Examination of the Adhesiveness of the Nanotube Layer on Anodized Commercially Pure Titanium Samples using the Micro-Limiting Dome Height Test and the Tensile Test.

Joshua Manohar Chinthapalli
joshmanohar25@gmail.com
ABSTRACT

EXAMINATION OF THE ADHESIVENESS OF THE NANOTUBE LAYER ON ANODIZED COMMERCIALLY PURE TITANIUM SAMPLES USING THE MICRO-LIMITING DOME HEIGHT TEST AND THE TENSILE TEST

Joshua Manohar Chinthapalli, M.S.
Department of Mechanical Engineering
Northern Illinois University, 2020
Dr. Jenn-Terng Gau, Director

Titanium oxide (TiO_2) nanotube is one of the most extensively studied nanotubes due to its wide applications in electronics and medical fields. In this study, we used electrochemical anodization to create nanotubes on commercially pure titanium (Cp-Ti) samples and examined the adhesiveness of the nanotube layer on the sample surface. Particularly we conducted micro-limiting dome height (µLDH) tests on anodized Cp-Ti foils of 38 µm thickness and 4 mm diameter at room temperature, 100°C, and 200°C. We also conducted tensile tests on standard tensile specimens of anodized Cp-Ti plate at room temperature and 200°C. The Hitachi S-4500 field emission scanning electron microscope was used to take the high-magnification images of the nanotubes on the surface of the Cp-Ti samples. The ImageJ software was used to analyze the shapes and qualities of the nanotubes on the surface of anodized Cp-Ti samples. The same process was also used to examine the integrity of the nanotube layers after the Cp-Ti samples underwent two tests.
For the best outcome of the nanotube layer on the foil samples, we tested anodization under varying voltages and anodization time through trial and error. We found that the combinations of 20V and 15, 30, and 45 minutes produced nanotube layers of sufficient quality. We also found that an increase in anodization time caused the nanotube layer to be unstable. Using the $\mu$LDH tests, we determined the maximum punch travel distance ($H_d$) that the Cp-Ti foil samples could withstand without damaging the TiO$_2$ nanotube layer on surfaces. We found that the samples prepared using 20V for 15 minutes tolerated a $H_d$ of 0.9 mm at room temperature. Samples prepared with a longer anodization time showed a lower $H_d$. Also, a higher testing temperature decreased $H_d$.

For the tensile testing samples, we found that the combinations for 20 V for 15, 30, 45, and 60 minutes anodization times produced nanotube layers of sufficient quality. Using the standard tensile test procedures, we found that the samples prepared at 20 V for 15 minutes withstood a maximum strain of 0.03 at the room temperature without damaging the nanotube layer on the surface. Samples prepared with a longer anodization time or tested under a higher testing temperature tolerated a lower strain without damage to the nanotube layer.

In summary, we found that the combination of 20V and 15-minute anodization time produced the best results in the creation of the nanotube layer on the surface of Cp-Ti samples in terms of its ability to withstand deformation and temperature changes. These results serve as careful considerations in further research and applications.
EXAMINATION OF THE ADHESIVENESS OF THE NANOTUBE LAYER ON ANODIZED COMMERCIALY PURE TITANIUM SAMPLES USING THE MICRO-LIMITING DOME HEIGHT TEST AND THE TENSILE TEST

BY

JOSHUA MANOHAR CHINTHAPALLI
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A THESIS SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

Thesis Director:
Dr. Jenn-Terng Gau
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And finally, I would like to thank my parents, Rajendra Prasad Chinthapalli and Shanthi Chinthapalli, and my sister, Jennifer Reshma Chinthapalli, for having confidence in me and for supporting me throughout my life.
DEDICATION

To my family and friends
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Chapter 1 INTRODUCTION AND LITERATURE REVIEW

1.1 Commercially Pure Titanium

Commercially pure titanium has light weight, high specific strength, high corrosion resistance, and biocompatibility due to which it has gained wide-scale recognition for medical and electronic devices. The corrosion resistance of Cp-Ti is due to the material's ability to form passive oxide films spontaneously (TiO$_2$) when it comes in contact with oxygen [1]. Because of its features, micro-manufactured components made of Cp-Ti have long-term reliability.

