

Titanium Surface Properties

A comparison of titanium from two suppliers

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Abstract English

This master thesis, completed at the company Alfa Laval studied the surface properties of grade 1 titanium from two different suppliers to examine if there were any significant differences between the two suppliers. Previously titanium from the two suppliers had performed differently at times when used in Alfa Laval's heat exchangers. The experiments performed were studies of surface energy, surface roughness, corrosion rates, Vickers hardness, surface chemistry using GD-OES, grain size and crystal direction using EBSD and tensile tests. Both titanium in sheet form and titanium that had been pressed into heat exchanger plates was tested.

The results showed that there were some differences between the suppliers. Supplier 1 had a smaller grain size, slightly higher surface energy and was softer. But the most remarkable difference was in corrosion rate. Supplier 1 titanium corroded as expected but Supplier 2 titanium barely corroded at all and became colored. The probable reason for this is that Supplier 2 has a higher carbon contentment in its surface thanks to differences in the production process between suppliers. This carbon causes the oxide layer of the titanium to grow in the corrosion tests instead of disappearing. This increased thickness of the oxide layer is what causes the color change. Note that this is only a theory and not verified in this report.

Abstrakt svenska

Denna är en rapport om examensarbete utfört på företaget Alfa Laval. I detta arbete har egenskaper hos grade 1 titan från två olika leverantörer jämförts för att se om det finns signifikanta skillnader mellan titanet från olika leverantörer. Vid ett tidigare tillfälle har titan från de två olika leverantörerna reagerat olika i en värmeväxlare från Alfa Laval. Experiment utföres för att studera ett flertal egenskaper hos titan prover från de olika leverantörerna. Test som utfördes för att studera egenskaper var ytenergi, ytfinhet, korrosionshastighet, dragprover, hårdhets test, ytkomposition med GD-OES och korn och kristallriktningar med EBSD analys. Test utfördes på både opressade plåtar och plattor som pressats för att användas i värmeväxlare.

Resultaten visade vissa skillnader mellan leverantörerna. Leverantör 1 hade mindre kornstorlek, något högre ytenergi och var mjukare än Leverantör 2. Men den största skillnaden var i korrosionshastighet. Leverantör 1 korroderar som väntat men Leverantör 2 korroderar knappt alls och prover får olika färger. En förklaring till detta kan vara att Leverantör 2 har mer kol nära ytan än Leverantör 1 tack vare skillnader i produktionsmetoder. Detta kol gör att oxidlagret växer istället för att tas bort i korrosionstest och denna skillnad i tjocklek gör att färgen ändras då ljus bryts annorlunda genom oxidlagret. Denna teori är ej verifierad i denna rapport.

Foreword

The report you are reading now is the result of my 20 weeks long master thesis work conducted at the Materials Technology and Chemistry department (MT&C) of the company Alfa Laval. And connected to the Centre for analysis and synthesis at the Lund institute of technology, within Lund university. The study was conducted during the spring and summer of 2018.

The purpose of this work was to study the surface properties of commercially pure grade 1 titanium from two different suppliers and examine if there are any significant differences between them.

Acknowledgements

To start with I would like to thank everyone at the company Alfa Laval who helped me during this thesis work. I would like to thank Jenny RehnVelut and Daniel Klint for giving me the opportunity to do this thesis work. Extra thanks to Daniel Klint for being my patient supervisor and helping me with all my questions and discussing ideas with me.

Thanks to Jonas Anehamre for showing me around the lab and keeping an eye on my experiments on days I was out of office. Thanks to Patrik Åkerlund for helping and teaching me how the tensile testing machine worked and many thanks to Roland Johansson and Niklas Olsson for teaching and helping me with sample preparation. Finally, a thank you to everyone else at Alfa Laval who has been friendly to me during my time there and answered my many questions!

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1. Introduction

1.1 The Alfa Laval Company and Heat Exchangers

With history tracing back all the way to 1883 the company Alfa Laval has been in business for a long time and specializes in separation, heat transfer and fluid handling. Today, Alfa Laval has over 17000 employees.

The company Alfa Laval offers several different types of products for heat transfer applications in industry. One family of these products are the plate heat exchangers. Plate heat exchangers are, as the name suggests built up by several plates that have patterns pressed in to them to increase the available surface area. Many of these plates are then joined together in to a complete heat exchanger as can be seen in Figure 1. Often a rubber gasket is put between the plates, but other alternatives include for example brazing or welding the plates together. A pair of plates that have been joined together is called a cassette. Media then flows over the plates and is met by either cooling or heating media flowing through the exchanger. An example schematic of a gasketed heat exchanger can be seen in figure 1.

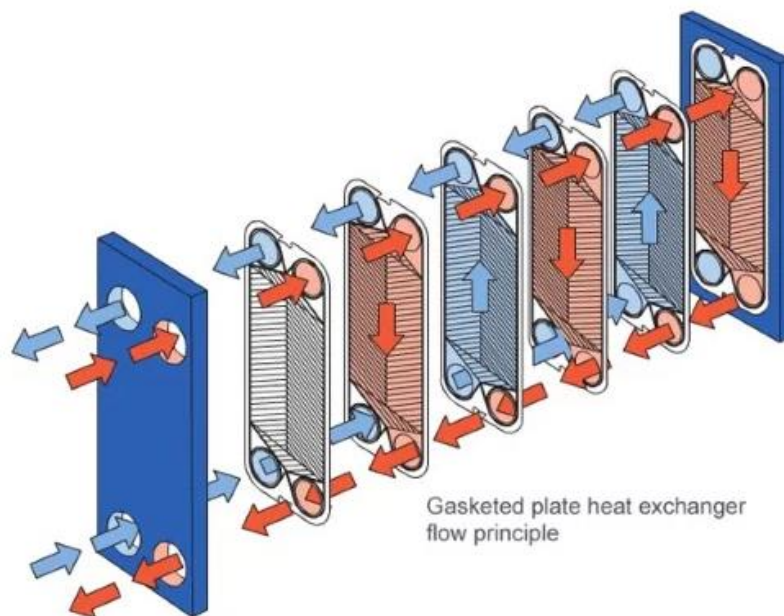


Figure 1 Schematic of a Plate heat exchanger (Alfa Laval copyright) [1]

The plates in heat exchangers can be made from different metals depending on the intended use of the heat exchanger and the desired price. For example, Titanium exchangers are useful in applications where the media is corrosive thanks to the good corrosion resistance of titanium metal in most solutions.

The titanium Alfa Laval uses for plates in heat exchangers comes from several different suppliers and Alfa Laval has strict restrictions on the production and purity of this titanium to ensure that products work as well as advertised. Two main suppliers are investigated in this report are called Supplier 1 and Supplier 2 so the supply companies can remain anonymous.

1.2 Titanium production and properties

Titanium is a silver coloured metal with a high strength to weight ratio, high ductility and excellent corrosion resistance [2]. This makes it useful for several purposes in several industries including the chemical, medical and aerospace industries. The titanium is either used commercially pure (CP) or alloyed with other elements to make the titanium assume the desired properties.

CP titanium is divided into different grades by organisations such as the American Society for Testing and Materials (ASTM) or Japanese Industrial Standards (JIS). Grades with a lower number mean purer titanium with less impurities, mostly regarding iron and oxygen see Figure 2.

	Chemical composition					
	H	O	N	Fe	C	Ti
JIS Type 1	≤ 0.013	≤ 0.15	≤ 0.03	≤ 0.20	≤ 0.08	Remainder
JIS Type 2	≤ 0.013	≤ 0.20	≤ 0.03	≤ 0.25	≤ 0.08	Remainder
JIS Type 3	≤ 0.013	≤ 0.30	≤ 0.05	≤ 0.30	≤ 0.08	Remainder

Figure 2 Chemical compositions and material properties of different titanium grades (JIS) [3]

It should be noted that Alfa Laval's internal requirements are even stricter than grade 1 titanium and requires even lower oxygen, carbon and iron content, see Figure 3.

		N	C	H	Fe	O	Ti
	Alfa Laval Requirement	≤ 0,03	≤ 0,05	≤ 0,013	≤ 0,06	≤ 0,06	Balance

Figure 3 Alfa Laval internal titanium requirements

1.2.1 General properties

Crystalline structure

Pure titanium has a HCP structure called α below 882 °C, over this temperature the titanium assumes a BCC structure called β . This transformation is affected by interstitial and substitutional elements and is thus dependent on metal purity where more impurities means that the α to β transition occurs at a lower temperature [4]. Impurities in the titanium also make it harder, increasing tensile strength and proof stress, see figure 2.

Grain size

In CP (commercially pure) titanium, grain size has some effects on the machinability of the titanium. Smaller grain sizes increase the strength of the titanium thanks to the higher amount of grain boundaries stopping dislocation movement in the material [5]. Since iron has limited solubility in the α form of titanium, small amounts of iron will form small “flocks” of β titanium. These flecks are harder and less ductile. Furthermore, the presence of these flecks reduces the grain size of the α titanium since they limit the grain growth during recrystallisation. [4]

Oxide layer

A titanium surface in the atmosphere or in water will quickly oxidize to form a thin layer of the ceramic TiO_2 protecting the metal surface from further corrosion. This layer breaks down at temperatures over 535°C [5]. The oxide layer grows rapidly from a thickness of 1 nm, but growth quickly tapers off see Figure 4 [6]. The layer can reach a thickness of around 25 nm after four years [7]. The oxygen content in the oxide layer decreases close to the titanium bulk forming Ti_2O_3 and TiO as it approaches the interface between oxide and metal [8]. When the oxide layer is created some oxygen will dissolve in the titanium, at high temperatures oxygen can have up to 14,5 % solubility. This thin layer of oxygen enriched titanium is harder and less ductile than the bulk of the titanium and is called α -case but as long as the titanium is not heated over a temperature of 550°C no significant amount of oxygen is dissolved into the titanium surface [4].

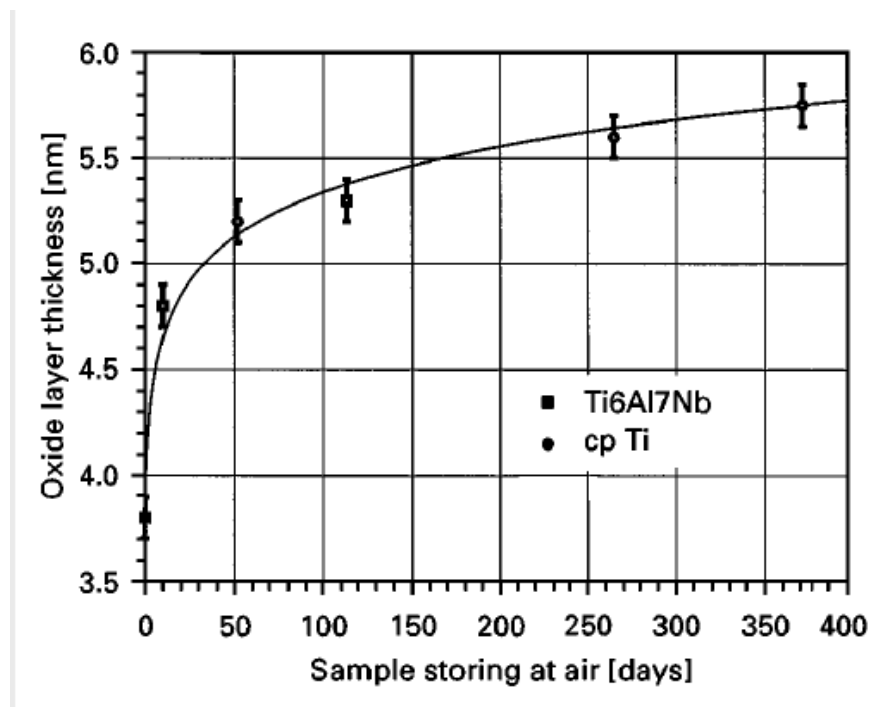


Figure 4 Growth of oxide layer on titanium [6]

1.2.2 Corrosion properties

Titanium has excellent corrosion properties. Thanks to this it is the metal of choice for many heat exchangers that have to perform over long lifecycles. These corrosion properties stem from the oxide layer on the titanium surface, the oxide layer is self-repairing in the presence of oxygen. This leads to great resistance to oxidizing agents such as chromic or nitric acid solutions. On the other hand, titanium lacks resistance to corrosion in the presence of reducing agents since these can cause breakdown of the oxide layer. An application of this can be seen in titanium production where hydrofluoric acids and nitric acid mixtures are used to pickle and chemically mill titanium. This breaks down the oxide layer exposing elemental titanium [4].

1.2.3 Titanium production

Raw material

The first step of titanium product production is the acquisition of elemental titanium from either rutile (TiO_2) or ilmenite (FeTiO_3). The ore is then chlorinated and reduced to elemental titanium using the Kroll process [4]. The resulting titanium is called titanium sponge.

Melting

The melting of titanium is one of the most critical steps in titanium production since it is the source of the majority of all defects in the titanium. The five most common defects are: type I defects also called high interstitial defects (HIDs), type II Alpha stabilized regions, beta stabilized regions, voids, and high-density Inclusions (HDIs) [4]. Once these defects appear they are very hard to remove.

The melting itself is commonly done using Vacuum Arc Remelting (VAR). In this process titanium sponge and desired alloying elements are mechanically compacted to form blocks, usually in a hydraulic press. These blocks are welded together in an inert gas chamber to form the first electrode. This electrode is then melted, cooled and remelted several times.

Processing

When the ingot from melting is finished and has been checked for defects, the ingot is often annealed for around 20-30 h at a temperature over the β transformation temperature, i.e. around 1100 to 1350 °C. The exact time and temperature used depends on the titanium alloy produced. The purpose of this annealing is to homogenize the ingot and is not used for all titanium alloys and some titanium producers skip this step altogether [4].

The ingot is then ground or lathe turned to smooth out the surface and remove stress concentrations. Care must be taken here since grinding can create local hotspots since the thermal conductivity of titanium is low.

The ingot is then hot pressed at temperatures about 150°C over β transformation temperature in to a square or round cornered square piece and the diameter is typically reduced 28-38 %. The ingot is then reheated to just below β transformation temperature and diameter is reduced by another 30-40 %. Finally, the ingot is heated to just over β transformation temperature and diameter reduced by an additional 30-40% and then rapidly cooled. This is to improve the structural uniformity of the metal [4]. After this the metal can be hot worked further, reducing the diameter by an additional 60%.

From here the process steps differs depending on the final product. In this report the focus will be on production of sheets since that is what Alfa Laval uses for their plate heat exchangers.

Sheet is hot rolled in a rolling mill where several sheets are often rolled together in a steel retort with parting agents between them to reduce oxidation and to prevent the sheets from sticking to each other. Sheet packets are often cross rolled to increase their width, this also reduces the degree of the texture of the sheets and has some effects on behaviour of the final product regarding formability [4].

After the hot rolling the sheets are extracted, some final processing in the form of pickling annealing or creep flattening is done. If extra thin sheet is required some final cold reduction can also be performed to reach the desired thickness. An example process for production of titanium sheet can be seen in

Figure 5.

The producers Supplier 1 and Supplier 2 differ slightly, Supplier 2 only vacuum anneals while Supplier 1 anneals in air and then pickles.

