

3.4.2.6. Final Coating

The top coat of the teflon coating was applied by using spray deposition technique. The sample was then baked at 315°C and held there for approx. 60 minutes to ensure that the final coating was cured properly. The white lustery surface of sample after final coating was checked.

Flowchart showing the process of teflon coating performed on Al-2219 T6 substrate according to **DuPont standards:[74]**



3.4.3. Qualification Tests

After the sample was prepared according to the Dupont standards, the sample was undergone certain qualification tests to see whether it was up to the standards or not. Various tests that performed were: Visible Inspection, Film thickness, Post boiling water fingernail test, and crosshatch test.

3.4.3.1. Visible Inspection

Teflon coated sample is visually inspected to see whether the coating is smooth, black colored, granular surface and free of blistering, pinholes, scratches, mud cracking or other defects. [74]

3.4.3.2. Film Thickness

Digital Coating thickness meter as mentioned in Section **3.3.3** was used for measuring the thickness of the sample and thickness should lie between the range 22-35 microns. The meter measures the thickness in unit micron. [71]

3.4.3.3. Post boiling water fingernail test

For 15 minutes, the sample was submerged in boiling water and then removed and cooled to room temperature. Then using a knife, a scratch was made in a straight line and coating was peeled off. The coating peeled off shouldn’t be greater than 6 microns. [76]

3.4.3.4. Crosshatch Test

The sample was put in boiling water for 15 minutes and then cooled to room temperature. Then using a single-edged razor blade, 100 small squares were made by first making 11 parallel cuts 2.4 mm apart and then repeating at right angle. Afterwards, a strip of transparent tape 25 mm wide was pressed on it and by ensuring maximum contact, the tape was pulled off firmly and rapidly. Then another tape was pressed at right angle and the process repeated. Good film shows no squares removed but less than 20% squares removed qualifies the test. [77]

3.4.3.5. Continuity Test

It was performed in a similar way as in Section **3.2.3** and since teflon coating is nonconductive. The samples cleared the test and were completely nonconductive. [67]

3.4.4. Characterization Techniques

After the process was performed, it was characterized to ensure that whether the coating obtained shows the desired properties. The techniques performed were contact angle measurement and tribometry. These techniques were chosen because they are necessary for the testing of the hydrophobic nature of the coating and its wear resistance.

3.4.4.1. Contact Angle Measurement

Contact angle is the angle between the liquid-vapor interface and the solid interface. By the young's equation it quantifies the wettability of a solid substrate by a liquid. The sessile drop method was used to measure the measure the contact angle of the water drops on teflon coated sample. In this a drop of water is placed on the sample surface with a light source at the back and a picture with a camera is taken. The picture is than later analyzed using Image J and the contact is then found. Contact angle less than 90° shows hydrophilic nature and greater than 90° shows hydrophobic nature. [64]

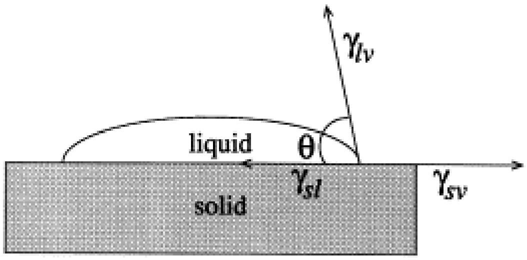


Figure 3.1 Sessile-drop contact angle schematic diagram [78]

3.4.4.2. Tribometry

Refer to Section **3.3.4.1.**

3.4.4.3. SEM and EDX

Refer to Section **3.2.4.1.**

Chapter 4: Results and Discussion

4.1. Passivation

4.1.1. Results of Qualification Tests

The qualification tests for Passivation, as mentioned by the ASTM A380 standard, were cleared by all the samples that were passivated under optimized conditions. The tests and their individual results are as followed:

Qualification Tests	Result
Visual Inspection	Relatively cleaner and monotone than before
Residual Pattern	No water spots or scarring seen
Free Iron Test	No Rust seen
Copper Sulphate Test	No copper deposited nor orange shade seen
Humidity	Survived 95 to 100 % humidity at 45°C for 24hr
Continuity Test	Conductive coating

Table 4.1.1 Qualification Tests

4.1.1.1. Visible test

The sample appeared cleaner and monotone, relative to the initial sample surface, indicating the formation of a passive layer. [53]

4.1.1.2. Residual Pattern Test

After heating for 20 minutes in an oven at 60°C no water spots or scarring was observed. This shows that the coat was adhered properly and therefore was not contaminated. [54]

4.1.1.3. Free Iron Test

As no reaction with the water took place and no oxides of iron were formed, which appear as rust, giving a visible indication that no free iron was present. Hence the passive layer didn't fail. [53]

4.1.1.4. Copper Sulfate Test

This test was performed for only the 300 series as no orange shade was seen, this shows that no copper was deposited indicating again that no free iron was present on the surface. [57]

4.1.1.5. Continuity Test

The samples cleared the continuity test using a multimeter in which they were all found to be conductors, as the layer formed by passivation is a thin film.[53]

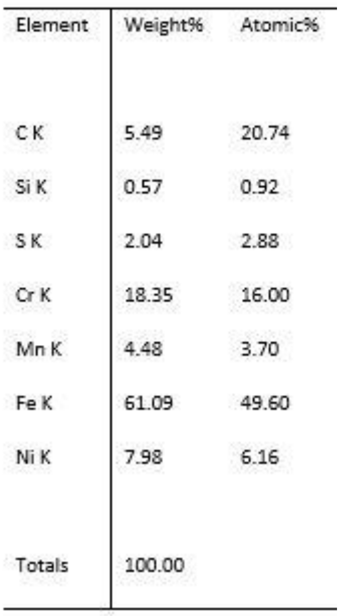
4.1.2. Results of Characterization

Different characterization techniques were used in order to check the credibility of the results and whether the coating had developed or not.

4.1.2.1. EDX

EDX was done for the samples before passivation in order to verify the samples composition. It was performed and then matched with the values found in the standard given in ***Table3.1.1***. The EDX results are as follows:

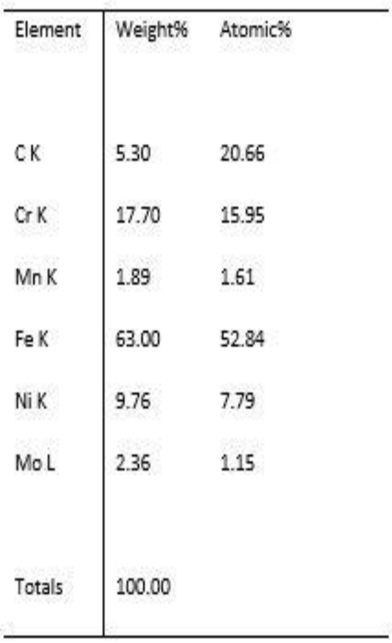
SS 304



Element	Weight%	Atomic%
C K	5.49	20.74
Si K	0.57	0.92
S K	2.04	2.88
Cr K	18.35	16.00
Mn K	4.48	3.70
Fe K	61.09	49.60
Ni K	7.98	6.16
Totals	100.00	

Table 4.1.4 SS 304 EDX

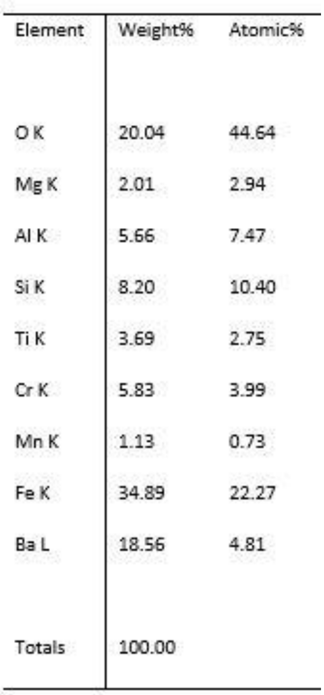
SS 316



Element	Weight%	Atomic%
C K	5.30	20.66
Cr K	17.70	15.95
Mn K	1.89	1.61
Fe K	63.00	52.84
Ni K	9.76	7.79
Mo L	2.36	1.15
Totals	100.00	

Table 4.1.3 SS 316 EDX

SS 420



Element	Weight%	Atomic%
O K	20.04	44.64
Mg K	2.01	2.94
Al K	5.66	7.47
Si K	8.20	10.40
Ti K	3.69	2.75
Cr K	5.83	3.99
Mn K	1.13	0.73
Fe K	34.89	22.27
Ba L	18.56	4.81
Totals	100.00	

Table 4.1.2 SS 420 EDX

The results of EDX obtained are matched with the standard value:

- From this we can see that the value of carbon is higher in all of the samples EDX and this can be easily due to the presence of surface impurities or even a finger print when placing the sample.
- The values of the other elements other than carbon found in SS 304 and SS 316 are similar to the value of the standard.
- The values of elements of SS 420 are very different as compared to the values given in the standard. Even titanium can be seen in an alarming quantity. This showed that there was some problem with the way the equipment was handled or the sample provided was not SS 420.