Stainless steel was the first metallic biomaterial used as an implant. Then other biomedical materials such as cobalt alloy and titanium alloys have come to use. A biocompatible material allows bone tissue growth to adhere to implants for a longer time compared to others. A newly discovered biomaterial, Cp-Ti, is considered to be the best among all the biocompatible metallic materials because of its surface properties resulting in the spontaneous build-up of a stable and inert oxide layer. Cp-Ti is widely used to fabricate implant devices such as artificial hip joints, artificial knee joints, bone plates, screws for fracture fixation, cardiac valve prostheses, pacemakers, and artificial hearts [2].
In electronics industries, there is a great need for lightweight and miniaturized components while maintaining high quality. The density of Cp-Ti is 60% of that of steel, but it has the same strength when compared to steel, making it the highest specific strength material among metals [3]. Because of these excellent properties, Cp-Ti has been widely used in fabricating miniaturized components in electronics products such as micro-gears, mobile phone components, resistor caps, contact springs, speaker diaphragms, etc.

1.2 Micro Metal Forming

Because of the expanding interest for miniaturized-scale components with features under 100μm in businesses, smaller-scale metal forming has aroused curiosity in the course of the most recent decade. Compared to the macro-scale manufacturing process, microforming reduces the consumption of both resources and energy required. As the equipment is scaled down, the mass of hardware is reduced dramatically and results in an increase of tool speed and improves production rate by reducing the manufacturing cycle [4].

Manufacturing microcomponents using advanced lithographic technologies and micromachining is not cost-effective in mass production and in using limited materials [5]. Because of the high production rate, low material scrap rate, net shape production, and improved mechanical properties due to work hardening, microforming is more suitable and cost effective. When features are scaled down to micro scale, the characteristics of a single grain of material involved in the deformation region will play a significant role in the mechanical behavior of the material. This phenomenon is called size effect [6], which is neglected in macro-scale manufacturing. Therefore, previous studies on macro scale in the past decades are invalid in microforming processes [7].
Size effects are deviations from intensive or proportional extrapolated extensive values of process characteristics that occur when scaling the geometric dimensions. Size effects occur depending on the fact that the ratio among all certain features cannot be kept constant according to process requirements [8]. Intensive variables do not affect change with mass, for example, temperature, density, etc. Extensive variables change with mass, for example, heat content, inertia force, etc.

In previous research, authors developed a resistance heating system for thin metallic materials and applied to the microforming process [9]. By reducing the flow stress of the worksheet by resistance heating, the developed system could improve the material formability. For further improvement in the real manufacturing process, control of temperature distribution in work materials is one of the important issues in microforming. Researchers in the past have studied the effects of various variables on formability. These variables are primarily divided into two categories:

1. Setup parameters (for example, strain rate, binding force, lubrication, and temperature)
2. Material properties (for example, anisotropy coefficients, strain hardening exponents, yield strength, etc.)

A previous study done by Zhang studied the effect of strain rate on the formability of Cp-Ti foil [10]. The researcher conducted a series of μLDH tests and two high speeds with a hemispherical punch of 4mm and 20 mm diameters, respectively. In the tests at the same strain rates at temperatures up to 300°C, there was an increase of about 80% in strain hardening exponent n. This increase shows the increase of the formability of Cp-Ti foil when increased in temperature.
1.3 Tensile Tests

Tensile tests provide data on the strength and ductility of materials under uniaxial stresses. This useful information is used to compare materials, alloy development, quality control, and design. For realizing the reliability and practicality of a material, tensile tests are performed. Tensile testing is imperative for ensuring safe and high-quality material. Types of tensile testing include:

1. Adhesion strength
2. Crimp joint pull-off force
3. Peel
4. Tear resistance

Even though surface modifications are treated with more importance, mechanical tests are also done on the nanotubes to test their properties. Previously researchers have done tensile testing on nanotubes. One study was about tensile testing on multiwalled carbon nanotubes using specialized equipment to grip the long nanotubes (~2mm) combined [11]. They have measured the average Young's modulus, and tensile strength obtained was 0.4560.23 TPa and 1.7260.64 GPa, respectively.

In another research, dog bone-shaped Type 4 specimens following ASTM D-638 standard were used for tensile testing. These samples had multiwall carbon nanotubes etched on them. This study was done to know the tensile strength of the sample and where it breaks [12]. Tensile tests from the study show an increase of 27% in the Young modulus value upon the addition of 1.0% of MWCNTs.
Previous studies show mechanical testing done directly on the nanotube layer, which is attached to the sample. In this study, we have performed tests on the sample which has a nanotube layer. The reason previous studies did that is to increase surface roughness when used for bone implants or to try to find the stress induced on the nanotubes when it is actually under usage. For both cases, the sample having nanotubes will be in contact with another surface, and the strength between them will be known when the properties of the nanotube layer are known. In our study, we are incorporating nanotubes to samples that are used for other applications such as electroluminescent devices, sensors, and electronic industries. That is the reason this study is one of a kind, and researchers are starting to recognize the importance of it.