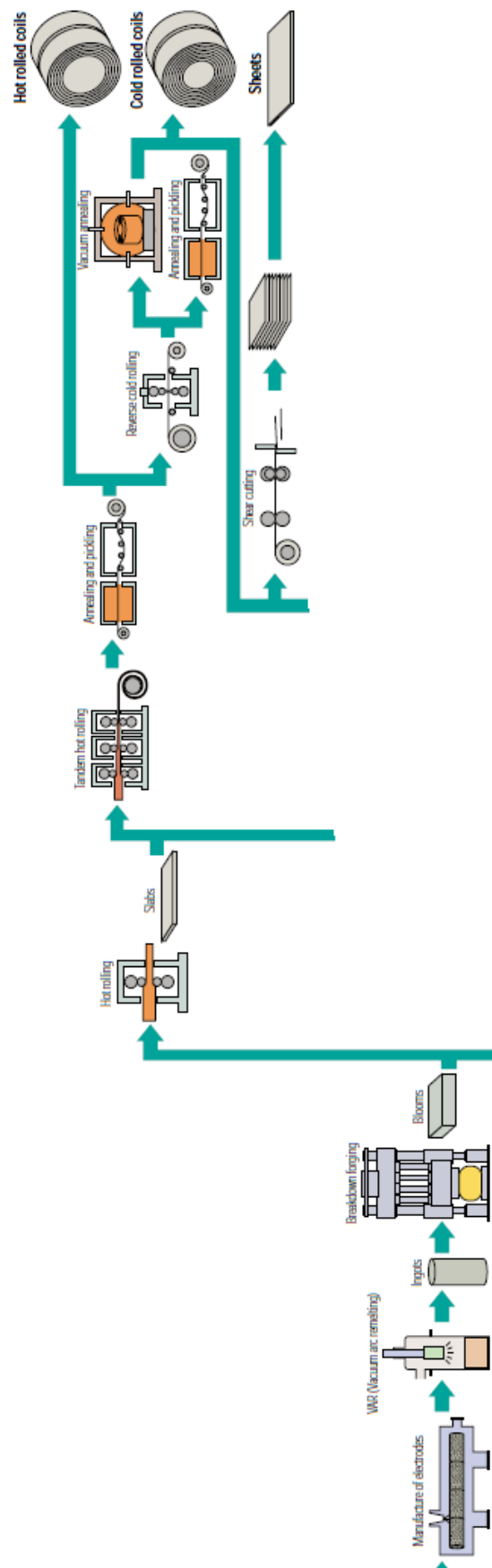


Figure 5 Sheet production process (cropped). [9]

1.3.1 Background

As stated earlier much of the grade 1 titanium Alfa Laval comes from two suppliers Supplier 1 and Supplier 2. On one occasion during a failure analysis of a titanium plate cassette from one a heat exchanger used for condensation of water vapor containing hydrochloric acid it was noted that the different sides of the cassette used titanium from different suppliers. Furthermore, one of the sides had corroded much more than the other. As can be seen in Figure 6 the edges of the N46958 plate looks jagged and much more brittle than the AT4376 plate does.

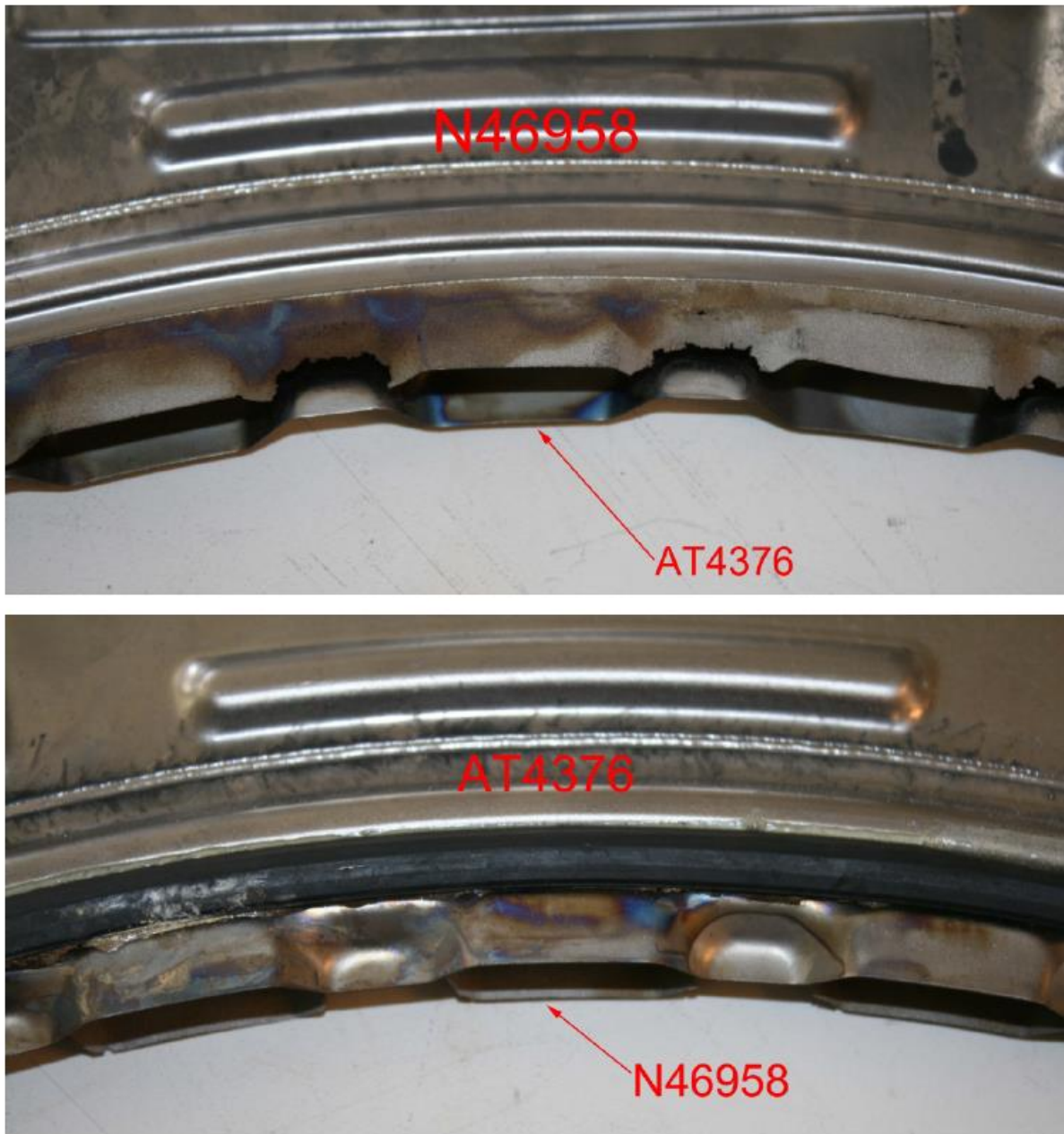


Figure 6 Corrosion on Titanium cassette with Supplier 1(AT) and Supplier 2 (N) marked [9]

When checked both batches of titanium were found to be within the allowed specifications Alfa Laval has for titanium [9]. Alfa Laval wants all their products to be of a high and consistent quality, and titanium from two different suppliers reacting differently makes consistency a problem.

1.3.2 Description of thesis work

This thesis work was created to study if any major differences in surface properties exists between grade 1 titanium from the two suppliers Supplier 1 and Supplier 2. The focus on surface properties stems from the fact that all titanium samples were in sheet form or pressed plate (from here on just called “plate”), and thus has large ratio of surface area compared to bulk volume. While the idea for this study arose from differences in corrosion rate differences in any material properties were of interest.

The study included both sheets and plates that had been pressed into shape for use in a heat exchanger in the Alfa Laval factory. This was to study how the pressing process affected the properties of the titanium and if the materials from the two suppliers were affected differently.

To study grade 1 titanium material from both Supplier 1 and Supplier 2 were provided. Every plate and sheet had a batch number with a document ensuring that the titanium properties were within Alfa Laval specifications.

The sheets and plates used in this study were gathered from Alfa Lavals production department. some of the sheets and plates were slightly damaged and care was taken to minimize the effects of scratches and bends on the measurements. The sheets and plates did not have a consistent size and there were some small variations in thickness, but no plate was thicker than 0.8 mm.

In the table below, there is a list of sheets and plates included in this study from Supplier 1 and Supplier 2. All Supplier 1 batch names starts with an **A** while all Supplier 2 batches stat with an **N**. Some batches had more than one sheet or plate, this is shown as an (number) at the end of the batch number to differentiate between different samples.

Table 1 Batch names of available Titanium sheets and plates from Supplier 1 and Supplier 2

Supplier 1		Supplier 2	
Sheets	Plates	Sheets	Plates
AK4394(1)	AK4184	N46936	N46864
AK4394(2)	AX0788	N66974	N57089
AX0226	AX1342	N67127(1)	N67127
AX0735(1)	AX1427	N67127(2)	
AX0735(2)	AX1656	N76179(1)	
AX0735(3)	AX1828	N76179(2)	
AX1828(1)	AX1850		
AX1828(2)			

As seen in Table 1 there was four unique batches of sheets and 7 unique batches of plates from Supplier 1. From Supplier 2 there were four unique batches of sheets and three unique batches of plates. Both Supplier 1 and Supplier 2 had one batch each where I had both sheet and plate from the same batch available.

2. Methods and Theory

2.1 Surface energy measurements

2.1.1 Theory

Knowing the surface energy of the titanium plates Alfa Laval uses can be very useful since surface energy has an impact on how well the rubber gaskets can be glued to the heat exchanger. This is because the surface energy of something affects how well it can be wetted and this is important for getting a good adhesion.

According to the nineteenth century scientist Thomas Young the surface free energy of a solid can be calculated by adding a drop of liquid with known surface tension on to the surface and measuring the contact angle by the equation:

$$\sigma_S = \gamma_{SL} + \sigma_L * \cos(\theta) \quad (1)$$

Where σ_S is the surface free energy of the solid, σ_L is the surface tension of the liquid, γ_{SL} is the interfacial tension and θ the angle between the drop and the surface see Figure 7. The interface between gas and the solid and liquid is ignored [10].

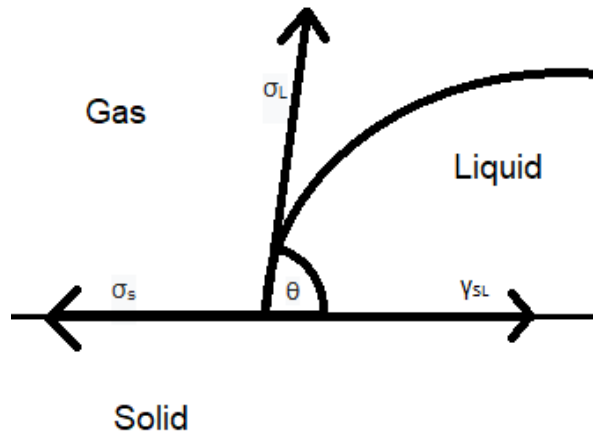


Figure 7 Schematic of surface energy measurement

The method used to calculate the surface free energy was the Owens, Wendt, Rabel and Kaelble method (OWRK). This method states that surface tension and surface free energy can be divided up into a polar and disperse part [10]. So σ_S and σ_L can be written as:

$$\sigma_S = \sigma_S^P + \sigma_S^D \quad (2)$$

$$\sigma_L = \sigma_L^P + \sigma_L^D \quad (3)$$

And the interfacial tension γ_{SL} can be written as:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2(\sqrt{(\sigma_S^D * \sigma_L^D)} + \sqrt{\sigma_S^P * \sigma_L^P}) \quad (4)$$

If one knows the disperse and polar fractions of two different liquids one can use equation (1), equation (4) and linear regression to find the surface free energy of the surface [10].

2.1.2 Experimental

The surface energy of the plates and sheets were measured by drop shape analysis using a KRÜSS MobileDrop hand held surface energy measuring device and the software KRÜSS Advance for evaluation. The liquids used were water and diiodomethane both of which had values of their polar and disperse fractions recorded in the Advance program.

The plates and sheets were washed with water, ethanol and acetone to make sure nothing at the surface interfered with the measurement, then ten drops of each liquid were dropped on the metal and the contact angle measured with the automatic measuring program in the Advance software. Since the plates are not flat the only place that could be measured was the rear side of the gasket groove, but on the sheet the drops were spread over a large measuring area.

2.2 Surface roughness

2.2.1 Theory

The surface roughness measurements is as the name suggests a way to evaluate how smooth the surface is. This can be measured by dragging a needle over the surface and recording the changes in elevation. The surface roughness can be expressed in several different ways for example Ra is the average surface roughness within the measurement area while Rz is the mean roughness depth which takes the average of the five highest deepest peaks and valleys. Rzmax on the other hand is the highest value of peak to valley.

2.2.2 Experimental

The surface roughness was measured using a Marsurf m400 instrument. The plates were measured at three different locations see Figure 8. The back of the gasket groove, on the ridge of the heating area and on the back of the gasket groove close to the opening. The sheets were measured once in the rolling direction and once in the transverse direction.

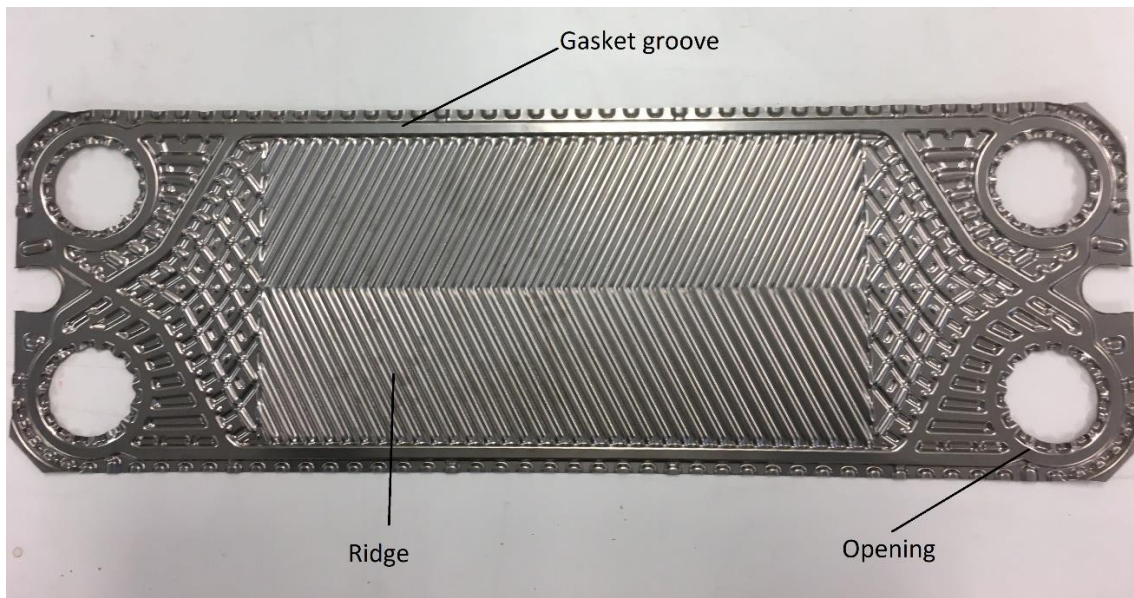


Figure 8 Measuring locations for pressed plates

2.3 Corrosion

2.3.1 Theory

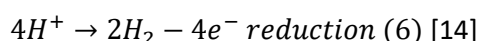
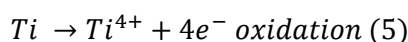
As mentioned earlier titanium will corrode in the presence of reducing acids such as hydrochloric acid or sulfuric acid, as long as there are no inhibitors present [11]. The speed of corrosion will increase both with concentration of the acid and with increasing temperature [12]. To test the corrosion properties of the titanium samples in this project the use of hydrochloric acid (HCl) was selected. This was because diluted HCl is relatively safe to handle and the lab facility already had HCl in stock. One corrosion test was also performed in sulfuric acid at room temperature, every preparation step was the same in the sulfuric acid test.

Grade 1 Titanium in a boiling solution of 1 % weight (% wt) HCl will corrode at the rate of 1.8 mm/year [11]. But one should note that the oxide layer on the surface of the titanium might have a small effect on the corrosion rate.