As a result, XRF was performed in order to confirm whether the titanium was present in the sample or not.

4.1.2.2. XRF

XRF was performed to confirm the results of the EDX and then to compare the results obtained from XRF and EDX with the standard value range.

The results obtained from XRF are as follows:

SS	Si	P	S	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Nb	Mo	W
420	-	-	-	0.11	0.15	10.84	0.6	87.63	0	0.32	0.19	0	0.05	0
304	0.14	0	0	0.03	0.10	19	1.9	69.59	0.15	8.14	0.67	0.01	0.12	0.04
316	0.18	0	0.01	0.02	0.05	17.33	1.7	67.62	0.15	10.07	0.74	0.02	1.93	0.08

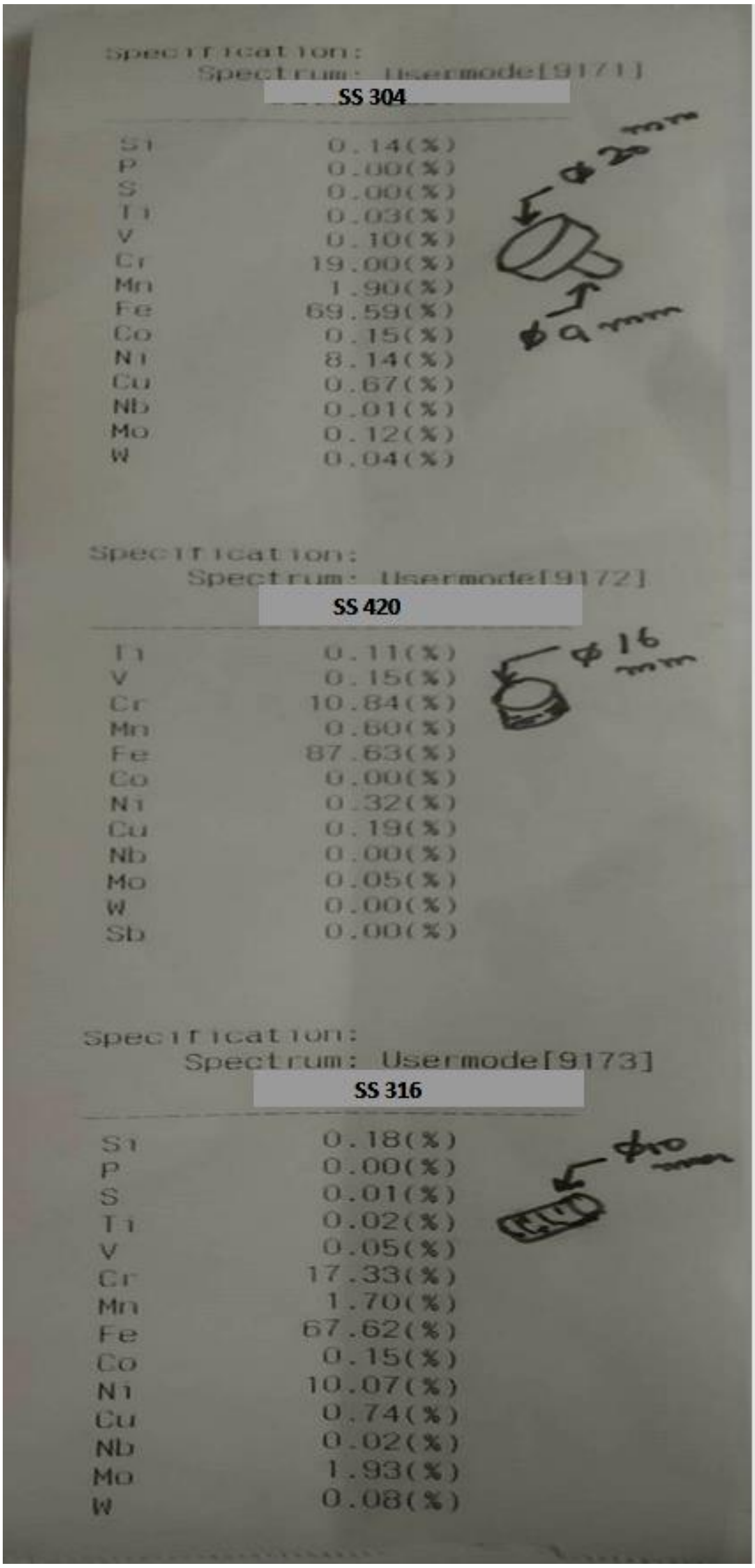
Table 4.1.5 XRF results

This result when compared to others indicated that:

- The presence of Titanium was in very small quantity i.e. 0.11 in SS 420. And even in other SS samples there was a very small amount.
- Also, the amount of Cr showed in XRF is very close to the values given in the standard.
- All of the values obtained by XRF are far more accurate than the values of obtained by EDX.
- After XRF it was confirmed that the samples were SS 420, 304, 316 and then the testing was done of the samples as only hard materials like 420 could be baked and for that the composition of the sample was to be known beforehand.

An XRF of the samples after passivation was not done, as after passivation no chemical composition changes take place. The elements being used by the layer formation are already present in SS therefore the total wt.% remains the same.

Machine generated XRF results:



```
Specification:
      Spectrum: Usermode[9171]
            SS 304
Si              0.14(%)
P               0.00(%)
S               0.00(%)
Ti              0.03(%)
V               0.10(%)
Cr             19.00(%)
Mn              1.90(%)
Fe             69.59(%)
Co              0.15(%)
Ni              8.14(%)
Cu              0.67(%)
Nb              0.01(%)
Mo              0.12(%)
W               0.04(%)

Specification:
      Spectrum: Usermode[9172]
            SS 420
Ti              0.11(%)
V               0.15(%)
Cr             10.84(%)
Mn              0.60(%)
Fe             87.63(%)
Co              0.00(%)
Ni              0.32(%)
Cu              0.19(%)
Nb              0.00(%)
Mo              0.05(%)
W               0.00(%)
Sb              0.00(%)

Specification:
      Spectrum: Usermode[9173]
            SS 316
Si              0.18(%)
P               0.00(%)
S               0.01(%)
Ti              0.02(%)
V               0.05(%)
Cr             17.33(%)
Mn              1.70(%)
Fe             67.62(%)
Co              0.15(%)
Ni             10.07(%)
Cu              0.74(%)
Nb              0.02(%)
Mo              1.93(%)
W               0.08(%)
```

Figure 4.1 XRF results of SS

4.1.2.3. XRD

XRD of stainless steel sample of 316 was performed before and after passivation, as shown below:

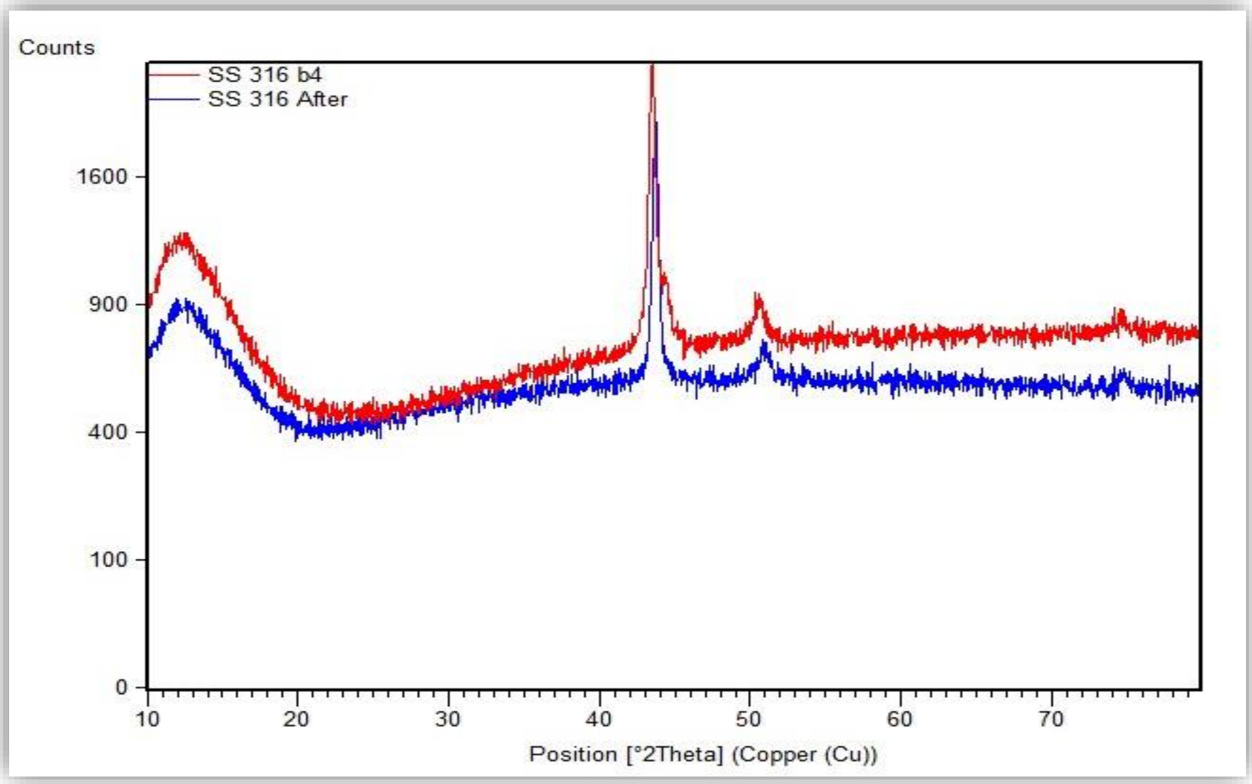


Figure 4.2 XRD of SS 316 before and after passivation

The red line indicates the result of the stainless steel 316 before passivation and the blue line, below the red line, indicates the stainless steel 316 after the passivation. The results upon analysis can be summarized by the following points:

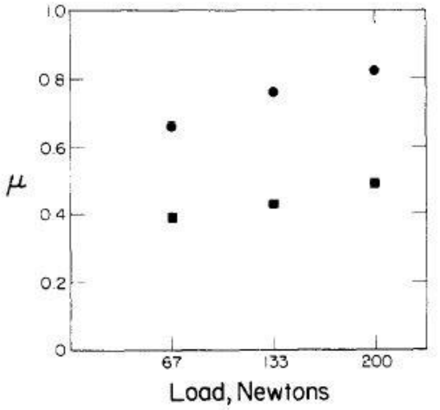
- First broad peak in the graph acts as a reference, which is obtained by placing the samples on a glass slide.
- The intensities of both the red and the blue peaks are similar.
- The sharp peaks show a shift, indicating a change in d spacing, according to Braggs law.
- This is a clear indication that chromium diffuses to the surface leading to a change in d spacing of the lattice.

- This clearly indicates that a reaction took place and chromium diffused to the surface to form its oxide and passivate the sample to protect it from corrosion.

4.1.2.4. Tribometry

Tribometry was performed for the passivated sample of SS 304. An average value of coefficient of friction obtained for the passivated sample was 0.463, with a standard deviation of 0.046.

This result is very close to the result that was published by Z.Y.Yang, M.G.S.Naylor, and D.A.Rigney from The Ohio State University, they tested the samples and found the coefficient of friction of SS 304 which was lower than that of SS 310 [79]. The low coefficient of friction allows for the stainless steel to be used in bearings, pistons etc. The graph, for reference, is given **Optimization of coating parameters**



Friction coefficient μ *vs.* normal load L for blocks of 304 and 310 stainless steel after prolonged sliding against M2 tool steel rings: ●, 310 stainless steel; ■, 304 stainless steel.

Figure 4.3 Coefficient of Friction graph of SS 310 and 304 [79]

The coating parameters that were optimized for passivation were: temperature, time and concentration of the baths.

- When the **temperature** was lowered keeping the other parameters constant it was noticed that complete passivation did not take place and for complete passivation **time** had to be increased. Whether passivation took place or not was tested by copper sulfate test and as copper was deposited it clearly showed lack of layer formation.

- When the **time** was decreased, incomplete passivation took place. Time was then increased it was observed that no change took place as the optimized time had already been provided for the process. All the other variables were kept constant.
- The **concentrations of the baths** played an important role, as the concentration of the bath was increased the passivation process got quicker and when decreased with other parameters constant, then passivation took place in spot form, incomplete layer was formed. This was again tested by the copper sulfate test.

Hence, the optimized parameters were found by testing on many samples and these parameters are mentioned in **Table 3.1.2**.

4.2. Anodizing

4.2.1. Results of Qualification Tests

All of the qualification tests were cleared by the anodized samples, according to the Military and ASTM standards. The tests and their individual results are as followed: [63]

Qualification Tests	Result
Visual Inspection	No black shade or spot or burning due to contact points
Continuity Test	Sample was Non-conductor
Coating Thickness	16.8 µm
Salt Spray Test	No corrosion observed

Table 4.2 1 Qualification Tests

4.2.1.1. Visual Inspection

No variations, burning or black spots were seen in the final samples prior to being sealed, under optimum conditions. Uniform, smooth, and permanent coloring was seen by sliding a finger across the sealing. When no sealing came of it showed that the sealing was now permanent.[66]

4.2.1.2. Continuity Test

The test was cleared by the samples that were completely nonconductive. The test was performed using a simple multimeter in which the contact lead was moved on the surface and the multimeter at any point gave no value other than 0. [53]

4.2.1.3. Coating Thickness Test

Digital coating thickness meter was used to measure the coating thickness in microns. The standard thickness to qualify should have been between 1.8µm~25.4µm, in order for the coating to qualify. Our coating achieved a thickness of 16.8um at the optimized voltage value.[63]

4.2.1.4. Salt Spray Test

The salt spray test was carried out to test the corrosion resistance of the coated sample. For the coating to qualify the standard ASTM B117, the sample was sprinkled with 5% NaCl solution and this was performed at room temperature and pressure for 15 days. And all the samples cleared the required test without any corrosion. [65]

4.2.2. Results of Characterization

Different characterization techniques were used in order to check the credibility of the results and whether the coating was qualified or not.

4.2.2.1. SEM and EDX

SEM and EDX both were done for the samples to check the structure and the compositional changes that occur in the sample after anodizing.

First is the EDX of the cross-section of a sample where no anodizing took place at Spectrum 1.

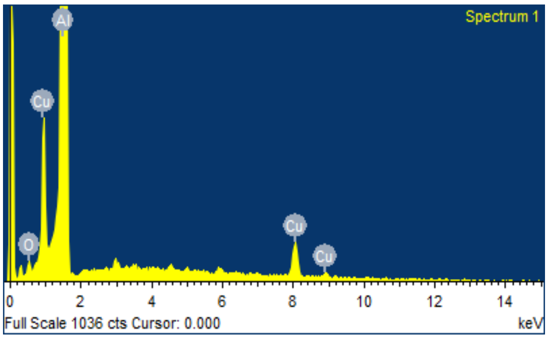


Figure 4.4 Compositional machine generated graph

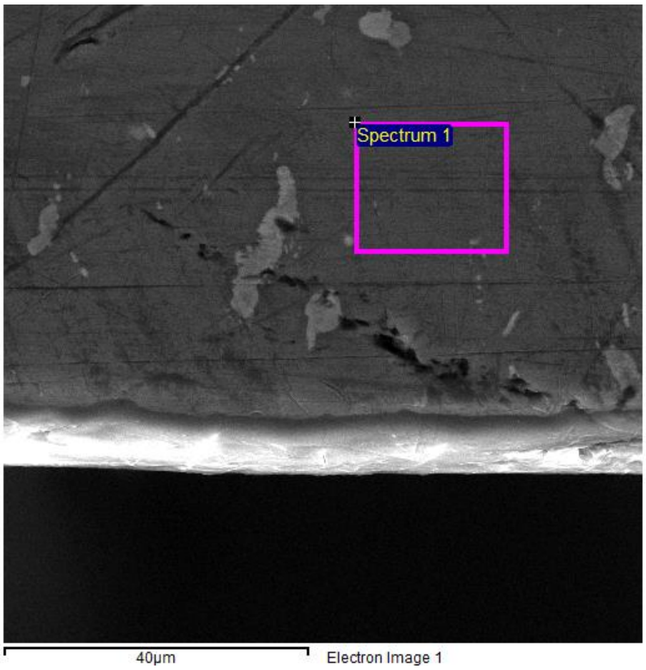


Figure 4. 5 SEM of Al-2219 T6 cross-section and EDX at Spectrum 1

The values obtained by the EDX are very similar to the values mentioned in Table 3.2.1 that gives the values of Al2219 T6 composition as mentioned in the standard.