In our study, we are trying to calculate the adhesive ability between the nanotube layer and the Cp-Ti foil. To calculate strain induced in the sample having the nanotube layer intact is the purpose of doing tensile tests on the sample. For our study, we are performing tensile tests using MTS tensile setup on ASTM standard specimens with the TiO$_2$ nanotube layer.

### 1.4 Material Properties of Cp-Ti

Due to the extensive applications and use of Cp-Ti, it was taken into consideration for this study. It is 38µm of thickness commercially pure grade 2 titanium foil, which was purchased from Arnold Magnetic Technologies in Marengo, Illinois. The mechanical, chemical, and physical properties are shown in Tables 1, 2, and 3.
Table 1  Mechanical properties of grade 2 Cp-Ti

<table>
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<tr>
<th>YOUNG'S MODULUS</th>
<th>SHEAR MODULUS</th>
<th>YIELD STRENGTH</th>
<th>POISSON'S RATIO</th>
<th>TENSILE STRENGTH</th>
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<tr>
<td>116 GPa</td>
<td>44 GPa</td>
<td>345 MPa</td>
<td>0.32</td>
<td>485 MPa</td>
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Table 2  Chemical composition of grade 2 Cp-Ti

<table>
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<tr>
<th>ELEMENT</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>Fe</th>
<th>O</th>
<th>Ti</th>
</tr>
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<tr>
<td>PERCENTAGE (%)</td>
<td>0.03</td>
<td>0.08</td>
<td>0.015</td>
<td>0.3</td>
<td>0.25</td>
<td>99.325</td>
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Table 3  Physical properties of grade 2 Cp-Ti

<table>
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<th>DENSITY</th>
<th>BETA TRANSUS</th>
<th>MELTING POINT</th>
<th>THERMAL CONDUCTIVITY</th>
<th>MAGNETIC PERMEABILITY</th>
<th>ELECTRICAL RESISTIVITY</th>
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<tr>
<td>4.48 g/cm³</td>
<td>915 °C</td>
<td>1668 °C</td>
<td>2.179 °C</td>
<td>Non-magnetic</td>
<td>0.53 µΩ*m</td>
</tr>
</tbody>
</table>
1.5 Titanium Nanotubes

The discovery of carbon nanotube (CNT) [13] has garnered much attention due to its attractive physical and chemical functions. Apart from CNTs, nanotubes can be formed using other inorganic materials like boron nitride (BN) [14] and molybdenum disulfide (MoS\textsubscript{2}) [15], vanadium oxide (V\textsubscript{2}O\textsubscript{3}) [16-18], aluminium oxide (Al\textsubscript{2}O\textsubscript{3}) [18], silicon dioxide (SiO\textsubscript{2}) [18,19], titanium oxide (TiO\textsubscript{2}) [20-26] and imogolite [27,28].

There has been extensive research on TiO\textsubscript{2} nanotubes because of its applications in making solar cells, hybrid electroluminescent devices, photocatalysis, and biomedical products. Researchers considered TiO\textsubscript{2}-based nanotubes with a high specific area, ion-changeable ability, and photocatalytic ability because of its extensive applications.

The following methods fabricate TiO\textsubscript{2} nanotubes:

1. Assisted-template method [29-31]
2. Sol-gel process [32]
3. Electrochemical anodic oxidation [33-38]

Titanium (Ti) nanotubes are one of the extensively studied nanotubes due to their light, corrosion-resistant, and durable nature [52-54]. The sol-gel method, electrophoretic deposition, and anodization are various methods to form titanium oxide nanotubes. For this study, vertically aligned TiO\textsubscript{2} nanotubes are formed on the Ti substrate by an anodization process. Take 1% hydrogen fluoride (H.F.) volume by weight solution as an electrolyte solution, and platinum is
considered as the anode while the Ti sample is taken as a cathode at 20 voltage for 45 minutes. The nanotubes are formed with this process on the surface of the sample.