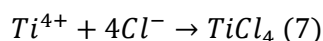
The mechanism by which the corrosion occurs is the following. First the oxide layer on the outside is attacked by the hydrochloric acid dissolving and creating titanium tetrachloride it by the reaction:



With the surface oxide layer removed the corrosion of the bulk of the titanium starts, this can be described as a redox reaction where:



The Titanium ions then react with the chloride ions in the acid creating titanium tetrachloride by the following reaction:



Corrosion is heavily inhibited by the presence of metallic cations or other oxidizing agents since the metal cations shifting the potential of the titanium in the noble direction [11]. Or by organic oxidising compounds forming a protective layer, shielding the titanium from corrosion [14]. Even a low concentration of metal cations would have a large effect on corrosion rate, for example a 100-ppm concentration of Fe^{3+} ions reduces corrosion rate in 5% boiling HCL from 29 mm/year to 0.025 mm/year [11].

2.3.2 Experimental

Pieces of titanium sheet were cut out firstly using a metal scissor then these cut out pieces were sawed into even smaller rectangular pieces using an automatic saw. After sawing the edges of the titanium coupons were hand grinded for approximately 10 seconds on every edge with 320-grit sandpaper using a sander. This was to remove the stress induced at the edges from the sawing.

The titanium plates proved difficult to cut using the metal scissor so large rectangular pieces of corrugated surface of the heat transfer area were instead cut out with an angle grinder. The pieces cut out with the angle grinder were quite large compared to the final corrosion coupons. This was a choice made so that the heat produced in the angle grinding did not affect the properties of the titanium plate coupons. After the angle grinding the squares of plate were small enough to fit in the saw and followed the same procedure as the sheets with grinding 10 sec on every edge.

The final size of the test coupons varied slightly from coupon to coupon, but attempts were made to make sure that all coupons in the same test were around the same size, approximately 30x30 mm.

An important note to make is that the coupons cut out from the heat exchange area of the plates have a larger surface area thanks to the ridges in surface. These ridges increase surface area by approximately 20% compared to a flat sheet [15]. An example of a corrosion coupon from a sheet and plate can be seen in Figure 9.

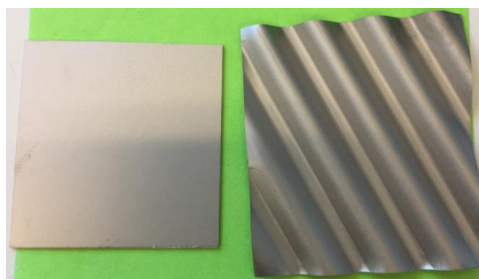


Figure 9 Coupon from sheet 34x34 mm (left) and plate 38x40 mm (right).

The corrosion setup used a reaction vessel with a volume of either 3 litres or 1 litres, depending on the number of coupons placed in the same corrosion test. This was according to ASTM standards stating that you need at least 0.2 millilitres of acid solution per square millimetre of test coupon surface area to ensure that acid concentration remains approximately unchanged over the duration of the test [16].

The mixing proportions was calculated using the formula:

$$\text{initial mass} * \text{start concentration} = \text{final mass} * \text{final concentration} \quad (8)$$

Since I had a 32% stock HCl solution and wanted a final mass of 1 kilo with a concentration of 1% HCl equation (8) becomes:

$$X * 0.32 = 1 * 0.01$$

Where **X** is the amount of 32 % HCl stock solution in kilos. This gives $X = 0.03125$ kg. Taking $1\text{ kg} - 0.03125\text{ kg} = 0.96875\text{ kg}$ gives us the weight of water in our desired 1 kg 1%wt HCl solution. For the 3L reaction vessel the weight values were multiplied by three.

The reaction vessel was filled with the desired weight of distilled water and placed on a heating plate. A magnetic stirrer was added since the reaction vessel had a tendency to break during heating if unstirred. A packing ring was added and a lid put on. Through the lid a thermometer was inserted and a reflux condenser was connected. The lid was then secured with a clamp and set to heat to 80 °C. An example of the experiment setup can be seen in Figure 10.

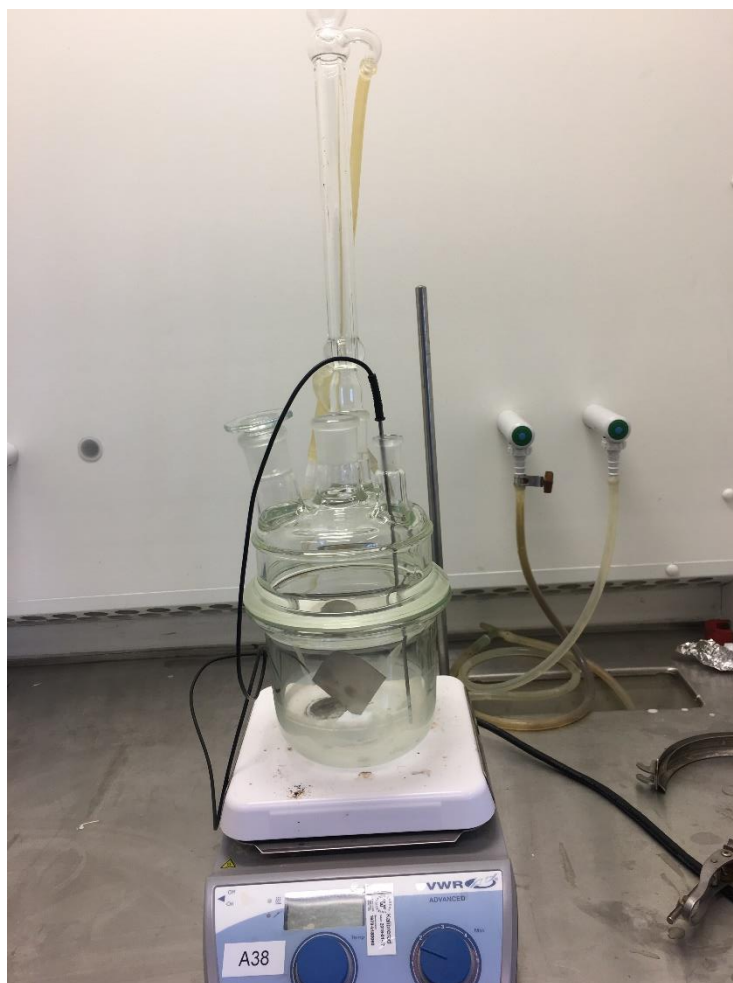


Figure 10 Corrosion experiment setup (no liquid)

While the water was heating the titanium coupons were washed with water, ethanol and acetone to clean them. Then they were weighed and their dimensions measured. After this they were fastened into groves in a mount made from Polytetrafluoroethylene (PTFE). Coupons were inserted in such a way as to minimize the amount of surface area of the coupons covered by the PTFE while still making sure that the coupons could not fall out of the mount.

When the test solution in the reaction vessel had reached 80 °C the lid was removed and the magnetic stirrer taken out, the mount with the titanium coupons were then quickly added and the lid put on again. The temperature was then increased to boiling and when the water started to boil the acid was added in. since no stirrer remained in the reaction vessel stirring was reliant on internal convection. The samples were left immersed in the acid solution for the desired time. The time varied between experiments but the most commonly used time was approximately 48 hours, longer tests would give a more reliable result since small changes in corrosion rate has time to stabilize [11].

After the desired time has been reached the lid of the reaction vessel was removed and mount with titanium coupons were taken out with a pair of tongs and quenched in water. The coupons were then removed from the mount and washed again in water, ethanol and acetone. The coupons were then weighed again and with the difference in mass one could calculate the corrosion rate in mm/year with the following formula:

$$\text{Corrosion rate in } \frac{\text{mm}}{\text{year}} = \frac{k*W}{(A*t*\rho)} \quad (8) \quad [16]$$

- Where k is a constant with the value of $8.76*10^4$.
- W is the mass loss in grams.
- A is the area of the coupon in cm^2 . Since the coupons were rectangular surface area was calculated with:

$$A = ((\text{Base} * \text{Height}) * 2) + ((\text{Thickness} * \text{Base}) * 2) + (\text{Thickness} * \text{Height}) * 2$$

As stated earlier plate coupons had an additional 20% surface area compared to a flat sheet so the area of a plate is equal to $A*1.2$.

- t is the time of exposure in hours.
- ρ is the density of the sample ($=0.00454 \text{ g/mm}^3$)

A total of 13 corrosion tests were performed, 12 in HCl and one in H_2SO_4 . In HCl three tests were run for approximately 24 hours, 5 tests ran for approximately 48 hours, one for 70 hours, one for 88 hours and the three longest tests for 169, 189 and 450 hours respectively.

The H_2SO_4 test ran for approximately 48 hours.

2.4 EDS Analysis

2.4.1 Theory

Energy-dispersive X-ray spectroscopy (EDS, EDX or sometimes XEDS) is a technique used with an electron microscope to gain information of the elemental content of the sample. In this technique the electron beam in the electron microscope excites or ejects electrons bound to atoms in the sample. When the atom returns to the ground state or an electron from a higher energy level falls down to fill the hole the difference in energy is compensated by the atom emitting an x-ray. Since all elements have unique energy levels the energy of these emitted x-rays are characteristic to a specific element [17]. Note since most atoms have several electron shells with several energy levels there are more routes than one an atom can take when it returns to ground state. This means that one element will not give out just one x-ray signal but several with different energy levels. The electron beam cannot excite electrons in an atom to levels requiring energy beyond the energy of the electron beam itself.

The emitted x-rays from the sample are picked up by a detector and counted. From the varying amounts of x-ray signals the elemental composition of the sample can be calculated.

2.4.2 Experimental

Samples were fastened on an aluminium stub with carbon tape and put into the FEI INSPECT™ S50 electron microscope. An SE picture was taken and the sample was analysed using the EDS detector with a beam energy of 10 keV. Results were compiled with the computer program AZTEK. Several scans over different areas were run to see if there were any regional differences in elemental composition.

2.5 Study using EBSD

Samples from both suppliers were studied using Electron Backscatter Diffraction (EBSD).

EBSD Analysis is performed using an electron microscope. The analysis provides you with information of the grain structure and crystalline directions of the sample surface.

When the electron beam in an electron microscope hits the sample, some incident electrons are backscattered back out of the sample. Since this is partly a diffraction interaction these electrons carry information of the crystalline lattice near the surface of the sample [18]. Because of the surface sensitivity of this method the sample surfaces need to be very flat.

The samples were analysed using the SEM in the Geology department of Lund University, with the help of Carl Alwmark.

The EBSD analysis was performed at two different occasions. With two Supplier 1 and two Supplier 2 samples analyzed at the first occasion, and one Supplier 1 with two Supplier 2 samples analysed during the second run.

Samples were prepared by cutting them out of the titanium sheet and then fixing them by hot moulding them in plastic. For this either a clear plastic or a special conductive plastic from Struers called ConduFast was used. All samples were oriented so that the rolling direction was out from the plane.

The samples were then polished in a polishing machine using SIC # 320 sandpaper, 9 µm diamond polish and finally a chemical polish "OP-Chem" from Struers. Sometimes 10% H₂O₂ and 10% ammonia was added to the OP-Chem mixture in an attempt to improve the polish, but this did not seem to yield any noticeable effect. After polish, the samples were inspected in an optical microscope and if the surface seemed flat enough they were cut or grinded down to a smaller size as to fit the size requirements of the electron microscope.

2.6 GD-OES

GD-OES or Glow Discharge Optical Emission Spectrometry, is an analysis method where the sample you want to analyse is ablated by argon ions in a low-pressure argon atmosphere. As atoms leave the surface of the analysis material and enter the surrounding plasma the optical emissions created by the de-excitation of the atoms is detected by an optical spectrometer and the elemental composition of the analysis material can be determined [19].

Since only the top layer of atoms can be ablated by the discharges a GD-OES analysis gives a picture of the elemental compositions of the layers of analysis material in very small increments. This makes this method very surface sensitive.

Since neither Alfa Laval nor LTH had a facility where GD-OES was available six samples were sent for external analysis by the company Swerea KIMAB. Each of the samples were tested two times and the results presented in this report is the mean of both results.

The requirement for analysis pieces to be relatively flat meant only sheets could be analysed. Pieces sent for analysis were N67127(2), N66974 and N46936 from Supplier 2 and AK4394(1), AX0226 and AX0735(3) from Supplier 1.

Alfa Laval has at an earlier time sent other samples for GD-OES analysis but the results of these are not included in the graphs below.

2.7 Tensile testing

2.7.1 Theory

In a tensile test a sample with known geometry is elongated by force until it breaks or to a preset elongation % from the start. From this several characteristics of the material can be determined. For example, the ultimate tensile strength, yield strength and fracture strength.

2.7.2 Experimental

Titanium sheets were cut in to a set width and length using a mechanical cutter. Three samples from every sheet was cut out. These titanium slips were then elongated in the tensile testing machine Zwick/Roell Z010. The elongation was set to 10, 20 and 30 % elongation. It should be noted that all of the pieces were not of the same thickness, so even though the pieces had the same length and width there were differences in sample geometry.

2.8 Hardness testing

2.8.1 Theory

Hardness testing tests the samples ability to resist plastic deformation. The titanium samples from the two suppliers were measured using Vickers hardness. This is measured by indenting the sample with a pyramid shaped indenter with a set load on it and then measure the area of the indentation.

2.8.2 Experimental

Since the hardness measurements require the samples to be flat, three samples each from sheets of the two suppliers were fastened in resin and polished in the same way as when samples were polished for EBSD analysis (2.4). The Vickers hardness was then measured using a Zwick/Roell ZHV μ machine 16 indentions per sample with 100 grams of force and a 10 sec dwell time.

2.9 Anova

The results of many of the experiments in this thesis comes in two or more groups since two different suppliers were investigated. Anova or analysis of variance is a statistic method for evaluating if two or more groups are significantly different by comparing the internal variance within the groups with the variance between groups. In this thesis the analysis tool pack addon in Microsoft Excel to perform the analysis.

Anova uses the null hypothesis that there is no difference between groups. The analysis outputs a value F that is compared to another value F_{crit} . if $F < F_{crit}$ the null hypothesis holds, and no significant difference can be detected between groups. But if $F > F_{crit}$ the null hypothesis is rejected and there is a significant difference between the groups.

3. Results

3.1 Surface energy

Results from the surface energy measurements are presented in Table 2 to Table 6. The results are similar between suppliers with Supplier 1 sheets having the highest mean surface energy and Supplier 2 plates having the lowest mean surface energy. Supplier 2 plates also had the highest standard deviation.

Anova analysis shown in Table 6 showed that there were significant differences Supplier 1 and 2 sheets and between the sheets and plates of Supplier 1. No significant difference could be shown between the plates from Supplier 1 and 2 nor from the comparison between sheet and plate from Supplier 2.