Element	Weight%	Atomic%
O K	1.15	1.98
Al K	93.76	95.81
Cu K	5.09	2.21
Totals	100.00	

Table 4.2.2 EDX compositional analysis of Al2219 T6

The SEM and EDX then done at the point where the coating was and the results are:

Element	Weight%	Atomic%
O K	13.49	22.58
Al K	69.15	68.63
Cr K	13.02	6.70
Fe K	4.34	2.08
Totals	100.00	

Table 4.2.3 EDX compositional analysis of Al2219 T6 at coated area

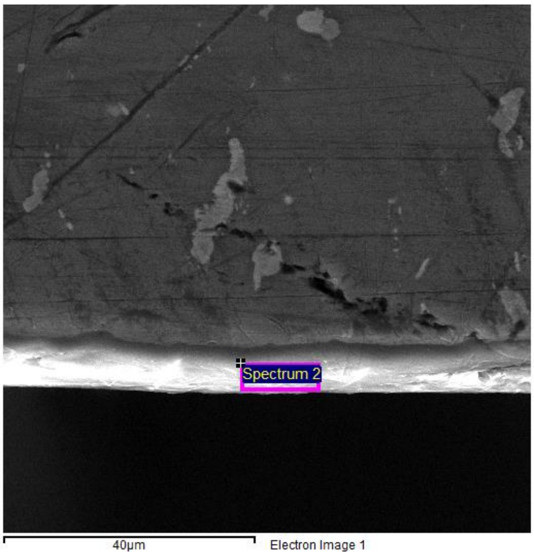


Figure 4.6 SEM of Al-2219 T6 cross-section and EDX at Spectrum 2

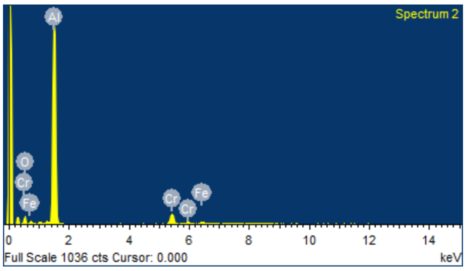


Figure 4.7 Compositional machine generated graph

The EDX result when compared to that of spectrum 1 shows that the sample has been anodized at the surface from which spectrum 2 has been taken. The sample as was sealed with potassium dichromate therefore as a result the surface coating has chromium present, and in a good amount as seen by the EDX result. There is also an increase in the amount of oxygen due to the anodizing reaction that takes place at the sample surface. This is a clear indication that anodizing has taken place. Furthermore, EDX was also done for the sample at the surface to see the surface composition and structure. And the results are similar and show that the anodizing reaction took place, along with sealing leading to compositional changes. And this can also be observed in Spectrum 4 on next page showing the EDX of sealed potassium dichromate sample.

The EDX below is of potassium dichromate sealed sample and the spectrum was taken of the sample surface. Showing that sealing took place because the amount of Cr increased.

Element	Weight%	Atomic%
O K	56.92	69.73
F K	2.79	2.88
Na K	0.43	0.37
Mg K	6.30	5.08
Al K	23.30	16.93
Si K	0.65	0.45
S K	2.82	1.72
Cl K	0.42	0.23
K K	0.42	0.21
Ca K	1.40	0.68
Cr K	4.55	1.71
Totals	100.00	

Table 4.2.4 EDX compositional analysis of Al2219 T6 at Spectrum 4

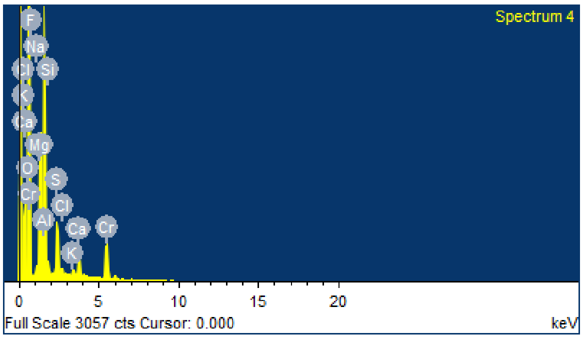


Figure 4.8 Compositional machine generated graph

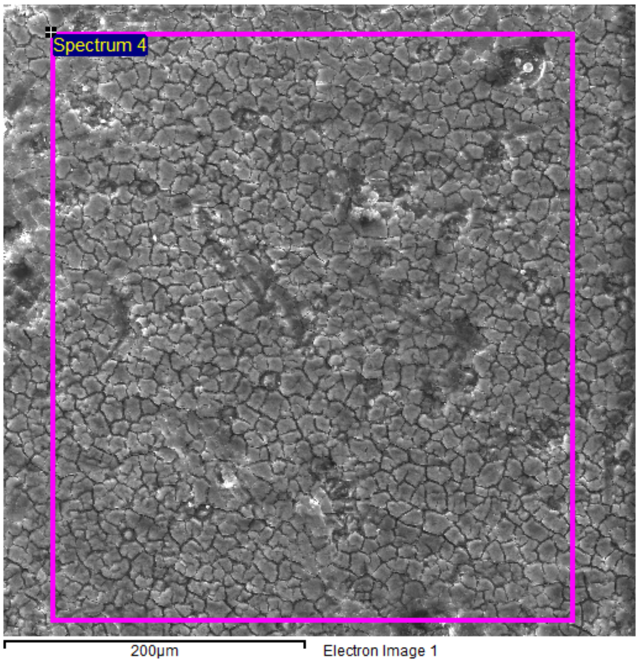
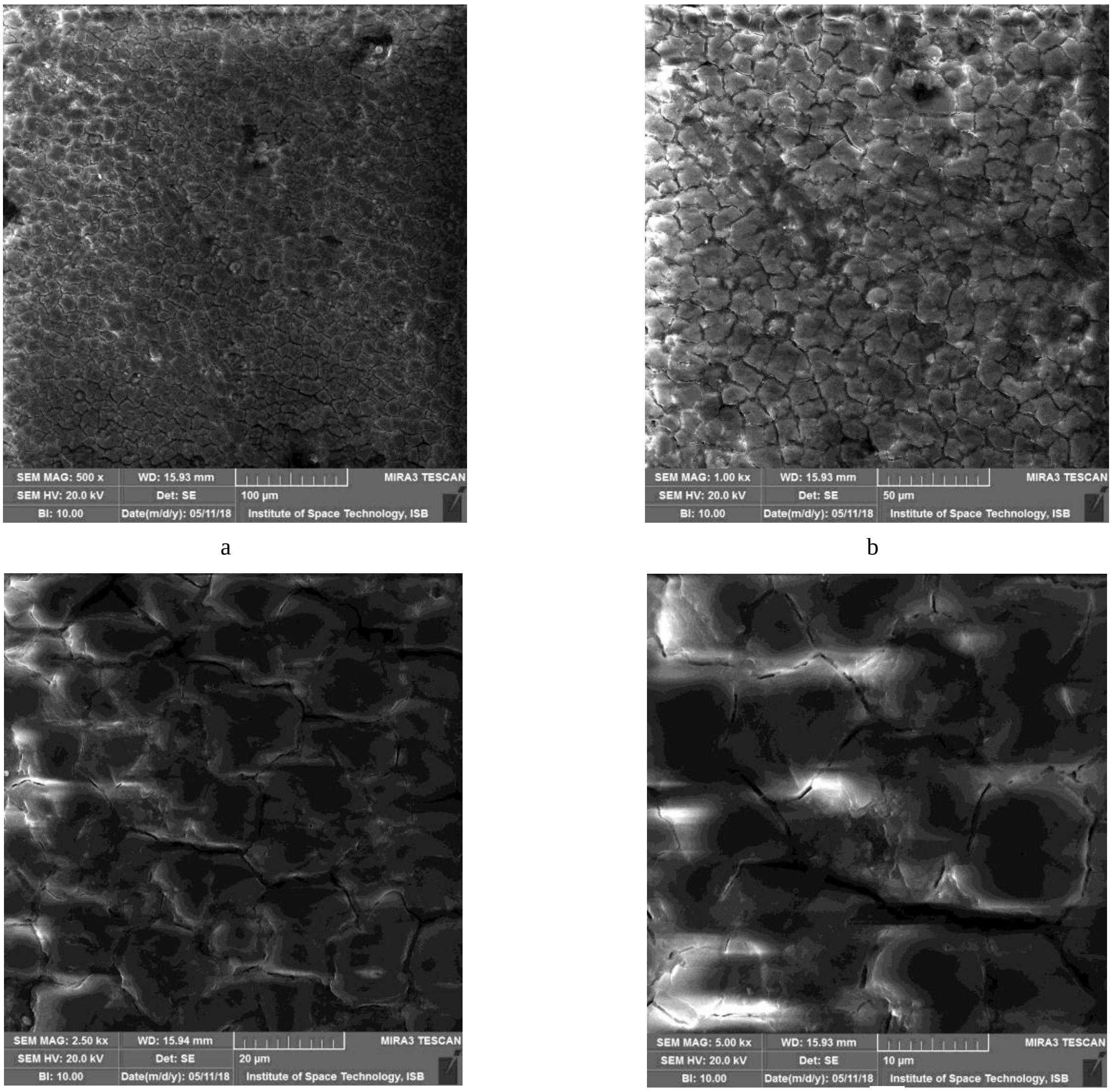


Figure 4.9 SEM of Al-2219 T6 potassium dichromate sealed surface

Figure 4.10 (a,b,c,d) showing surface of potassium dichromate sealed Aluminum



a

b

c

d

The figures show SEM at different magnification (increasing from a to d) of the potassium dichromate sealed surface of Al2219 T6. The surface shows honeycomb structure has developed. Due to the sealing in between these hexagons a depth can see that depicts that there was a pore present that has been successfully sealed. Now these areas where these hexagonal type structures meet are of high energy and from where cracks can propagate, specially from the triple points. In short SEM results showing a honeycomb structure clearly show the formation of an anodized layer on the Al 2219 surface.