Titanium being relatively inert cannot directly bond to bone, and osseointegration via the natural oxide (TiO$_2$) is a long process (55,56). Therefore, research has been going on to reduce the time needed for osseointegration. For enhancing the interaction of cell implant and increase the lifetime, bioactive ceramic-based coatings are applied to Ti implants, for example, hydroxyapatite (H.A.) [57-60]. Later TiO$_2$ has been used as a potential alternative to H.A. coatings.

The advantage of using TiO$_2$ is that it can be grown directly on the Ti surface by affordable methods such as anodic oxidation [61-63]. The main problem with H.A. coatings is poor adhesion strength at the H.A./Ti interface [57-60]. Using electrochemical anodic oxidation, TiO$_2$ is formed with a chemical bond between oxide and Ti substrate, resulting in enhanced adhesion strength. Researchers have suggested that TiO$_2$ with 3-D nanoporous structure improves apatite formability when compared to dense TiO$_2$ [63]. The study done by Gong et al. [64] has shown that TiO$_2$ coatings consisting of uniform self-assembled nanotube arrays are formed on the surface of Ti by anodic oxidation.

TiO$_2$ nanotubes are formed in F- containing electrolytes and are the result of two electric field-assisted processes. Hydrolysis process of Ti metal is done to create TiO$_2$ by the following reaction [65-67]:

$$Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+$$ \hspace{1cm} (1)

In addition, chemical dissolution of TiO$_2$ at the oxide/electrolyte interface occurs in the formation of [TiF$_6$]$^{2-}$ [65-67]:

$$TiO_2 + 6HF \rightarrow [TiF_6]^{2-} + 2H_2O + 2H^+$$ \hspace{1cm} (2)
The growth of nanotubes is divided into three main processes:

1. Initial barrier formation
2. Formation of uniformly distributed pores
3. Separation of interconnected pores into nanotubes

During the onset of anodization, a barrier oxide layer begins to form, causing an exponential decrease in the anodic current density. In fluorine-free electrolyte solutions, both the thickness of the barrier layer and current density reach steady state [65,67-69]. However, in fluorine-containing electrolyte solutions, a nanoporous structure begins to form due to the chemical dissolution of the barrier oxide layer (Eq. 2). Current density increases during this process. After a particular time, pores become assembled in an ordered fashion and become unconnected. Once the nanotube structure is established, the current density again stabilizes at a greater value than that in a fluorine-free solution [65,68,69]. From this point, further anodic oxidation simply increases the length of the tubes without significantly affecting the tube structure or the anodic current density.

The exact mechanism by which nanopores are formed is still under a lot of research. Several researchers have suggested that nanopore formation occurs by the random local dissolution of the TiO₂ surface, which helps in the creation of pores [68-70]. Nanotubes formed by this process reduces the film thickness locally, increasing the electric field intensity at the bottom of the pore and developing the new oxide. Thus, the reactions given above (Eqs. 1 and 2) take place simultaneously at the bottom of the pore and cause further growth into the Ti substrate [67,69]. Beranek et al. [68] suggest that pore formation takes place at random locations initially, and self-ordering is merely a product of competition between growing pores. Raja et al. [65] suggested that
local surface perturbations result in the ordering of pores. The increase in strain energy of the oxide film may be caused by variations in dielectric constant and electrostriction coefficient. Mor et al. [69] suggested that the unanodized regions between pores are susceptible to field-assisted oxidation/dissolution, causing voids between nanopore regions. Thus, nanotubes are the result of the simultaneous growth of pores and voids. Raja et al. suggested that the separation of pores may be a result of repulsive forces between cation vacancies. Macak et al. [70] indicated that these ridges are the result of current oscillations during the anodization process.

Two types of tests are done in this research with different sample sizes. First, 4mm diameter samples are taken, and anodization is done to get the titanium nanotube layer on it. These specimens are used to do micro-limiting dome height tests. Then high-magnification images are taken using a scanning electron microscope to study the nanotube layer affected by dome tests in different temperatures. The second test is done using a standard tensile specimen formed by using a water jet machine. Then the anodization process is done for these specimens to form nanotubes. Then tensile tests are done using a tensile machine, and data is recorded using a laser extensometer. This data is then studied along with the images from SEM to know the adhesiveness of the nanotube layer formed on the specimens.