Table 2 Surface energy for Supplier 1 sheets

Supplier 1 sheet	Surface free energy [mN/m] OWRK	STD	Mean Supplier 1 sheet	Pooled STD
AK4394(1)	67.66	4.18	59.39	5.86
AK4394(2)	58.38	5.21		
AX0226	62.27	6.59		
AX0735(1)	59.45	4.72		
AX0735(2)	53.88	8.6		
AX0735(3)	60.23	6.36		
AX1828(1)	64.33	4.73		
AX1828(2)	48.94	5.26		

Table 3 Surface energy for Supplier 2 sheets

Supplier 2 sheet	Surface free energy [mN/m] OWRK	STD	Mean Supplier 2 sheet	Pooled STD
N46936	55.03	6.67	50.63	6.24
N66974	48.4	5.75		
N67127(1) side 1	51.58	7.14		
N67127(1) side 2	55.94	5.58		
N76129(1)	46.65	5.81		
N76129(2)	46.17	6.35		

Table 4 Surface energy for Supplier 1 plate

Supplier 1 plate	Surface free energy [mN/m] OWRK	STD	Mean Supplier 1 plate	Pooled STD
AX0788	49.78	12.75	52.4	9.19
AX1342	60.25	8.65		
AX1427	56.06	11.95		
AX1656	47.49	4.42		
AX1828	48.07	3.45		
AX1850	52.74	9.73		

Table 5 Surface energy for Supplier 2 plate

Supplier 2 plate	Surface free energy [mN/m] OWRK	STD	Mean Supplier 2 plate	Pooled STD
N46864	57.95	10.94	51.9	13.56
N57089	53.13	7.62		
N67127	44.52	4.98		

Table 6 Anova comparisons for surface energy

Anova comparison (alpha =0.05)	F	F crit
Supplier 1 sheet Vs. Supplier 2 sheet	9.53	4.75
Supplier 1 plate Vs Supplier 2 plate	0.018	5.59
Supplier 1 sheet Vs. Supplier 1 plate	5.48	4.75
Supplier 2 sheet Vs. Supplier 2 plate	0.118	5.59

3.2 Surface roughness

Results of surface roughness presented in Table 7 and Table 8.

For Supplier 1 the Ra values were higher for measurements in the rolling direction, 0.324 vs 0.296 μm . While the opposite is true for Supplier 2 where the values were 0.238 vs 0.302 μm . Supplier 1 sheets had higher values of Rz and RzMax than Supplier 2 sheets. For plates the value measured on the ridge of the heating area where the highest in all categories for both Supplier 1 and 2.

Results of Anova comparisons can be seen in Table 9 to Table 14. In these one can see that there are no significant differences between rolling or transverse direction for either of the Supplier sheets. For Supplier 1 plates there are significant differences between gasket groove and ridge, and between opening and ridge. Between gasket groove and opening there is no significant difference. For Supplier 2 there are no significant differences between any of the measurements.

When comparing Supplier 1 and Supplier 2 the only significant differences are in the Rz and RzMax values of the sheets.

Table 7 Surface roughness of sheets

Sheets	Ra (μm)	Rz	RzMax
Mean and STD Supplier 1 Rolling	0.324 \pm 0.108	3.303 \pm 0.489	4.686 \pm 0.558
Mean and STD Supplier 1 Transverse	0.296 \pm 0.0768	2.883 \pm 0.562	3.995 \pm 0.933
Mean and STD Supplier 2 rolling	0.238 \pm 0.0525	1.590 \pm 0.374	1.986 \pm 0.609
Mean and STD Supplier 2 transverse	0.302 \pm 0.0697	1.792 \pm 0.369	2.035 \pm 0.374

Table 8 surface roughness of plates

Plates	Ra (μm)	Rz	RzMax
Mean and STD Supplier 1 Gasket groove	0.477 \pm 0.236	3.513 \pm 1.342	4.743 \pm 2.17
Mean and STD Supplier 1 Ridge	0.868 \pm 0.273	5.445 \pm 1.580	7.187 \pm 2.1
Mean and STD Supplier 1 Opening ridge	0.394 \pm 0.124	3.777 \pm 1.019	5.741 \pm 2.11
Mean and STD Supplier 2 Gasket groove	0.362 \pm 0.0352	2.276 \pm 0.212	4.388 \pm 2.266
Mean and STD Supplier 2 Ridge	0.912 \pm 0.413	5.297 \pm 2.316	7.31 \pm 3.852
Mean and STD Supplier 2 Opening ridge	0.498 \pm 0.365	3.402 \pm 2.606	4.533 \pm 3.824

Table 9 Anova comparisons between Rolling and transverse directions Supplier 1

Anova comparison sheets Supplier 1 (alpha=0.05)	F	F crit
Rolling Vs. Transverse Ra	0.321	4.6
Rolling Vs. Transverse Rz	2.396	4.6
Rolling Vs. Transverse RzMax	3.11	4.6

Table 10 Anova comparisons plate measurements Supplier 1

Anova comparison plates Supplier 1 (alpha=0.05)	F	F crit
Gasket groove vs. Ridge Ra	8.234	4.747
Gasket groove vs. Ridge Rz	6.41	4.747
Gasket groove vs. Ridge RzMax	4.77	4.747
Gasket groove vs. Opening Ra	0.972	4.747
Gasket groove vs. Opening Rz	0.068	4.747
Gasket groove vs. Opening RzMax	0.529	4.747
Ridge vs. Opening Ra	18.911	4.747
Ridge vs. Opening Rz	6.406	4.747
Ridge vs. Opening RzMax	2.265	4.747

Table 11 Anova comparisons between Rolling and transverse directions Supplier 2

Anova comparison sheets Supplier 2 (alpha=0.05)	F	F crit
Rolling Vs. Transverse Ra	2.663	4.964
Rolling Vs. Transverse Rz	0.122	4.964
Rolling Vs. Transverse RzMax	0.0241	4.964

Table 12 Anova comparisons plate measurements Supplier 2

Anova comparison plates Supplier 2 (alpha=0.05)	F	F crit
Gasket groove vs. Ridge Ra	2.609	7.709
Gasket groove vs. Ridge Rz	2.789	7.709
Gasket groove vs. Ridge RzMax	0.0473	7.709
Gasket groove vs. Opening Ra	0.511	7.709
Gasket groove vs. Opening Rz	0.63	7.709
Gasket groove vs. Opening RzMax	0.0098	7.709
Ridge vs. Opening Ra	0.196	7.709
Ridge vs. Opening Rz	0.0165	7.709
Ridge vs. Opening RzMax	0.00216	7.709

Table 13 Anova comparisons between sheets from Supplier 1 and Supplier 2

Anova cross comparison sheets (alpha=0.05)	F	F crit
Rolling Supplier 1 Vs. Supplier 2 Ra	2.723	4.747
Rolling Supplier 1 Vs. Supplier 2 Rz	43.857	4.747
Rolling Supplier 1 Vs. Supplier 2 RzMax	63.59	4.747
Transverse Supplier 1 Vs. Supplier 2 Ra	0.0219	4.747
Transverse Supplier 1 Vs. Supplier 2 Rz	16.214	4.747
Transverse Supplier 1 Vs. Supplier 2 RzMax	22.785	4.747

Table 14 Anova comparisons between plates from Supplier 1 and Supplier 2

Anova cross comparison plates (alpha=0.05)	F	F crit
Packing Supplier 1 Vs. Supplier 2 Ra	0.512	5.318
Packing Supplier 1 Vs. Supplier 2 Rz	2.419	5.318
Packing Supplier 1 Vs. Supplier 2 RzMax	0.0047	5.318
Opening Supplier 1 Vs. Supplier 2 Ra	1.178	5.318
Opening Supplier 1 Vs. Supplier 2 Rz	0.0366	5.318
Opening Supplier 1 Vs. Supplier 2 RzMax	0.0255	5.318
Ridge Supplier 1 Vs. Supplier 2 Ra	0.432	5.318
Ridge Supplier 1 Vs. Supplier 2 Rz	1.127	5.318
Ridge Supplier 1 Vs. Supplier 2 RzMax	1.429	5.318

3.3 Corrosion testing

3.3.1 Corrosion tests in 1 % HCl

Results from corrosion testing presented as mean values in Table 15. Supplier 1 sheet and plate has a corrosion rate quite close to the expected value of 1.8 mm/year [11]. Supplier 2 sheet and plate had almost no mass loss and sometimes gained some mass. Supplier 2 coupons also switched colour from the grey of titanium to a brownish yellow or sometimes red, see Figure 11.

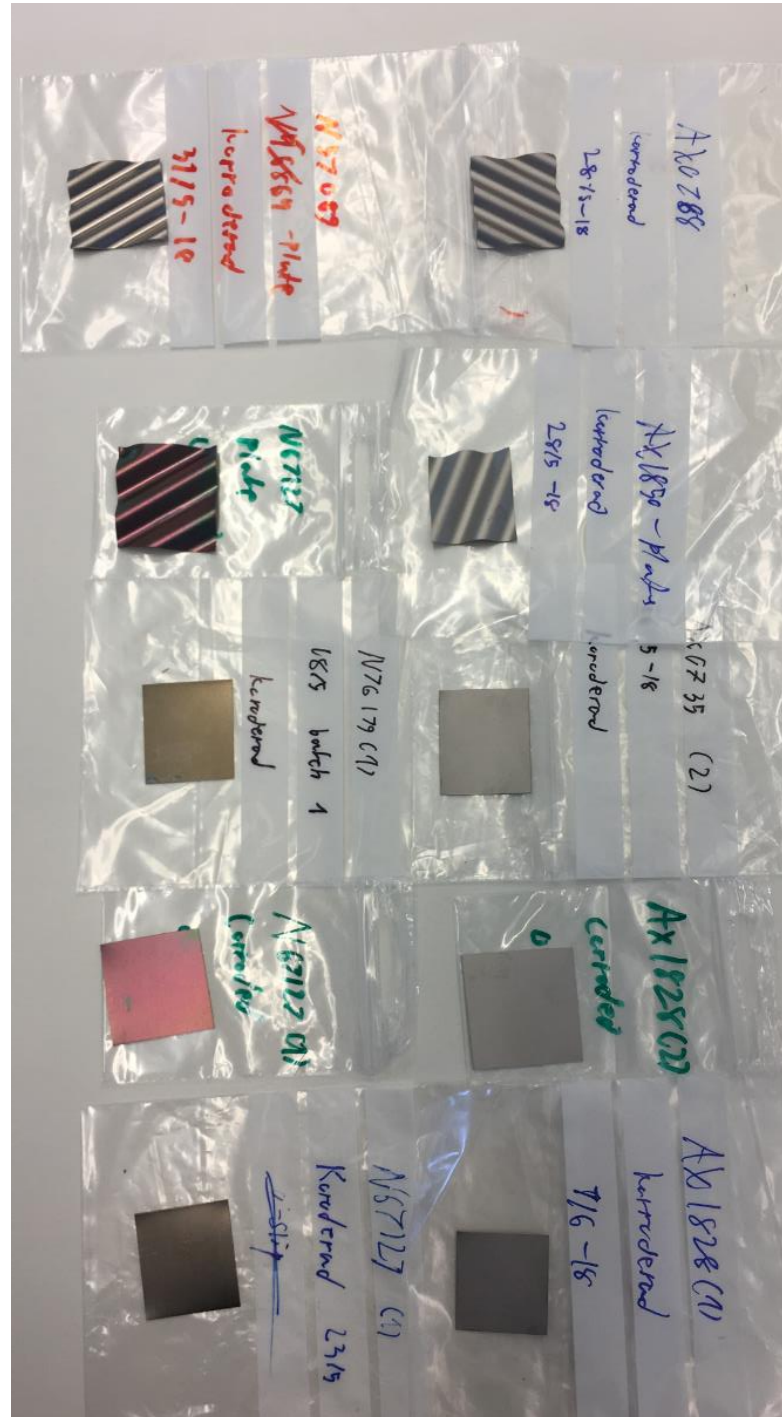


Figure 11 Corroded Supplier 1 and Supplier 2 pieces. Left column is Supplier 2 and right column is Supplier 1

Table 15 Mean corrosion rate of titanium samples

Supplier 1				Supplier 2			
Sheets	Corrosion rate mm/year	Plates	Corrosion rate mm/year	Sheets	Corrosion rate mm/year	Plates	Corrosion rate mm/year
AK4394(1)	1.65	AK4184	1.71	N46936	-0.023	N46864	-0.0019
AK4394(2)	1.58	AX0788	1.79	N66974	-0.071	N57089	-0.0017
AX0226	1.52	AX1342	1.8	N67127(1)	0.0021	N67127	0.0023
AX0735(1)	1.71	AX1427	1.75	N67127(2)	0.0089		
AX0735(2)	1.64	AX1656	1.76	N76179(1)	-0.023		
AX0735(3)	1.59	AX1828 ¹		N76179(2)	-0.023		
AX1828(1)	1.63	AX1850	1.7				
AX1828(2)	1.97						
Mean	1.66		1.75		-0.021		-0.00043
STD	0.14		0.041		0.031		0.0024

1. All experiments with AX1828 went wrong in some way and the only reliable results are from experiments with other acid concentrations that 1% HCl so no values from that plate was used when calculating mean or STD.

Anova tests were performed to study if there was a significant difference between Supplier 1 and Supplier 2 sheets and plates. And if there were significant differences between sheets and pressed plates from the same supplier. Results of anova analysis in Table 16.

There were significant differences in corrosion rate between Supplier 1 and Supplier 2 but no significant difference between sheet and plate within the suppliers.

Table 16 Anova comparison from corrosion tests

Anova comparison Alpha = 0.05	F	F crit
Supplier 1 sheets Vs. Supplier 2 sheets	863.788	4.747
Supplier 1 plate Vs. Supplier 2 plate	5181.46	5.591
Supplier 1 sheet Vs. Supplier 1 plate	2.417	4.747
Supplier 2 sheet Vs. Supplier 2 plate	1.546	5.591

In one of the tests the acid in the container switched colour from clear to a clear pink. The pink colouring of the liquid seemed to come from the red or brown silicon plastic packing ring which had come into contact with acidic gas in the reaction vessel and melted into the solution. this did not seem to affect the corrosion rate of the titanium.

During the three longest tests performed the reaction vessel eventually was covered in a white layer that was hard to remove. Once this coincided with a melted packing ring. In longest test performed, running for approximately 450 hours there were not only a white layer on the reaction vessel but also loose white and blue precipitate in the form of flakes on the mount and the bottom of the reaction vessel. The blue precipitate was centred around the Supplier 1 pieces in the experiment. Samples were of the white and blue precipitates taken both from the experiment where the ring had melted and from the longest experiment, the samples where dried and analysed using EDX to determine the elemental content. When drying the blue precipitated faded to white.

3.3.2 EDX Analysis of residue

One of the results of EDX analysis of precipitate from the experiment where the packing ring melted can be seen in Figure 13 and Figure 13. The rest where similar and can be seen in the appendix. The EDX analysis showed a high amount of carbon, oxygen, silicone and some small amounts of chlorine and titanium.