4.2.3. Optimization of coating parameters

The coating parameter that was optimized for anodizing was the **Voltage**. The rest of the variables were kept constant. The graphs are given below:

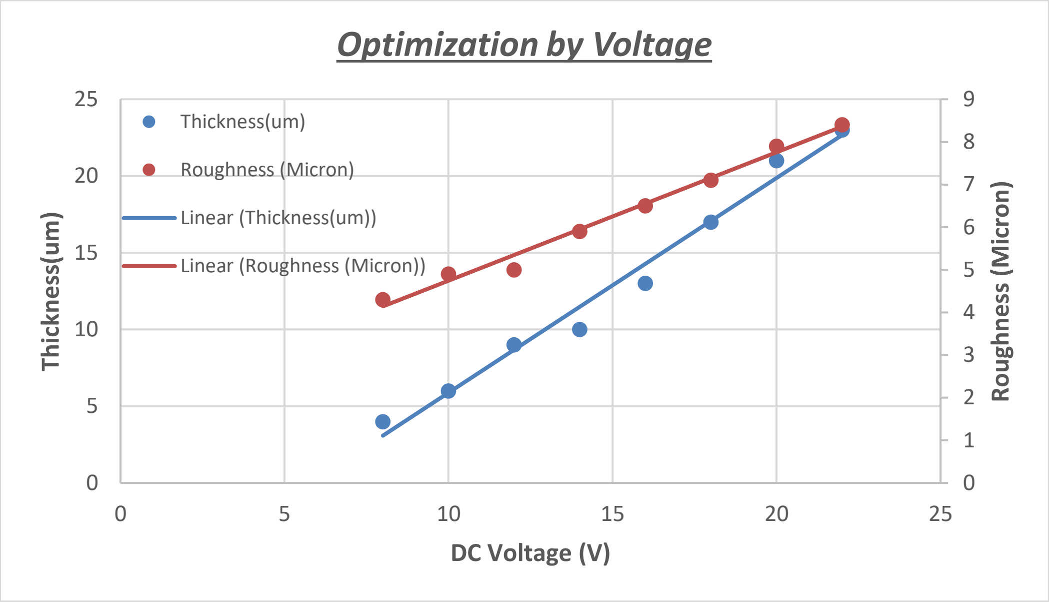


Figure 4.11 Graph showing the relationship between voltage, thickness and roughness

Sample No.	Voltage (Volt DC)	Thickness(um)	Roughness (Micron)
1	8	4	4.3
2	10	6	4.9
3	12	9	5
4	14	10	5.9
5	16	13	6.5
6	18	17	7.1
7	20	21	7.9
8	22	23	8.4

Table 4.2.5 Thickness and roughness values according to changes in the voltage

As seen by the graph, an increase in voltage causes an increase in thickness of the coating as well as they show a linear and direct relationship. Now for the thickness to increase more reaction takes place in this continuous process, which means the development of more pores. Upon these pores more, chemical reaction takes place that causes an increase in roughness of the surface being anodized. This relation of roughness with voltage is also shown on the graph. The application of our process requires a porous anodized layer with a thickness that was being achieved at 18 DC volt. This is how the anodizing process was optimized as required by our application.

4.3. Metaflex

4.3.1. Results of Qualification Tests

All of the samples cleared the qualification tests for metaflex, according to the ASTM and AkzoNobel standards. The tests and their individual results are as follows:

Qualification Tests	Results
Visual Inspection	Smooth yellowish film obtained
Coating Thickness	41.5 micron
Adhesion Strength	6.62 Mpa
Salt Spray Test	No corrosion observed
Continuity Test	Sample was Non-conductor

Table 4.3.1 Qualification Tests

4.3.1.1. Visual Inspection

The sample was free from any defects and a uniform, yellowish colored coating was obtained. This qualified the AkzoNobel standard. [36]

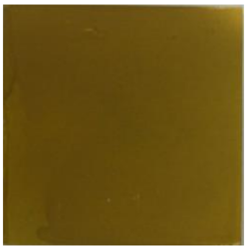


Figure 4.12 Metaflex sample

4.3.1.2. Coating Thickness

Digital coating thickness meter was used to measure the coating thickness in microns. It used the principle of eddy current to measure the thickness. The coating achieved a thickness of 41.5 micron, which was up to the standard.

Figure 4.13 meter

4.3.1.3. Adhesion Strength

Adhesion test was performed on the metaflex samples to find out the adhesion strength of the coating according to ASTM D4541. The test was performed by using Elcometer 510 Model S UK origin, with a dolly size of 20 mm and a pull rate of 0.7 Mpa per second, according to the international standard. As a result, the adhesion strength on average was found to be 6.62 Mpa. [72]

Figure 4.17 Dolly attached to the sample

Figure 4.16 Puller attached to the dolly

Figure 4.14 Adhesion testing meter

Figure 4.15 Multimeter

4.3.1.4. Salt Spray Test

The salt spray test was carried out to test the corrosion resistance of the coated sample. For the coating to qualify the standard ASTM B117, the sample was sprinkled with 5% NaCl solution and this was performed at room temperature and pressure, for 15 days. All the samples cleared the test without any corrosion. [65]

4.3.1.5. Continuity Test

The metaflex samples were tested to completely nonconductive, which was required. The test was performed using a simple multimeter, in which the contact lead was moved on the surface and the multimeter at any point gave no value other than 0. [53]

4.3.2. Results of Characterization

Different characterization techniques were used in order to check the credibility of the results and whether the coating had developed up to mark or not.

4.3.2.1. Tribometry

Pin on disk tribometer was used to measure the coefficient of friction of the metaflex sample. Metaflex coating should cause a decrease in the coefficient of friction of the surface. The coefficient of friction for metaflex was found to be 0.135, with a standard deviation of 0.126. The metaflex sample has a low friction factor and the surface of the sample being smooth gives a constant wear rate.

4.3.2.2. SEM and EDX

To characterize the coating and to find the compositional analysis of the coating to match it with the given standard EDX was done along with SEM. The results of EDX are as shown below.

The metaflex coating composition obtained through the EDX was compared with the Akzonobel (Table 2.1 and 2) and a similar composition had been achieved.

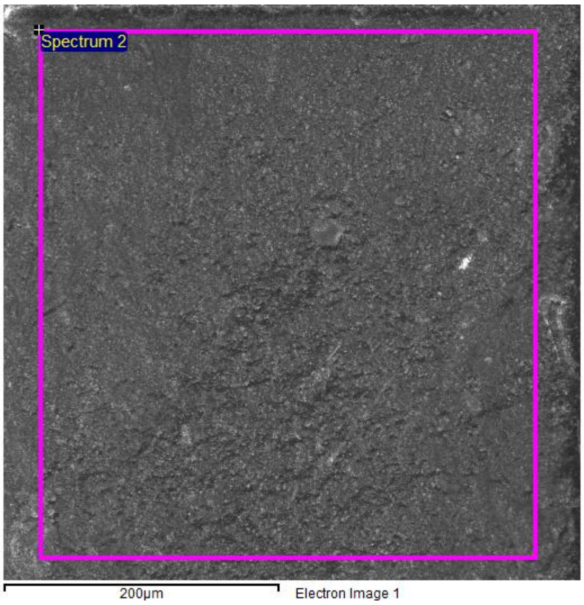


Figure 4.18 SEM micrograph of Metaflex sample for EDX analysis

The presence of chromium shows that the metaflex coating is a type of chromate conversion coating.