1.6 Scanning Electron Microscope

A scanning electron microscope collects the reflected electrons from the electron beam focused on the sample and creates an image. When the electron beam is projected onto the sample, stigmators, as seen in Figure 1, are used to direct the beam to a focal point. This is very important while taking high-magnification pictures because the image would be out of focus.
Figure 1  Schematic diagram of the SEM [71].
1.6.1 Astigmatism

Astigmatism is popularly known as a medical condition that causes visual impairment in adults. Relating to electron microscopy, astigmatism arises due to imperfections in the lens system. At high magnification, this effect is seen; the spherical objects appear as an elliptical object (Figures 2 and 3).

Figure 2  Over and underfocusing the image, the image was astigmatic due to the visible elongation in perpendicular directions [72].

Figure 3  (A) underfocused (B) When stigmatic and in focus, the image is crisp and (C) overfocused [72].
Chapter 2 MICRO-LIMITING DOME HEIGHT TESTS (µLDH)

2.1 Sample Preparation for Dome Tests

Commercially pure titanium (Cp-Ti) grade 2 foils are cut into 1-inch by 1-inch square pieces using a paper cutter. Wearing gloves is necessary while doing this process to reduce the fingerprints and smudges attaching to the samples.

Before doing the electrochemical anodization, each sample must be cleaned and prepared. This process includes cleaning the sample with distilled water and acetone and dried. The first sample is submerged in distilled water, and the small beaker is kept in a sonicator for 10 minutes. The same process is done next with the sample held in acetone and then finally in distilled water. Then it is kept drying before taking it to the anodization, as shown in Figure 4.

Figure 4  Anodization setup for dome test samples.
For electrochemical anodization (Figure 5), a beaker is taken and filled with 200 ml of distilled water and then 2 ml of H.F. is added, which is 1% of weight volume [73]. This H.F. solution is kept on a magnetic stirrer and starts to mix the solution with the help of a small magnet in the solution. Then platinum foil with part number 267244-350MG, 0.025mm thickness, and 99.9% pure is attached to the cathode, which is connected to the power supply using alligator clips and a stand to support the alligator clips. Then the Ti foil is connected to the anode, and both are suspended into the H.F. solution until the alligator clip end; do not touch the solution, which would, in turn, jeopardize the experiment. While the solution is being stirred at low speed, power supply is switched on and the constant voltage of 20V is kept for about 45 minutes.

![Diagram](image)

Figure 5  Representation of electrochemical anodization process.
2.2 Anodization Process on Dome Test Samples

With 20 constant voltage and submerging the sample in an electrochemical solution of 1% hydrofluoride solution, these samples are formed with titanium nanotubes. For these samples, different conditions are checked to get the nanotube layer. The optimization of the process is done by the "trial and error" method. Four different constant voltages are used, i.e., 5V, 10V, 15V, and 20V, at different process times, i.e., 15, 30, 45, 60, and 75 minutes.

It is observed that in the samples prepared, a constant 20 voltages facilitated to form nanotube layer and is therefore utilized for further experimentation. The samples that are developed at 60 minutes and 75 minutes anodization process are very thin and fragile, so the experiments done showed inconsistent results. Therefore, for performing further dome tests, only samples formed from anodization process of 15, 30, and 45 minutes are considered.
2.3 SEM Images of Dome Test Samples

Figure 6  A dome test sample prepared at 20V 15 min taken at 80kx magnification.

Figure 7  A dome test sample prepared at 20V 30 min taken at 80kx magnification.

Figure 8  A dome test sample prepared at 20V 45 min taken at 80kx magnification.

Figure 9  A dome test sample prepared at 20V 60 min taken at 80kx magnification.
Figure 10  A dome test sample prepared at 15V 45 min taken at 80kx magnification.

Figure 11  A dome test sample prepared at 10V 45 min taken at 80kx magnification.

Figure 12  A dome test sample prepared at 5V 45 min taken at 80kx magnification.
2.4 Experimental Procedure of Dome Test

Micro-limiting dome height tests are done in the materials lab on the electromechanical machine named MTS model 43 (MTS - Methods for Testing and Specification). A punch and die setup are used. Moreover, the whole tests are done in MTS environmental chamber. Also, before the tests, blanking is done to get samples of a diameter of 4mm.

2.4.1 Blanking Process

Blanking is the metal fabrication process in which a part of the metal workpiece is removed when it is punched through. The removed material is called a blank, and which is, in our case, the 4 mm diameter sample. Samples that are already prepared from electrochemical anodization are taken, and blanking is done. The samples are kept face down and marked lines on the backside of the sample. This was done to avoid confusion between two sides of the Cp-Ti foil. The blanking and dome test is done on the same side of the foil. The setup can be seen in the above Figure 13. The controller in the MTS model 43 can control crosshead speed, which is used for the blanking process.