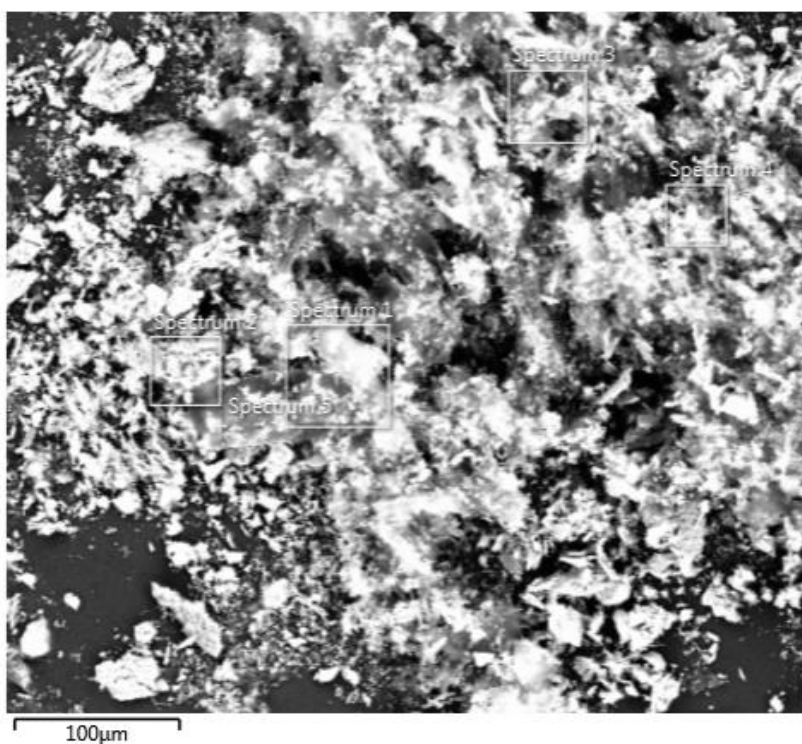


Figure 12 SE image of precipitate sample from experiment with broken packing ring

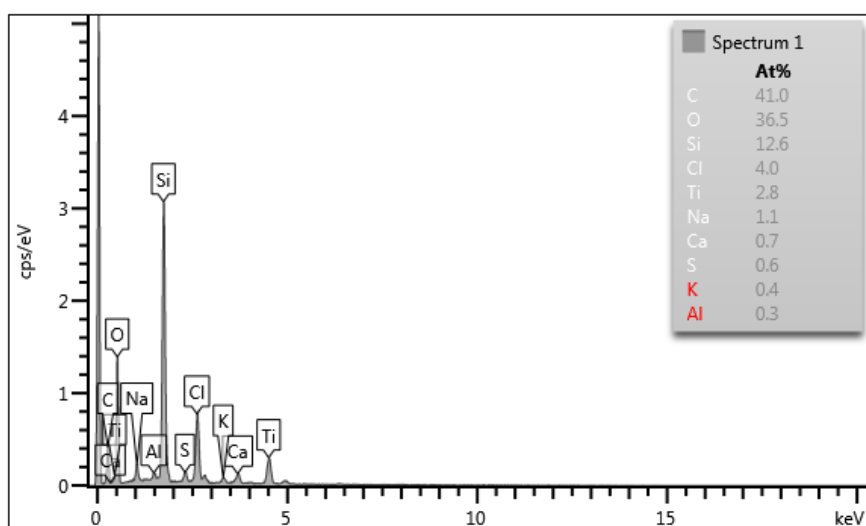


Figure 13 EDX analysis of precipitate from experiment with melted packing ring

The results of three EDX analyses of precipitate from the longest test shown in Figure 14 to Figure 19. Samples were taken from the wall of the reaction vessel, from white flakes of precipitate covering the mount and bottom of the reaction vessel. Finally, some of the blue precipitate from around the Supplier 1 samples were collected. The samples of the blue precipitate are called blue even though by the time they were analysed in the EDX the sample had turned white and were indistinguishable from the white precipitate.

The results show that the samples contain mostly oxygen and titanium in all three cases.