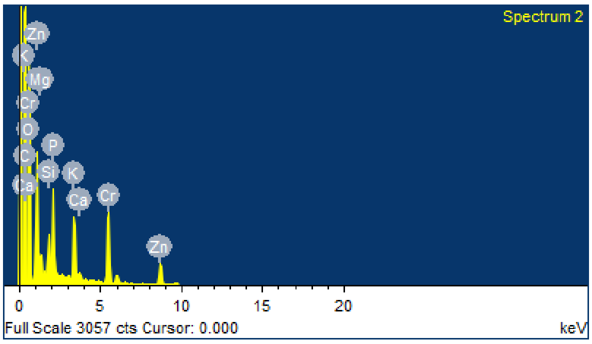
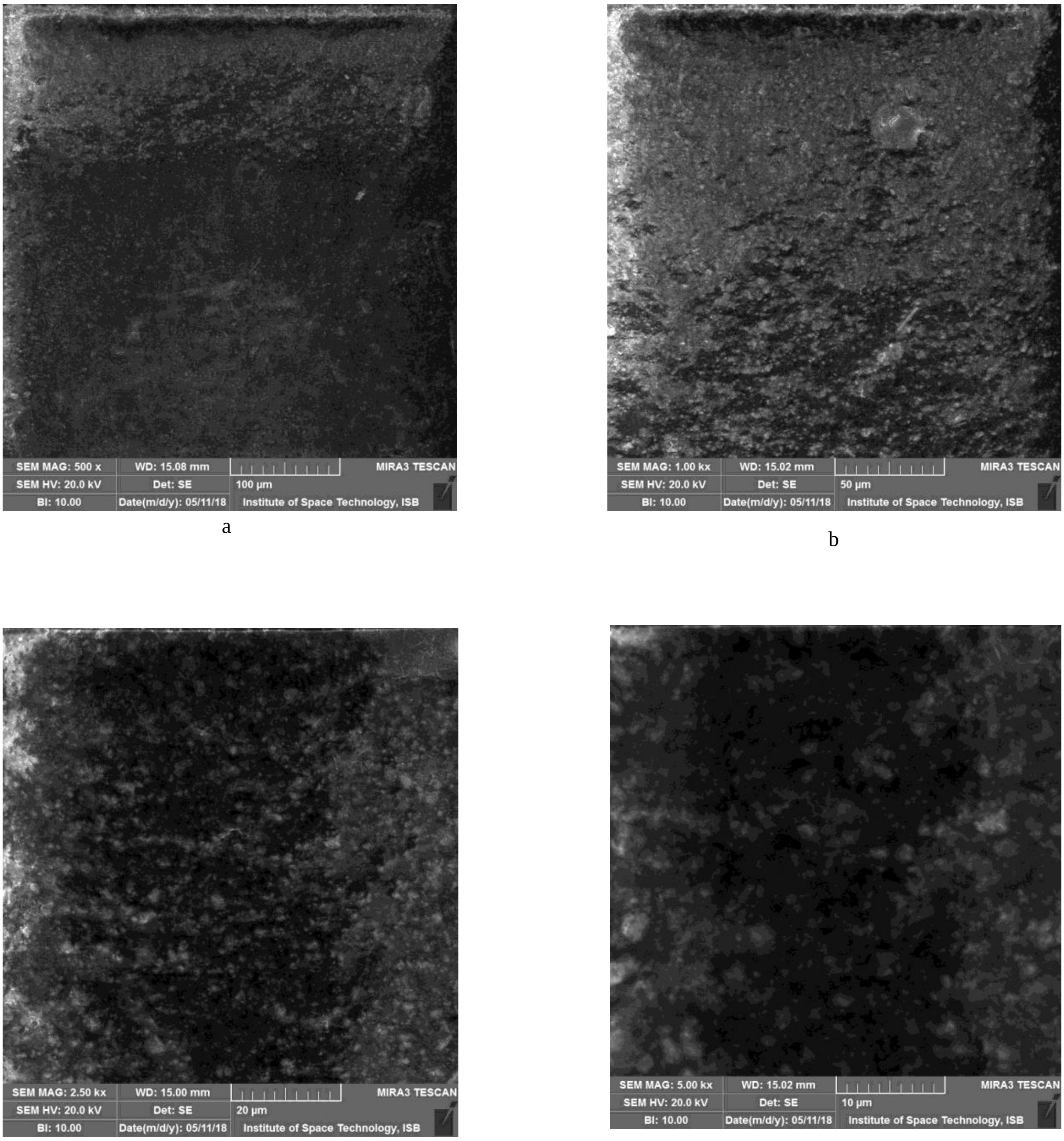


Figure 4.19 Compositional machine generated graph

Element	Weight%	Atomic%
C K	51.13	64.33
O K	31.63	29.87
Mg K	0.71	0.44
Si K	0.87	0.47
P K	2.36	1.15
K K	2.13	0.82
Ca K	0.17	0.06
Cr K	5.23	1.52
Zn K	5.77	1.33
Totals	100.00	

Table 4.3.2 EDX compositional analysis of Al2219 T6 metaflex coated sample at Spectrum 2

Figure 4.20 (a,b,c,d) SEM mircogrpahs of Metaflex coating on Al2291T6



a

b

c

d

The metaflex coating was performed on Aluminum substrate which was sandblasted and it can be seen in the SEM as well. Along with roughness there is no change in contrast that shows that there was smooth deposition of the metaflex coat.

4.3.3. Optimization of coating parameters

The metaflex coating was optimized by the conditions of pressure that was applied during sandblasting. A change in pressure lead to a change in roughness that ultimately effects the thickness. Now as the metaflex coating is a mechanical anchoring process, better roughness means better adhesion due to better anchoring and therefore same number of coats lead to a higher thickness value. The results are as shown:

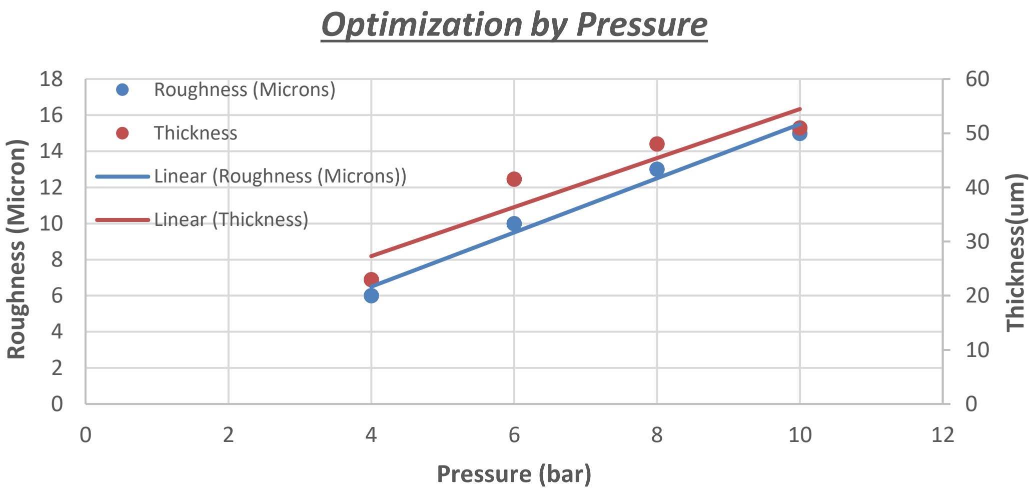


Figure 4.21 Optimization by pressure

Sample No.	Pressure (bar)	Roughness (Microns)	Thickness (Microns)
1	**4.0**	**6.0**	**23**
2	**6.0**	**10**	**41.5**
3	**8.0**	**13**	**48**
4	**10**	**15**	**51**

Table 4.3 3 Optimization by pressure values

Furthermore, the time is not a factor in this as the coating is dried in air. The only main factor that can affect the coating is the **room temperature and humidity**. Higher the temperature of the room, quicker the coating will dry.

Humidity can also affect the coating when it is being applied. This is because the coating is a type of chromate conversion coating and for this reaction humidity is a favorable thing to a controlled limit.

Coating thickness can be increased or decreased by changing the quantity of primer being deposited by the spray deposition. Also, the spray deposition method was performed by following the international standards to get an optimized coating.

4.4. Teflon

4.4.1. Results of Qualification Tests

All of the qualification tests for teflon were cleared according to the ASTM and DuPont standards by all of the samples. The tests and their individual results are as follows:

Qualification Tests	Results
Visual Inspection	Smooth black color film obtained
Coating Thickness	25 microns
Post Boiling Fingernail Test	No scratch marks
Crosshatch Test	Less than 20% peel off (no failure)
Continuity Test	Sample was Non-conductor

Table 4.4.1 Qualification Tests

4.4.1.1. Visual Inspection

The coating obtained was smooth and black colored. The surface was granular and free of blistering, pinholes, scratches, mud cracking and other defects. This qualified the DuPont standard. [74]

Figure 4.22 Teflon coated sample

4.4.1.2. Coating Thickness

Digital coating thickness meter was used to measure the coating thickness in microns. It used the principle of eddy current to measure the thickness of the teflon coated sample. The coating achieved a thickness of 25 micron up to the standard which states that the coating should be in between 22-35 microns. [76]

4.4.1.3. Post Boiling Fingernail Test

For 15 minutes, the sample was submerged in boiling water, then removed and cooled to room temperature. Then by using a knife, a scratch was made in a straight line and the coating was peeled off. The coating that peeled off, for multiple samples, was less than 6 microns, therefore the test was cleared and the samples qualified.[76]

4.4.1.4. Crosshatch test

Under the test the samples showed no peel off, few samples showed no removed square and the few that did less than 20 squares was removed, which was up to the standard value. Therefore the coating qualified. [77]

4.4.1.5. Continuity test

The teflon coated samples cleared the test and were completely nonconductive as when the test was being performed using a simple multimeter in which the contact lead was moved on the surface and the multimeter at any point gave no other value other than 0. [53]

4.4.2. Results of Characterization

Different characterization techniques were used in order to check the credibility of the results and whether the coating was qualified or not.