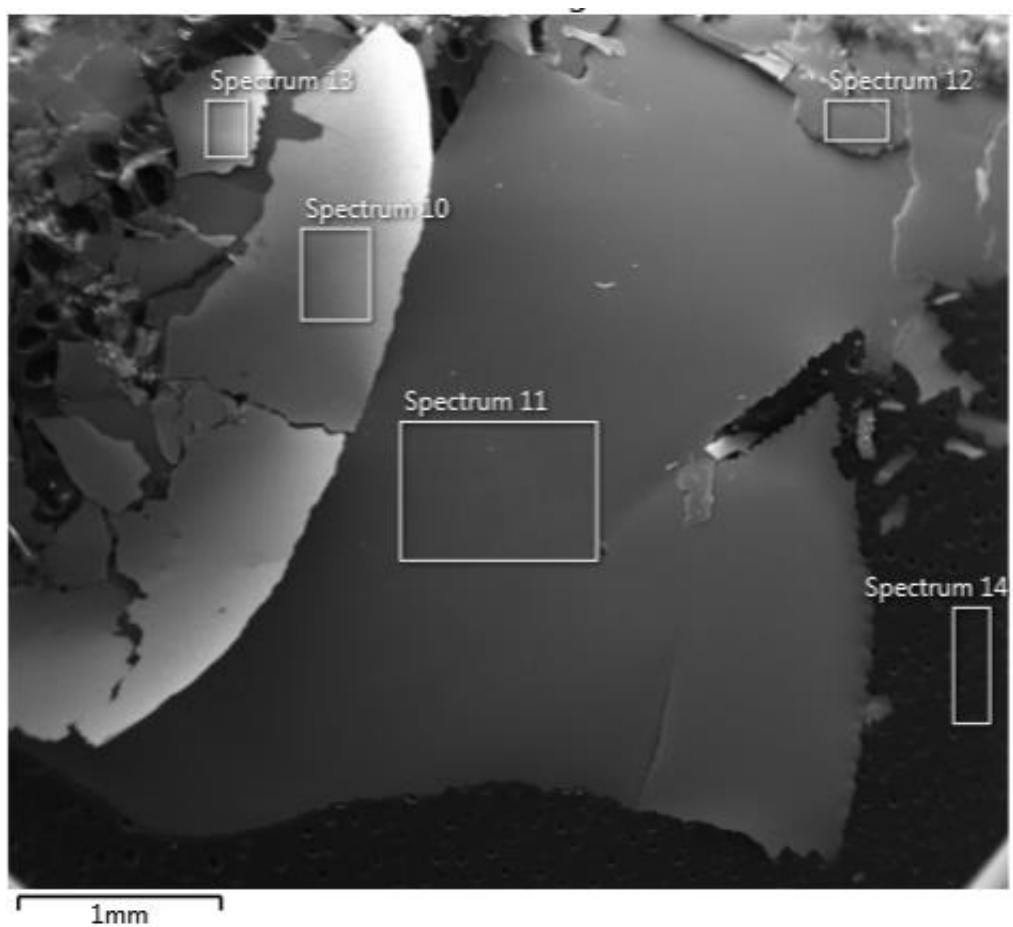


Figure 14 SE image of wall precipitation from longest corrosion test

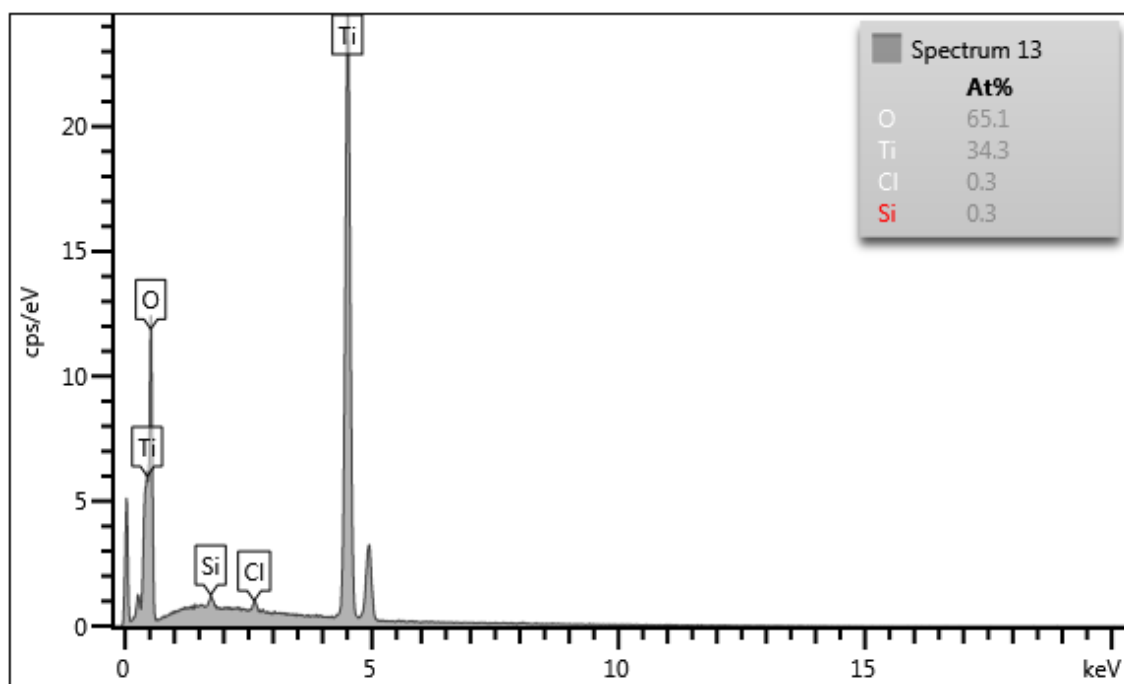


Figure 15 EDX analysis of wall precipitate from longest corrosion test

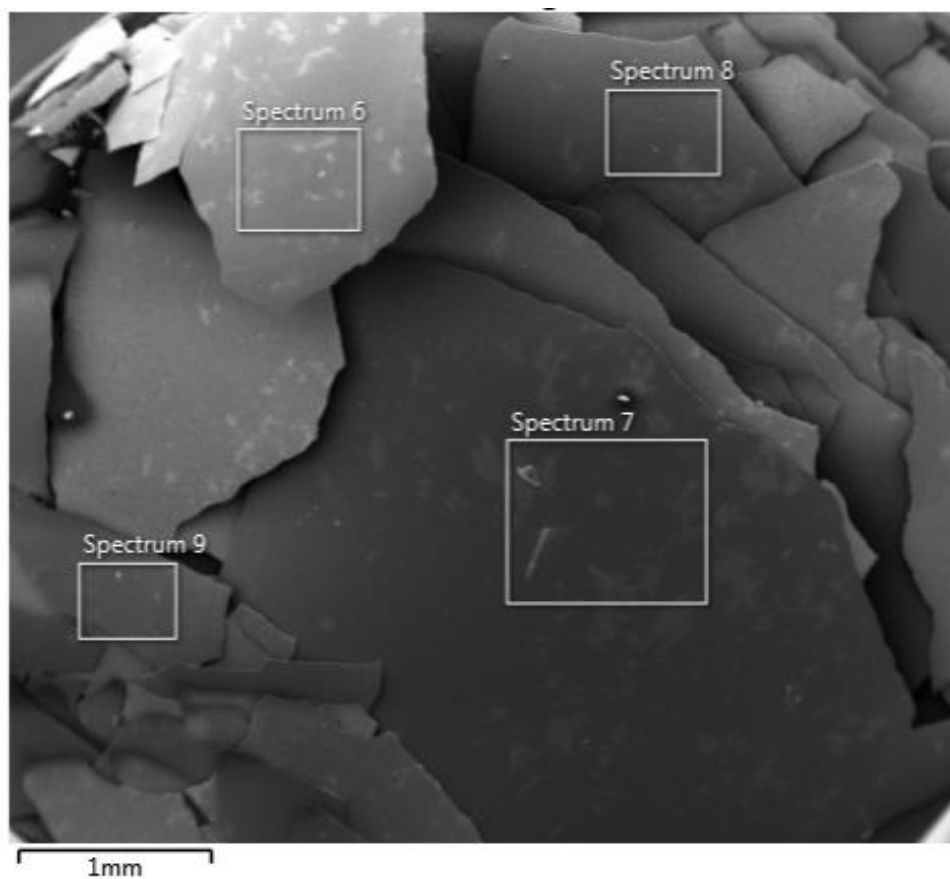


Figure 16 SE image of precipitate from the bottom of reaction vessel

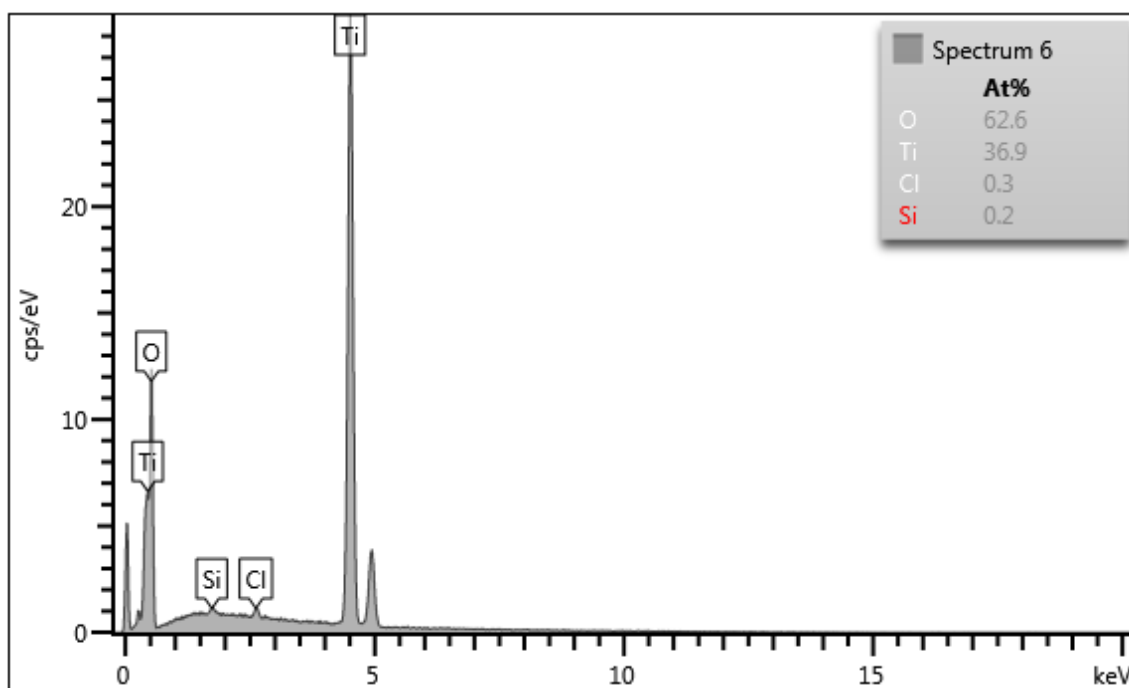


Figure 17 EDX analysis of precipitate from the bottom of reaction vessel

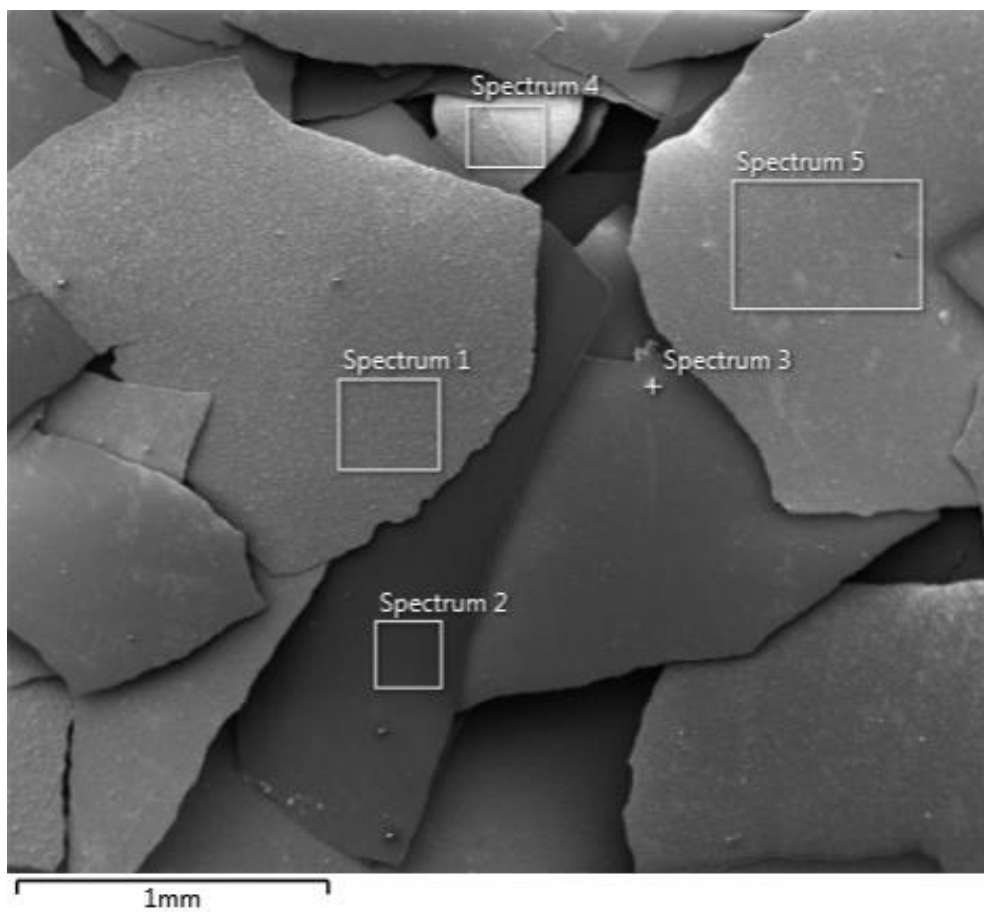


Figure 18 SE image of blue precipitate from longest corrosion test

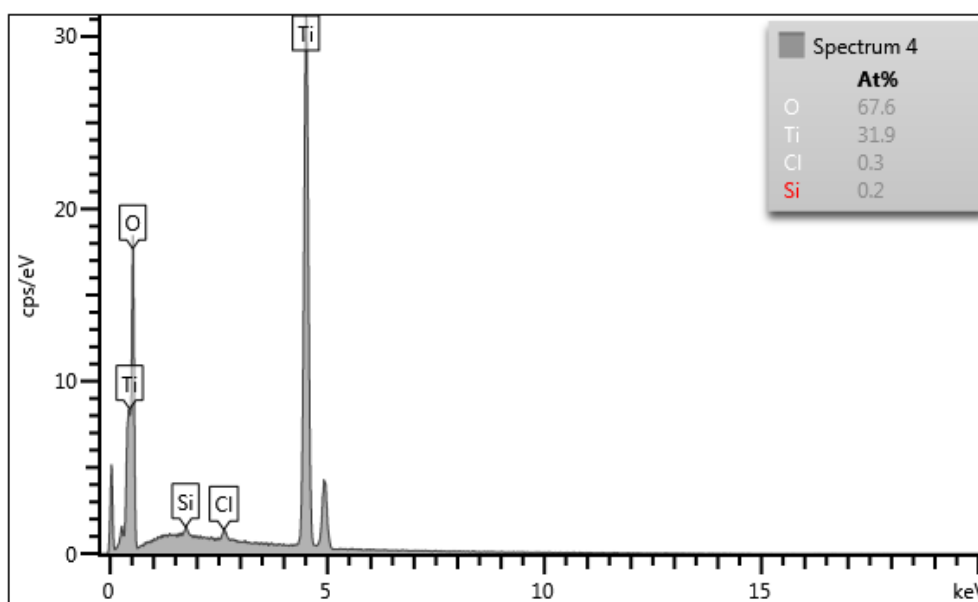


Figure 19 EDX analysis of blue precipitate from longest corrosion test

3.3.3 Other corrosion tests

Some corrosion tests were run with an acid concentration of 2 % instead of 1%. The same patterns were present there, only Supplier 1 sheets corroded while there was minimal effect on Supplier 2 plates.

One test was also run in sulphuric acid 10% at room temperature. In the sulphuric acid the Supplier 1 sheet was corroded but only a small amount of mass loss had occurred on the Supplier 2 sheet same as in the HCl. See Table 17.

Table 17 Results of corrosion test in H_2SO_4

Sheet	Corrosion rate mm/y
Supplier 1 AX0735	0.55
Supplier 2 N67127(2)	0.17

3.4 EBSD study

Pictures from the two EBSD studies can be seen in Figure 20 to Figure 26. Black pixels in the image means that the SEM did not get a diffraction signal from that spot at all. In the tables below these are called zero solutions other pixels are majority Titanium with a hexagonal crystal structure (alpha) and small fraction titanium with a cubic crystal structure (beta) these fractions are presented in Table 18 to Table 24. As can be seen, Supplier 1 pieces give more complete images when compared to the Supplier 2 pieces. The Supplier 2 pieces were also much more difficult to polish properly. Requiring several attempts to get a relatively smooth surface. Even then the roughness of the surface varied over the sample and the EBSD analysis was run on the smoothest patch that could be found.

The EBSD images show that Supplier 1 samples has a smaller grain size then Supplier 2 samples. The crystal directions of the grains on the other hand does not show any apparent pattern.

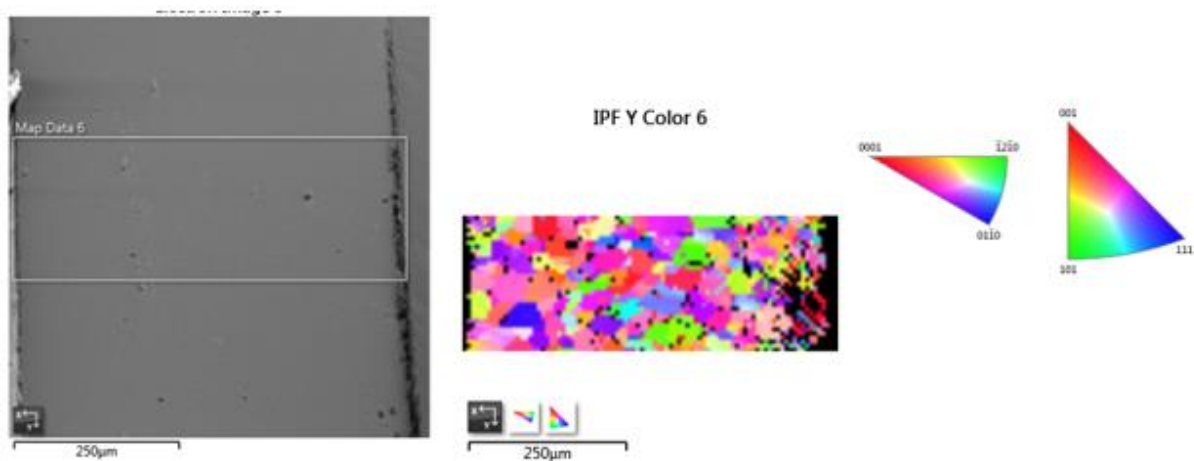


Figure 20 AK4394 (1) SE and EBSD image

Table 18 Phase fractions AK4394(1)

Phase Name	Phase Fraction (%)
Ti α	86.15
Ti β	0.03
Zero Solutions	13.82

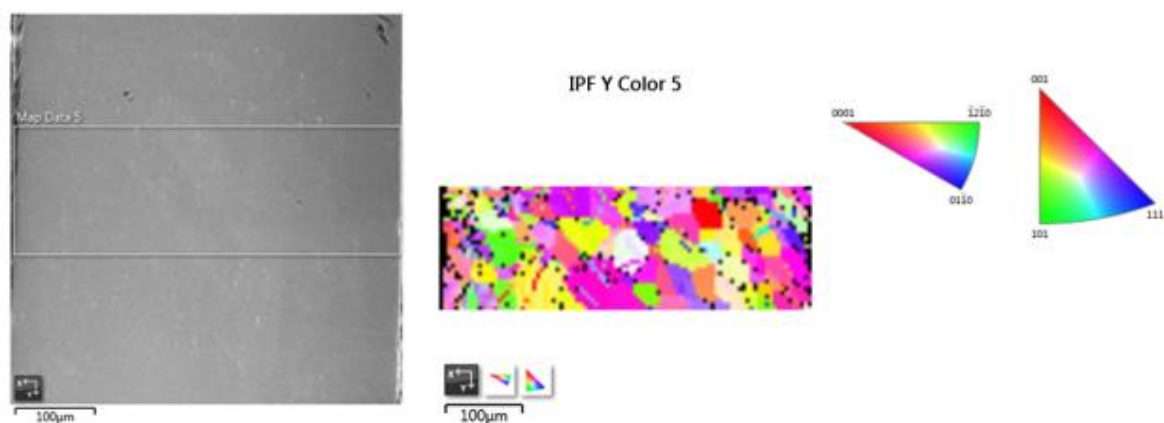


Figure 21 AX1828 (2) SE and EBSD image

Table 19 Phase fractions AX1828(2)

Phase Name	Phase Fraction (%)
Ti α	91.67
Ti β	0.03
Zero Solutions	8.3

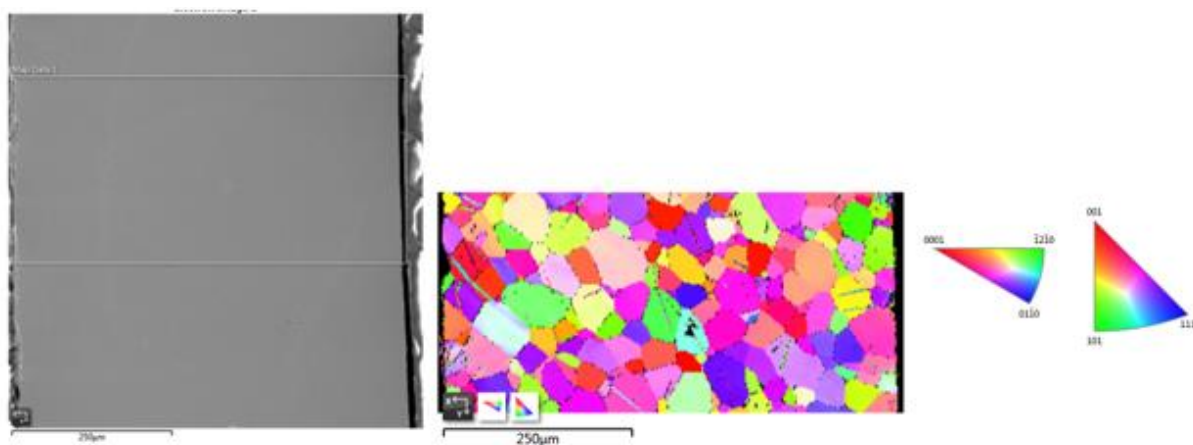


Figure 22 AX0735(1) SE and EBSD image

Table 20 Phase fractions AX0735(1)

Phase Name	Phase Fraction (%)
Ti α	94.04
Ti β	0.05
Zero Solutions	5.91

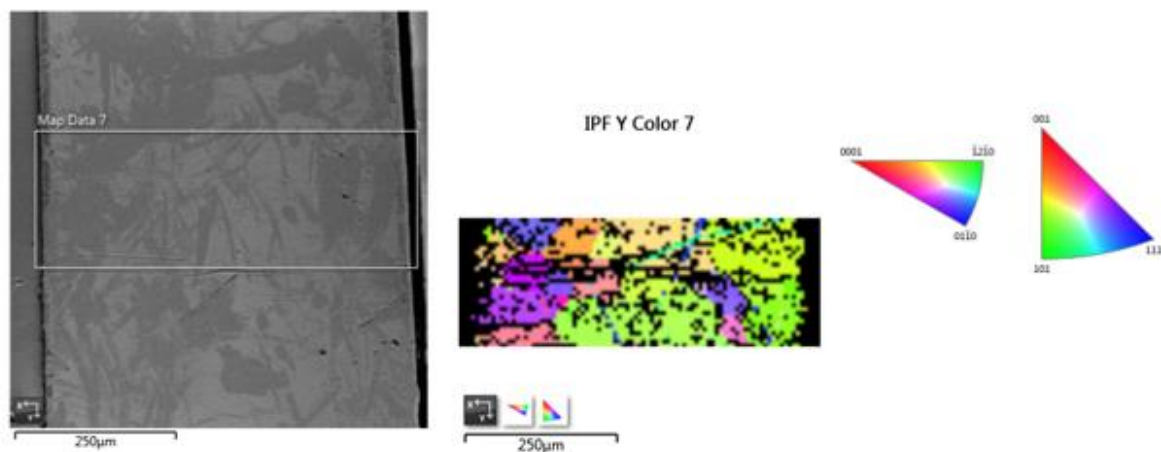


Figure 23 N66974 SE and EBSD image

Table 21 Phase fractions N66974

Phase Name	Phase Fraction (%)
Ti α	59.52
Ti β	0.07
Zero Solutions	40.41

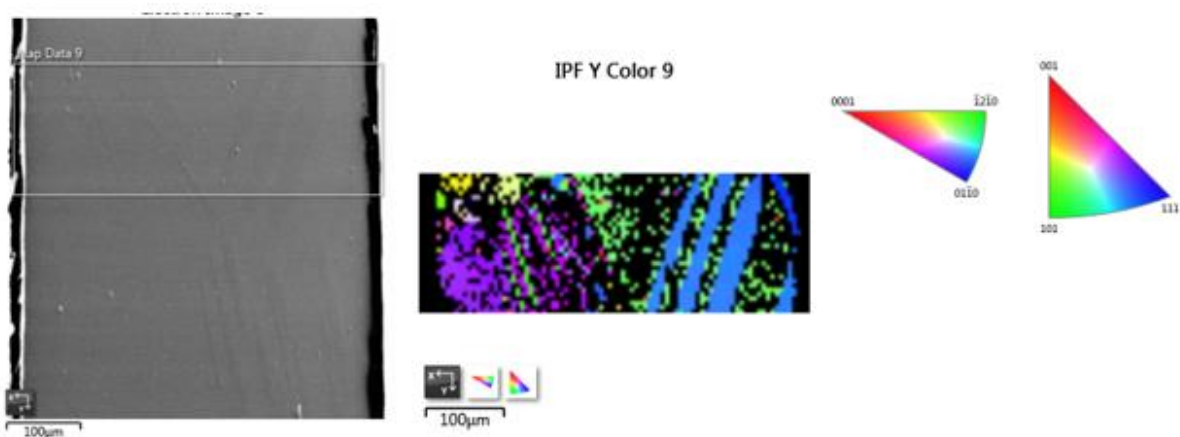


Figure 24 N67127(1) SE and EBSD image

Table 22 Phase fractions N67127 (1)

Phase Name	Phase Fraction (%)
Ti α	41.61
Ti β	0.07
Zero Solutions	58.32

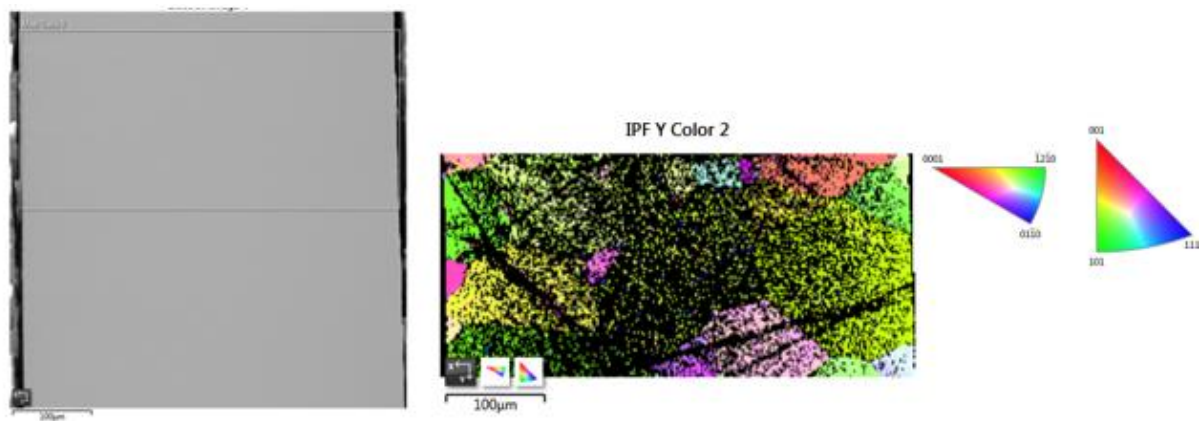


Figure 25 N67127(1) SE and EBSD image attempt two

Table 23 Phase fractions N67127(1) attempt two

Phase Name	Phase Fraction (%)
Ti α	37.3
Ti β	0.66
Zero Solutions	62.04

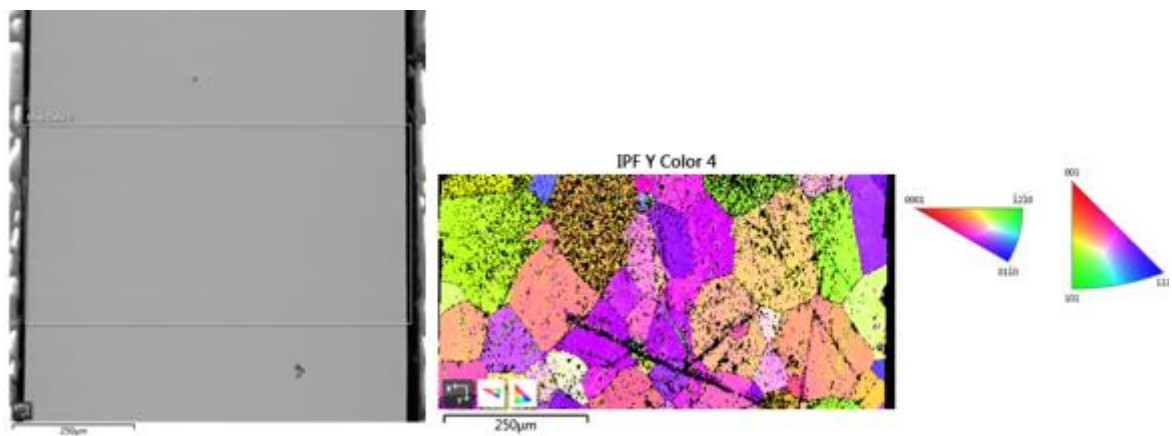


Figure 26 N46936 SE and EBSD image

Table 24 Phase fractions N46936

Phase Name	Phase Fraction (%)
Ti α	80.29
Ti β	0.16
Zero Solutions	19.55

3.5 GD-OES

Six pieces of titanium, three from each of the suppliers were analysed at two different locations see Figure 27.



Figure 27 samples after GD-OES testing

All the elemental ratios near the surface are quite far off from the ratios required by Alfa Laval internal specifications. But The expected bulk concentration is reached at around 0.7 micrometres for most elements all elements. One notable exception is oxygen content which did not go down to the expected 0.06 %Wt but only reached approximately 0.2 %Wt at the deepest measuring depth of 1.45 μm .

From this study one can see that the Supplier 2 sheets have a slightly higher carbon content close to the surface as can be seen in Figure 28 this was also true for a previous GD-OES study conducted by Alfa Laval. Oxygen content as seen in Figure 29 is high in the first couple of nanometres. Probably a result of the oxide layer that forms on the surface of titanium as it flattens out at around 20 nm, which is how thick the oxide layer is on titanium older than four years. There are also some small differences in the content of some other elements close to the surface, for example iron and nickel see Figure 30 and Figure 31. Very close to the surface there are relatively large differences even within the two suppliers as can be seen with AX0735 in Figure 30.

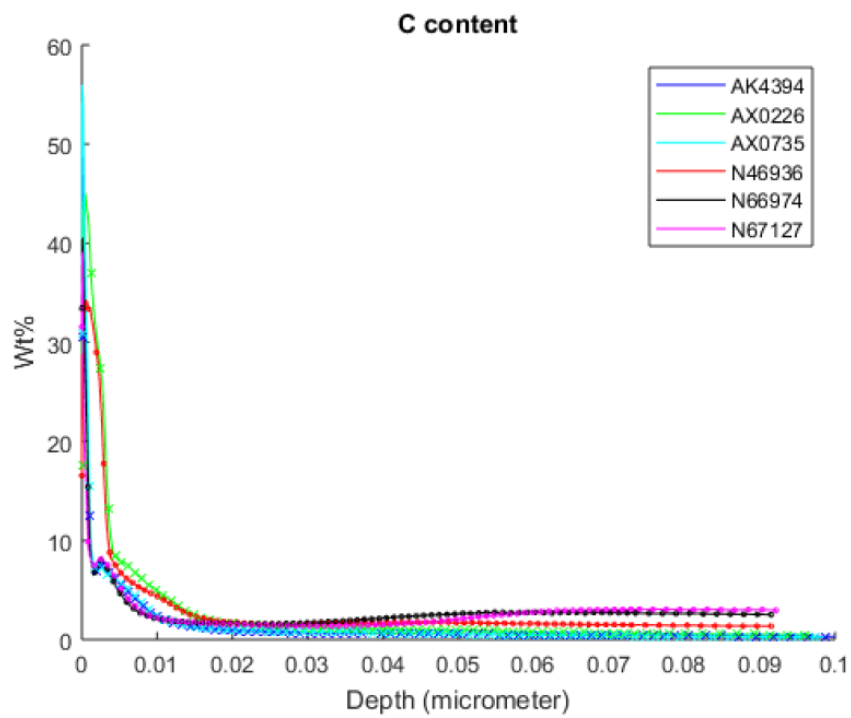


Figure 28 Carbon content vs Analysis depth (cropped)

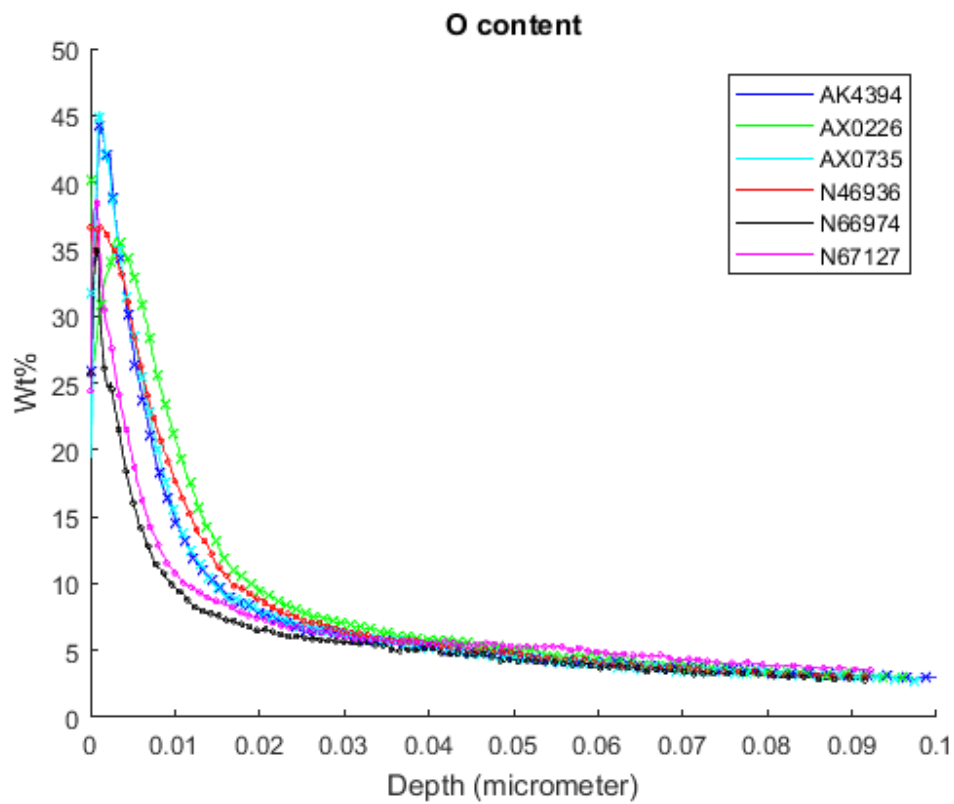


Figure 29 Oxygen content vs Analysis depth (cropped)

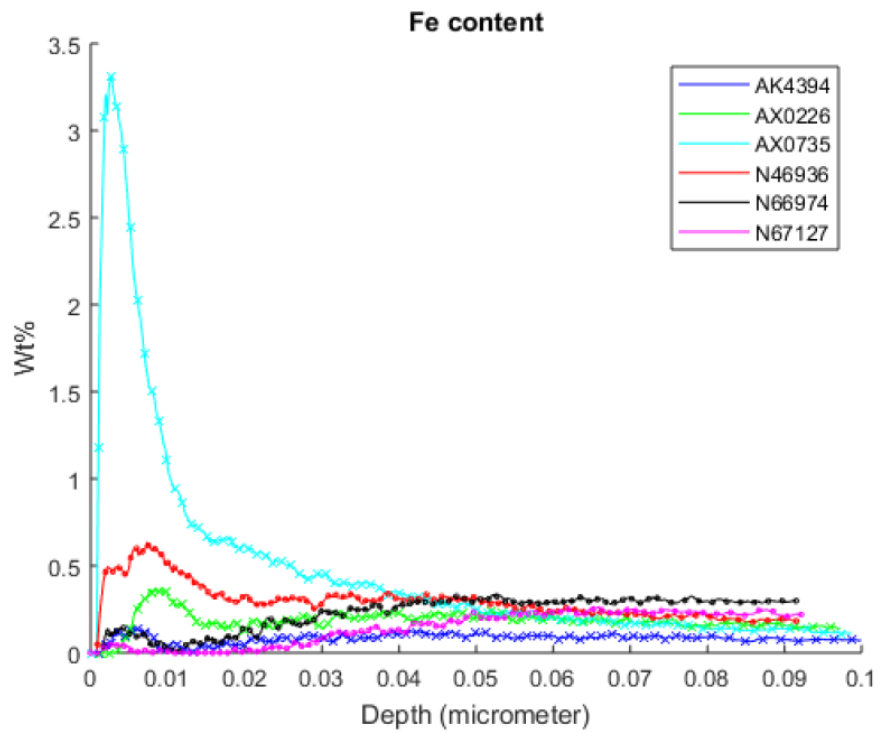


Figure 30 Iron Content vs Analysis depth (cropped)

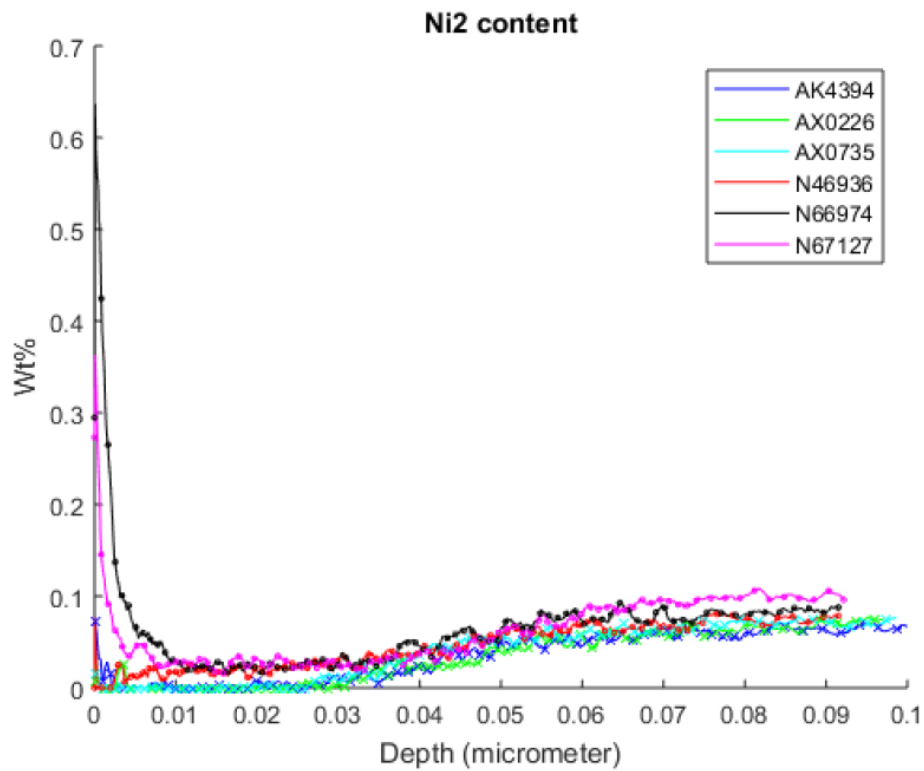


Figure 31 Nickel content vs analysis depth (cropped)

3.6 Tensile testing

All of the sample pieces except for one could be strained to 30% without breaking. But at 30% elongation necking occurred in the majority of the pieces see Figure 32. The two that did not neck and the one that fractured at 30% elongation were the two thickest and the thinnest respectively.

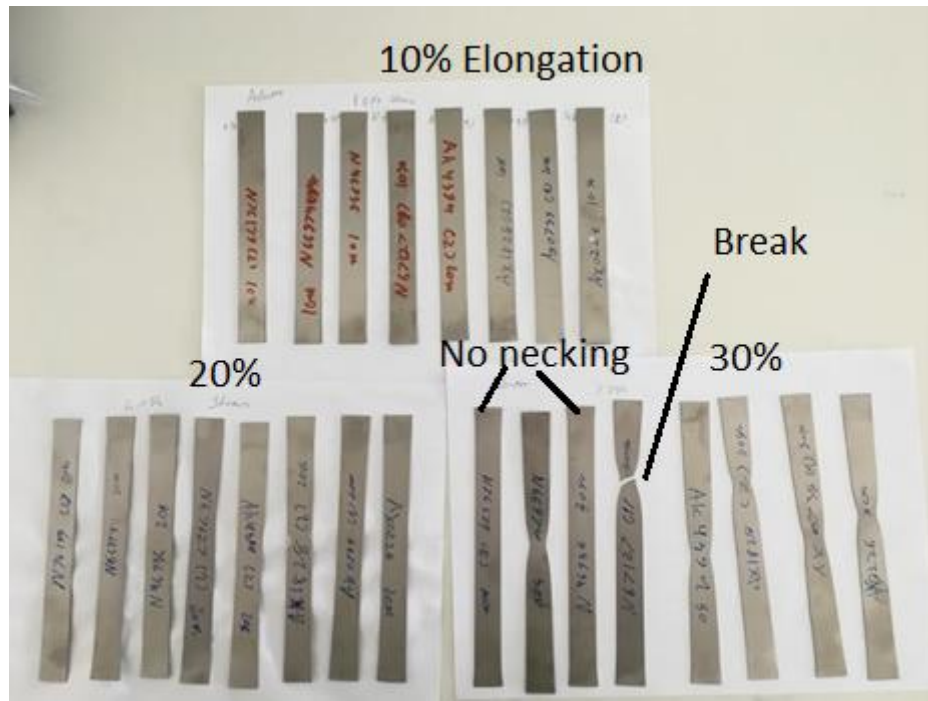


Figure 32 results from tensile testing 10%, 20% and 30 % elongation

After elongation the surface of the Supplier 2 samples became rougher. This effect became more pronounced with increased strain. This did not happen to the Supplier 1 samples. for a comparison between a 30% elongated Supplier 2 and Supplier 1 sample see Figure 33.