4.4.2.1. Contact Angle Measurement

Contact angle is the angle between the liquid-vapor interface and the solid interface.

Figure 4.23 Sessile drop of water on teflon coated sample

The contact angle of the teflon coated sample was measured multiple times for different samples and the average contact angle was calculated to be 93.5°. This shows that the film is hydrophobic in nature as the contact angle measured is greater than 90°. The sample if tilted even at small angles, lets the water roll of it which keeps the surface of the sample clean and shows the nonstick nature of the Teflon coating.

4.4.2.2. Tribometry

Pin on disk tribometer was used to measure the coefficient of friction of the teflon coated sample. Theoretically Teflon should decrease the coefficient of friction as it is nonstick. Due to this nonstick behavior the sample is sand blasted prior to the application of the Teflon coating so that it can adhere to the surface. As a result, the surface roughness is increased and so the wear rate fluctuates, for the sample a lot. The coefficient of friction for Teflon was found to be 0.124 with a standard deviation of 0.030.

A study by J. C. Burton, P. Taborek, J. E. Rutledge in University of California suggest a few values of coefficient of friction of teflon coated sample as given below: [80]

By looking at the graph and comparing the values at room temperature of both the static and kinetic friction coefficient it can be seen that the value that was obtained by tribometry is of the around the same value as that found by J. C. Burton.

Hence the value of coefficient of friction of 0.124 gives teflon quite an advantage over specific coatings especially in non-stick applications.

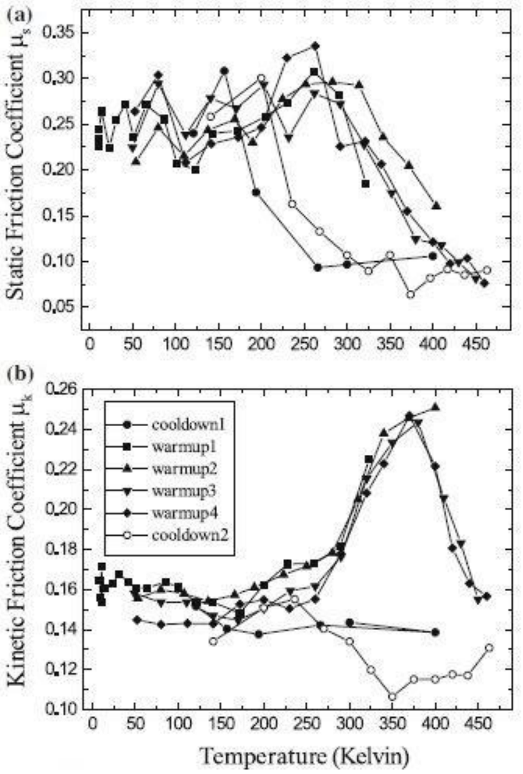


Figure 4.24 coefficient Friction of between steel and PTFE [80]

4.4.2.3. SEM and EDX

To characterize the coating and to find the compositional analysis of the coating to match it with the given standard of DuPont EDX was done along with SEM. The results of EDX are as shown below:

Element	Weight%	Atomic%
F K	99.07	99.42
Si K	0.66	0.45
Ca K	0.26	0.13
Totals	100.00	

Table 4.4.2 EDX analysis of Teflon coated sample at Spectrum 1

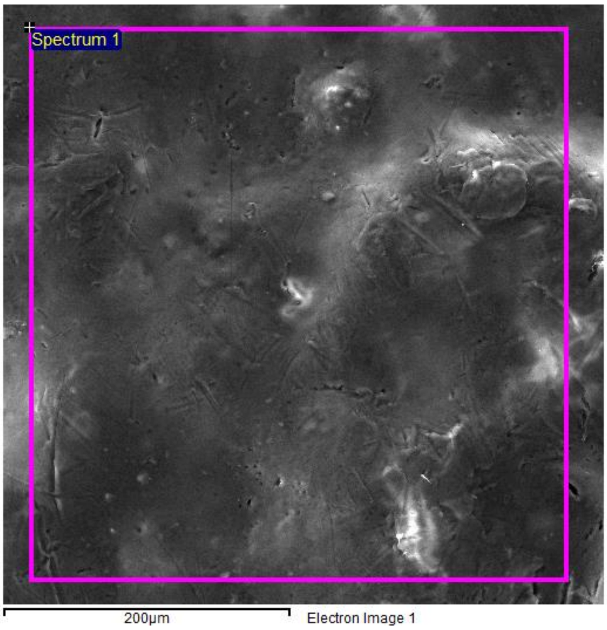


Figure 4.25 SEM micrograph of teflon coated sample on Al 2219 T6

The teflon coating composition was found using EDX, filtering carbon out. Therefore, the results don't show the amount of carbon present.

Also, the presence of other elements is not shown in EDX as shown in Table 2.3 since after baking most of these compounds evaporate, especially water which is not seen in the EDX results.

From EDX it can be seen that the main elements are fluorine and carbon (as it consists of a carbon backbone). So, the final compound can be stated to be PTFE.

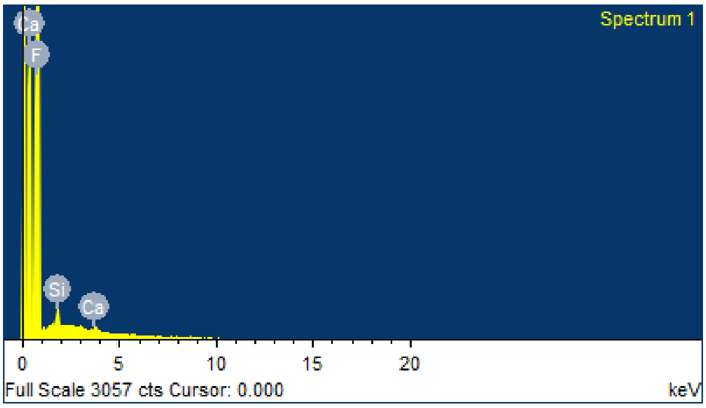
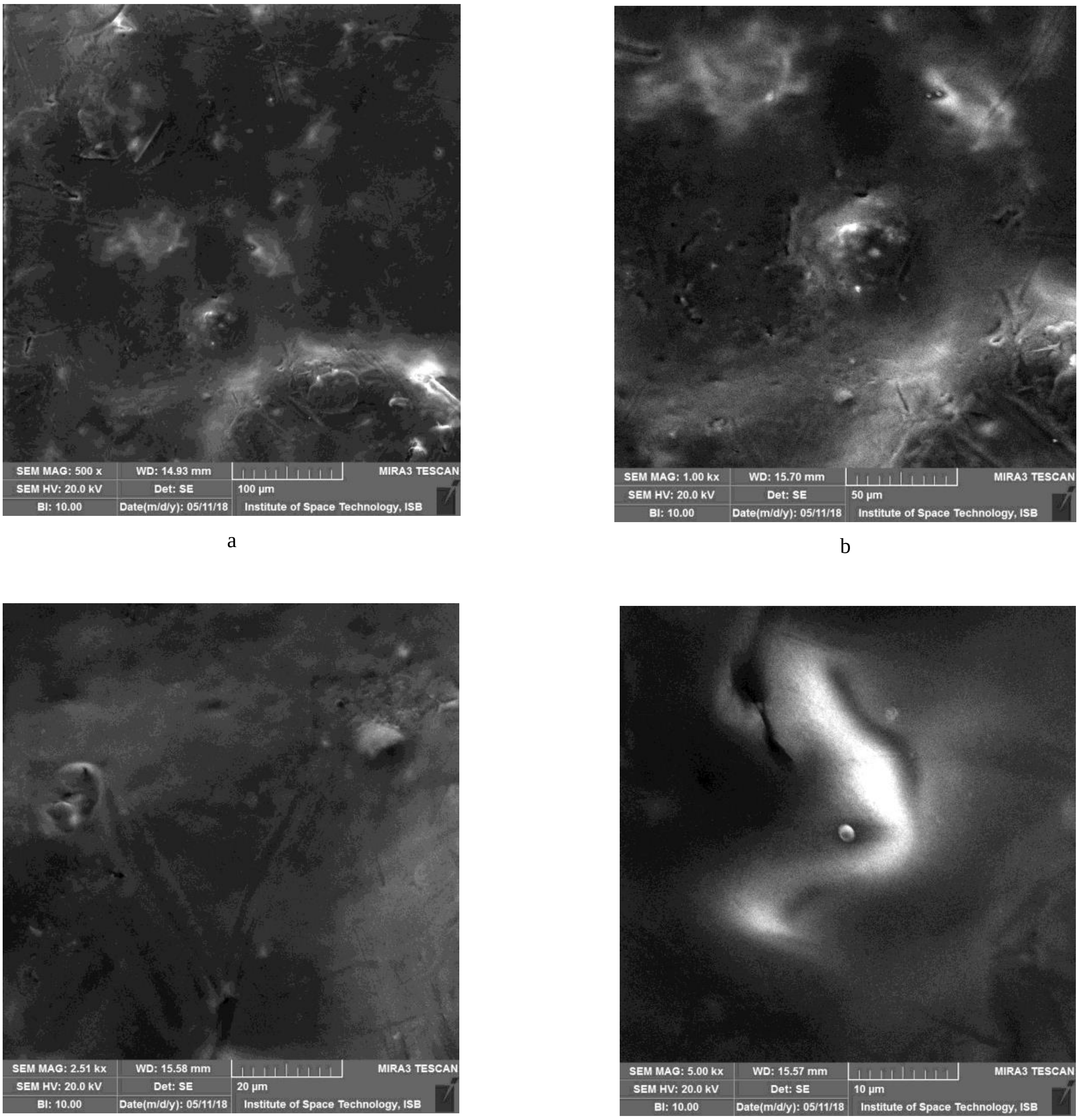