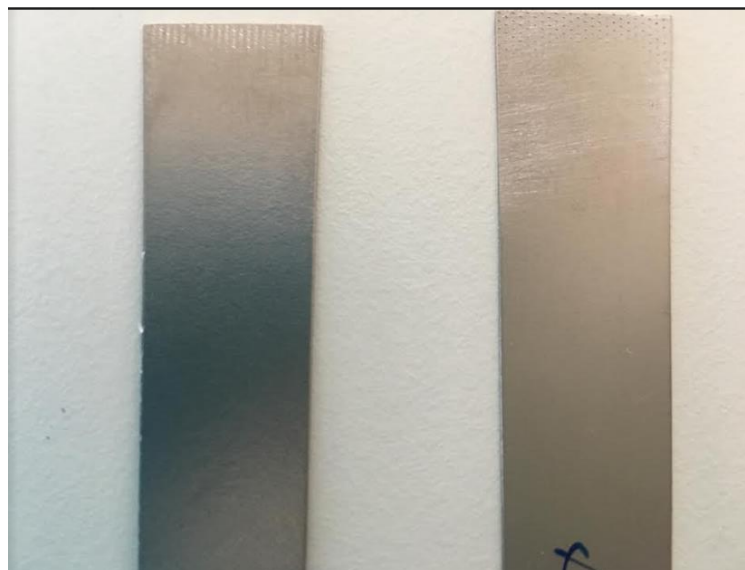


Figure 33 Difference between Supplier 2 and Supplier 1 30% elongation Supplier 2 left Supplier 1 right

3.7 Hardness testing

As with the EBSD Analysis Supplier 2 was harder to polish than Supplier 1. Resulting in a less even surface for the Supplier 2 samples as can be seen in Figure 34 and Figure 35.

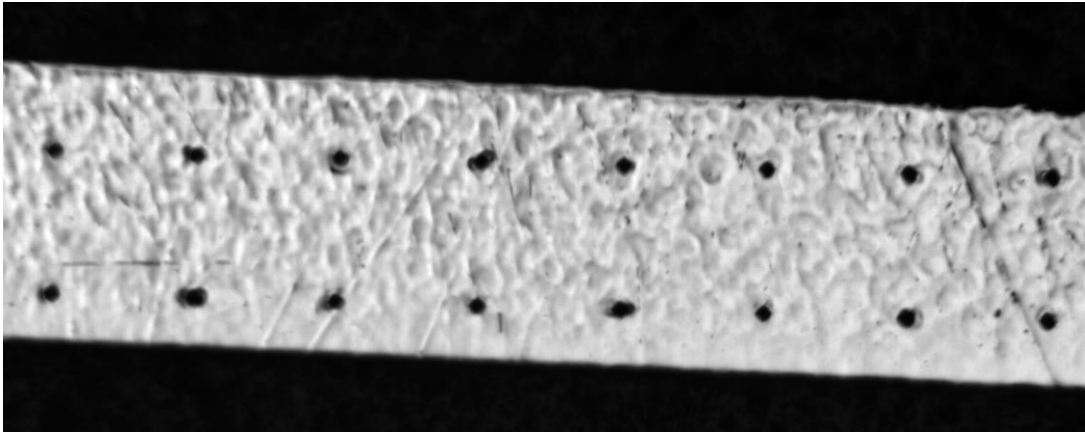


Figure 34 Hardness test of Supplier 2 sample N76179(2)

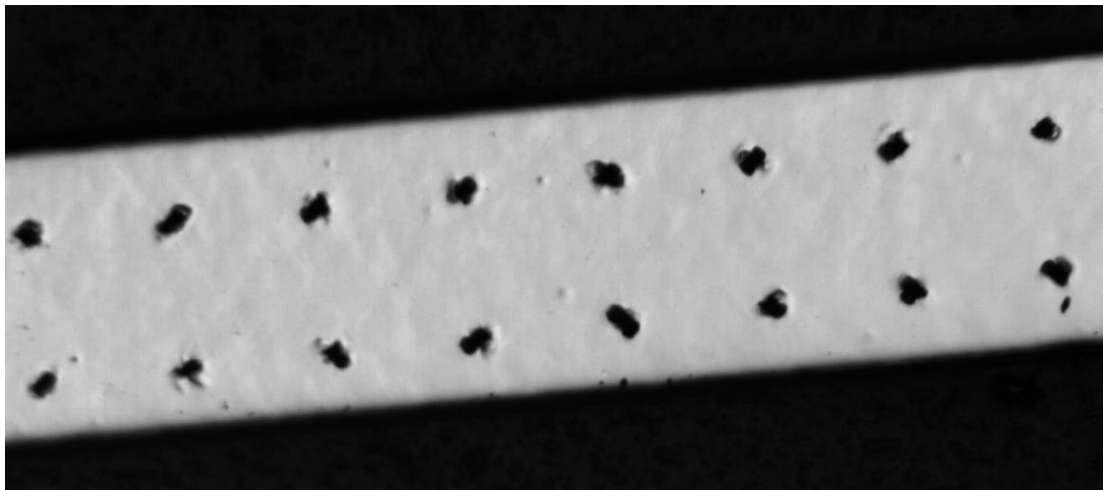


Figure 35 Hardness test of Supplier 2 sample AX0735

Supplier 2 was slightly harder than Supplier 1 see Table 25. Anova tests showed no significant differences between supplier one samples but there were significant differences between all supplier two samples and between Supplier 1 and Supplier 2 samples. Since there were no significant differences between Supplier 1 samples, results from all three samples were considered one large sample called “Full Supplier 1” in Table 26 and compared to Supplier 2 samples.

Table 25 Vickers hardness for Supplier 1 and Supplier 2

	AK4394(2)	AX0735	AX1828(2)	Mean Supplier 1	N66974	N67127(2)	N76179(2)	Mean Supplier 2
Mean (HV)	92	95.5	96.4	94.6	124.8	116	143.6	128.1
STD (HV)	14.6	9.2	5.3	10.7	10	7.5	6.2	14.2

Table 26 Anova comparisons of Hardness tests

Anova comparison Alpha = 0.05	F	F crit
AK4394(2), AX0735 and AX1828(2)	0.74	3.2
N66974, N67127(2) and N76179(2)	44.65	3.21
N66974 and N67127(2)	7	4.18
N67127(2) and N76179(2)	117.2	4.18
N66974 and N76179(2)	38.5	4.17
Full Supplier 1 and N66974	96.5	4
Full Supplier 1 and N67127(2)	51.08	4
Full Supplier 1 and N76179(2)	297.67	4

4. Discussion

4.1 Surface energy

Supplier 1 has slightly higher surface energy than Supplier 2 samples. In sheets there is a significant difference between Supplier 1 sheets and Supplier 2 sheets. This difference might stem from the last production steps causing a difference in the surface layer of the samples from different suppliers.

In Supplier 1 samples the pressing of the plates has reduced the surface energy slightly. In Supplier 2 it is harder to draw conclusions about the plates since there were so few samples. The plate measurements all have quite high standard deviations. This large standard deviation for the plates can partially be explained by the fact that back of the gasket groove was a tight fit for the measuring instrument and light coming in from the sides disturbed the measurement program used.

Higher surface energy would be useful if a gasket needs to be glued onto the plates. It is hard to draw conclusions about Supplier 2 plates since there are so few samples, but if one assumes that both suppliers are affected equally by the pressing process the Supplier 1 plates would have a slightly higher surface energy than Supplier 2, since Supplier 1 sheets have higher surface energy than Supplier 2 sheets.

4.2 Surface roughness

For Supplier 1 and Supplier 2 sheets there were no significant differences between the measuring directions. But if you compared Supplier 1 and Supplier 2 sheets there were significant differences in the Rz and RzMax value but not in the Ra value. This might mean that the surface of Supplier 2 plates are more uniform but with more bumps while Supplier 1 has fewer more extreme bumps in the surface since the average measurement (Ra) is similar while the extreme values (Rz and RzMax) differ.

For the Supplier 1 plates the gasket groove and opening had no significant differences in their surface roughness. This was expected since the opening measuring position is actually also a part of the gasket groove. There were significant differences with the ridge where the roughness was much higher. This can be the result of a process called orange peel. Discussed further in section 4.6 of this report.

For Supplier 2 plates no significant differences could be seen between the three measuring positions. As said in 4.1 the low samples size of Supplier 2 plates giving a variance might be the cause of this.

4.3 Corrosion test

As can be seen in Table 1 Supplier 1 titanium is much more heavily corroded than Supplier 2 titanium, this is independent on whether the titanium is in sheet or plate form. This is unexpected since what inspired this thesis in the first place was a situation where a Supplier 2 plate had corroded more than the accompanying Supplier 1 plate.

In some cases, the Supplier 2 titanium coupons had an increased mass after the corrosion tests and the colour change of some of the pieces seems to indicate a chemical bonding to the surface of the titanium. It is known that through light interference an increased thickness of the oxide layer on the titanium surface can create many different colours depending on oxide layer thickness [4] [3]. Prime Metals has noted that the production path of the titanium has an effect on the amount of discoloration because of pickling removing TiC that has formed on the titanium surface from lubrication during cold rolling. This TiC reacts with acid to form more TiO₂ in acid increasing the oxide layer thickness [3]. This hypothesis is supported by the GD-OES analysis where all Supplier 2 samples had higher carbon content than the Supplier 1 samples.

It is possible that the TiC might be expended if the samples is left in a corrosive environment for a long time for example over a year. Supplier 2 might then start to corrode as the Supplier 1 samples do. This could be interesting to test in the future.

If the corrosion tests were left for a long time precipitation seemed to cover the reaction vessel. This happened in all three of the longest tests with the 450 hour one having a significant amount of precipitation on the bottom of the vessel too.

The EDX analysis of the precipitate from the first time this happened showed several elements not present in the EDX analysis of precipitate from the longest test. Elements such as silicone and carbon. The source of this is assumed to be material from the packing ring of silicone plastic mixing with the precipitate.

But in the precipitate from the longest test only oxygen and titanium were present in significant amounts indicating that the white precipitation is titanium oxides. The cause of this is probably that the acid solution after a while becomes saturated with titanium ions and causes equation (4) to reverse creating new titanium oxide in the solution.

The blue coloured precipitate around the Supplier 1 samples in the longest corrosion test was most likely Ti^{3+} and Ti^{4+} ions since these are blue in colour and when left in air the colour quickly faded to white since the ions would react with air and create titanium oxides. This is supported by the EDX results since the previously blue precipitate had a similar composition to the other two samples.

4.4 EBSD analysis

The EBSD analysis seemed to have clearer results for the Supplier 1 than for the Supplier 2 pieces. The Supplier 2 pieces were much harder to polish properly and the image quality was much worse as can be seen in Figure 24 for example. Luckily, some of the grains can still be seen with the help of some imagination. Why the Supplier 2 pieces are so much harder to polish is not known at this time. It might have something to do with the larger grain size. If more tests were run it would be a good idea to electropolish the samples instead of polishing with grinding. This might give better results but there was no availability to do this at my location.

Supplier 1 samples have a much smaller grain size then the Supplier 2 samples. This indicates some difference in the production process of Supplier 1 and Supplier 2. The crystalline directions are not fully structured, but Supplier 1 crystalline direction seems to be more on the red to purple line while Supplier 2 has less of the red direction and more of the yellow directions. But it is hard to draw conclusions from the small amount of usable grains from Supplier 2.

There does seem to be slightly more beta titanium in the Supplier 2 samples with sample two of N67127(1) being a large outlier. But with so many zero solutions it is hard to tell if this difference means that there is more bcc titanium in Supplier 2 samples. Perhaps the bcc crystals are easier to detect in the EBSD and since there are less solutions of alpha titanium for Supplier 2 the value might be only proportionally larger since we cannot see all alpha titanium solutions.

4.5 GD-OES

There are some differences in elemental content for all elements and all samples but as stated in the results the carbon content and the iron content sticks out. The carbon content seems to support the TiC theory for the corrosion tests. The differences are not very large, but more carbon near the surface could indicate more TiC in the surface layer of Supplier 2 samples changing the corrosion properties.

The oxygen content near the surface of the titanium seems to match the thickness oxide layer described in section 1.2. The titanium oxide layer does not have a stop point, the oxygen content slowly lowers the further in you go. Still the oxygen content in general is quite high, oxygen content does not lower to the 0.06 Wt% required by Alfa Laval for either of the suppliers but the oxygen content seems to slowly lower the further into the material you get so it is possible that the required bulk concentration is reached further in than the GD-OES analysis max analysis depth.

Some of the oxygen shown in Figure 29 might be from oxides of the other elements present in the titanium, for example it is a possibility that some of the iron detected in the GD-OES analyses was iron oxides.

The difference in iron content is also small but might affect the hardness slightly as stated in the introduction, iron content in titanium changes the crystal structure to the harder BCC structure. But this should only impact the hardness close to the surface since values have gone down to the expected levels after approximately 0.7 micrometres.

4.6 Tensile test

The differences in thickness of the sheets is what effected the necking and breaking of the samples. But the interesting thing here is the rough surface of the Supplier 2 sheets after the tensile test. This effect of the surface getting rougher is called "orange peel" named after the fact that the surface has visual similarities to the surface of the aforementioned fruit. This arises from the fact that during tensile testing the individual grains thinness slightly differently [20]. The larger the grains and the larger the deformation the more pronounced this effect becomes [20]. Since the Supplier 2 samples has a larger grain size as seen in the results from the EBSD analysis orange peel affect them more than the Supplier 1 samples.

4.7 Hardness test

The Supplier 2 metal is slightly harder than the Supplier 1 metal. As stated in the GD-OES analysis the iron content in the Supplier 2 samples are higher close to the surface. But since measurements were made on the cross-section of sheets this should not affect the measurement results. Since the Supplier 1 samples have a smaller grain size the Hall-Petch effect should make them harder than the larger grained samples from Supplier 2. But this was not in line with results.

The EBSD analysis showed higher amounts of beta titanium in Supplier 2 samples, and beta titanium is harder than alpha titanium, so the difference could be because of this. But since EBSD results of Supplier 2 are of low quality it is hard to know if this difference is something that could affect the hardness of the samples.

Supplier 1 is softer than the table value of CP grade 1 titanium which is 127 to 134 HV [11]. Supplier 2 lands within the 127-134 range. It should be noted that Alfa Laval's internal standards has even more strict restrictions on iron content than CP grade 1 titanium this should mean that the titanium they use are even softer than CP grade 1 titanium.

5. Conclusions

There are some clear differences between the two suppliers most likely arising from the differences in their production processes, perhaps the most unexpected difference is the difference in corrosion properties. This study found the Supplier 2 metal to be more corrosion resistant, most likely because of higher carbon content. This was unexpected since the find that started this project was that a Supplier 2 plate had corroded more than a Supplier 1 plate.

The other large difference is the grain size, Supplier 2 has a larger grain size than Supplier 1 which seems to indicate that Supplier 2 cools slower in the production process. This grainsize leads to orange peeling when elongated but does not seem to have a large effect on the surface roughness when pressed into plates.

Other differences are not as apparent but Supplier 1 having slightly higher surface energy might make it very slightly easier to glue gaskets to the plates.

There are some differences in elemental content close to the surface of the samples as can be seen in the GD-OES results this could be the source of the difference in corrosion properties.

There is also a difference in hardness between suppliers, but it is hard to draw conclusions as to why. The higher beta titanium content in Supplier 2 might be a reason for the increased hardness but since the EBSD results are so varied in quality it is difficult to say if this is actually the case.

6. Ideas for future tests

In this report the corrosion of titanium was only tested in the reducing acids HCl and sulphuric acid. It might be interesting to try a corrosion test in an oxidising acid even though titanium should be resistant to corrosion in such acids there might be differences in behaviour from the two suppliers just as in reducing acids. Another corrosion test that could be interesting to perform would be using the scanning vibrating electrode technique (SVET). This could give information if the corrosion rate is constant over the sampling area of approximately 100mm².

It would also be interesting to try to remove the top layer from Supplier 2 to see if this effected the corrosion rate, since the TiC should only be present close to the surface if my theory is correct.

Either way testing the TiC theory in some way is recommended.

If one is interested in further EBSD analysis electropolishing of the samples is a good idea. This would hopefully eliminate the polishing problems present from the grinding polish and would give clearer pictures.

If performing more EBSD experiments is not a possibility, x-ray diffraction analysis could perhaps also be used to gain a better understanding of the crystalline content and examine if there really is a difference in the alpha and beta content between suppliers.

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