Figure 4.26 Compositional machine generated graph

Figure 4 27 (a,b,c,d) SEM mircogrpahs of Teflon coating on Al2291 T6



a

b

c

d

The SEM micrographs of Teflon coated samples show the melt flow process that occurs while the Teflon coating settles on the sand blasted sample. The grooves and the valleys result in a granular structured surface that show the mechanical anchoring done by the melt flow process. The image d shows the smooth formation of the film, hence depicting strong mechanical anchoring of the Teflon coat.

4.4.3. Optimization of coating parameters

The coating parameter that was optimized for the Teflon coating was the **pressure for sand blasting**. Sandblasting, as mentioned above, is needed to allow the best possible mechanical anchoring to take place so that the coating is well adhered to the surface. Therefore, the pressure was optimized so that that optimum roughness could be achieved that allowed better adhesion of the coat, as per the Du Pont standard.

The size of the sand was kept constant as the pressure was changed to achieve a variation of roughness. The optimum pressure was chosen i.e. 6 bars giving an average roughness of Ra= 10 microns (as per the requirement of the standard).

The practical data is given below along with the graph:

Sample No.	**Pressure (bar)**	**Roughness (Microns)**	**Thickness (Microns)**
1	4.0	6.0	16
2	6.0	10	25
3	8.0	13	27
4	10	15	30

Table 4.4.3 Pressure and Roughness relationship

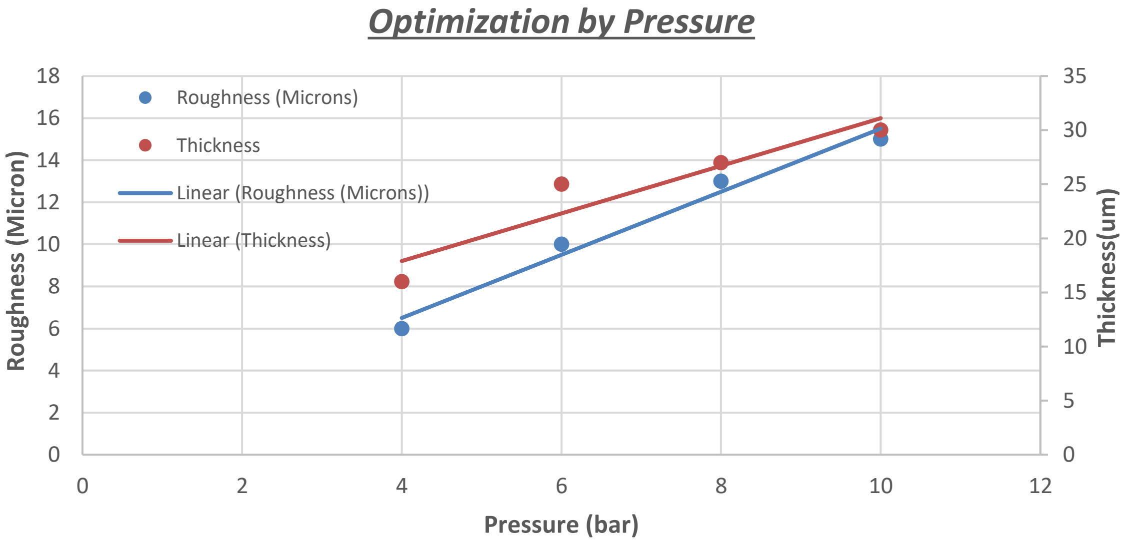


Figure 4 28 Shows the graphical relationship between the pressure of sand blasting, the roughness of the surface and the change in thickness.

Chapter 5: Conclusion

Four different types of coatings were developed at lab scale in order to pave the way for the opening of a coating center in SCME and all these coatings are optimized and up to international standards.

5.1. Qualification Tests

All the coatings performed: Passivation, Anodizing, Metaflex, and Teflon; all of them qualified the required tests according to International standards i.e. Military, ASTM, AkzoNobel and DuPont.

5.2. Characterization of Coatings:

The coatings were all characterized and the required results were achieved:

- Samples to be passivated were checked for composition and XRF results that were more reliable than EDX were chosen as EDX showed higher quantity of an element present like Titanium in stainless steel 420.
- Sample of Stainless steel 316 grade had XRD performed on it before and after passivation. The result was that it indicated a change in the d-spacing due to the diffusion of the chromium from within the bulk to surface for passivation.
- Anodized samples were checked by SEM and EDX. EDX showed how the composition of the samples surface was changed before and after anodizing showing that a reaction took place.
- SEM was done to see the structure of the sealed sample of the anodized aluminum by potassium dichromate. The result was that cracks were seen on the surface with a high roughness and sealed pores were seen.
- Metaflex sample had SEM and EDX performed on them because this lead to the confirmation of the composition of the coating that it was the same as Akzonobel standard and that the coating after being applied have a chromate conversion reaction leading to a different composition on surface.

- Teflon sample also had SEM and EDX performed on them because it to led to the conclusion that all the water and binder evaporated leaving only PTFE in the coating.
- Furthermore, Teflon coating was found be hydrophobic due to its contact angle being greater than 90 degrees.
- Also, all the coatings expect anodizing had tribometry performed on them to find out the coefficient of friction.

5.3. Optimization of Coatings

The coatings were all optimized according to the requirement:

- Passivation was optimized by controlling the concentration of the baths, temperature, and time leading to complete and uniform coating.
- Anodizing was optimized by controlling the voltage that lead to change in the thickness of the coating and the relation between the two was found to be direct and linear. Also, as the coating thickness increases so does the size of the pores and when sealing is done there is more cracking and more roughness is seen on the surface.
- Metaflex was optimized by the following the international standards for manual spray deposition method to get an optimized coating. And by controlling the humidity to a controlled level.
- Teflon was optimized by changing the pressure of the sand blasting leading to a change in the roughness. As the pressure was increased so was the roughness. An optimized value of roughness of Ra 10 microns was chosen as that provided the best adhesion and the best mechanical anchoring.

This is how all the coatings were optimized to achieve coatings that were up to military and international standards.

The table below summarizes the important results:

	Passivation	**Anodizing**	**Metaflex**	**Teflon**
Coating Thickness	N/A	16.8 microns	41.5 microns	25 microns
Conductivity	Conductor	Non-Conductor	Non-Conductor	Non-Conductor
Substrate	300 and 400 series of SS	Al and it alloys, Non-ferrous alloyss	Al and its alloys	Al, ferrous and Non-ferrous alloys
Adhesion	N/A	N/A	6.62	N/A
Principle of Coating	Chemical Conversion	Chemical Conversion	Mechanical Anchoring	Mechanical Anchoring
Application	To protect against corrosion	To protect against corrosion	To protect against corrosion	Non-stick application
Coefficient of friction	0.463	-	0.135	0.124

Table 5.1 Summary Table

From the Summary Table 5.1, it can be concluded that:

- The Passivated sample coating thickness couldn’t be found because it is in the scale of few nanometers.
- If application requires the use of conductive coating on stainless steel than passivation can be done and if non-conductive anyone of the other three can be done which will depend on other required conditions as well.
- Passivation can only be done on stainless steel and metaflex can only be done on Aluminum and its alloys. Anodizing and Teflon can be done on different type of samples.

- Adhesion test cannot be done for coatings whose principle revolves around chemical conversion and it cannot be performed teflon as well because teflon is non-stick so adhesion test for it cannot be performed.
- All the coatings are for protection against corrosion but only teflon is the one that provides non-stick application unlike others.
- Also, teflon coated samples can be used at relatively high temperatures up to 260 degrees Celsius.
- Teflon coated samples provide the least friction coefficient and hence where this application is desired teflon can be coated.

In the future, hybrid coatings can be done i.e. two or more coatings done on the same substrate at once, for example, this can be performed by first coating anodizing and then doing teflon over it or metaflex over it. Then checking the properties to see whether the result is enhanced or not. In this way new coatings can be developed by using these coatings and better properties can be achieved.

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