![Blanking equipment setup.](image-url)
2.4.2 μLDH Tests

All the Cp-Ti foil samples which had nanotubes and blanked into 4 mm diameter were taken. Each sample was kept facing down so as not to make the punch contact with the face where nanotubes are present, which was more comfortable to recognize from the marker lines on the samples. Then the setup was arranged, as shown in Figure 14.

![Micro-limiting dome height test setup](image)

Figure 14  Micro-limiting dome height test setup.

The punch was guided to the die holder, where the sample is secured inside. After that, the chamber is closed and rests for 30 minutes for the temperature to reach 100°C and then 200°C. This heating chamber is shown in Figure 15. The temperature of the chamber was controlled by the setup, as shown in Figure 16. After reaching that temperature slowly, the punch is guided down onto the sample by the knob on the controller until the load started to increase.
When the load value started to increase from 1N to 4N, manual loading was stopped, and then the software MTS Test Suite is opened and run. The program was created by Zhang, a former student who already researched these tests [10]. At first, experiments were done at speeds of 0.01 mm/s, but it damaged the test sample and a more substantial crack formed. To minimize the crack, the rate at which the load was applied reduced to 0.001 mm/s, and then experiments were done.

Figure 15  MTS machine with a heat chamber.

Figure 16  Heat chamber controller.
2.5 Precautionary Steps Taken During Dome Tests

Consider the surfaces of Cp-Ti foil called as side one and side two. Side one is the surface faced away from platinum cathode and side two faces platinum cathode. Both the surfaces of the Cp-Ti have nanotubes formed, but it is more prominent on the side facing the platinum cathode (side two). While doing μLDH tests, the punch is in contact with the sample on side one, which by that time does not have many nanotubes left. The blanking process removes the nanotube layer on the contacted side.

Both the punches for blanking and μLDH test applies pressure on side two. Therefore, side one of the samples having nanotubes is not affected by contact with blanking punch and μLDH test punch. Therefore, the only effect by the strain caused inside the material is due to the μLDH test.

2.6 Formability

Three different conditions are considered while doing the μLDH test: one is at room temperature, the second is at 100°C temperature, and the third is at 200°C temperature. The previous study shows that the increase in temperature increases the formability of the Cp-Ti foil without nanotubes. In this study, after doing dome tests, the fractures were analyzed using ImageJ software at each temperature. From this, a forming limit curve (FLC) was generated using the ASTM E2218-02 standard (2008) for each FLD. Then the FLC’s low points and plane strain values reveal that the formability of Cp-Ti increases as temperature increases. However, in our study, the rise in temperature decreases the forming nature of the Cp-Ti samples.
2.7 Studying the Results from Dome Tests

Using Hitachi S4500 field emission scanning electron microscope (SEM), images are captured at higher magnification. Analysis of SEM images for μLDH tests done at different punch travel distances was carried out. Punch travel distance is the distance traveled by the punch at 0.0001 mm/s to form dome shape on the sample that defined the height of the dome formed on the sample (H_d). Then for analyzing the SEM images, three to five circles of diameter 1 inch are drawn at the center of the picture. After calibration, we found out the area covering the circle is approximately 0.2172 µm². Counting and marking the number of nanotubes inside the circles of said area are done using ImageJ software. The results from these samples are compared with different samples to know the H_d, where the μLDH test is not affecting the nanotube layer.

First, the H_d (punch travel distance) is known when the dome forms crack due to strain, and then the experiments are done in decrements of H_d. While doing these tests, it is observed that even though there is no crack visually in the sample, the nanotube layer gets separated when observed from SEM. Therefore, the value before this particular H_d is the minimum punch travel distance at which there is no loss in the number of nanotubes. It also represents the most strain the sample can induce without affecting the nanotube layer.
2.8 Dimensions of TiO$_2$ Nanotubes

Figures 17 - 20 show dome test samples taken using SEM to calculate the length, inner diameter, and wall thickness of the nanotubes. The samples are mounted at 45 degrees inclination before scratching the nanotube layer to create an opening. Data is collected using ImageJ software to determine the dimensions of the titanium oxide (TiO$_2$) nanotubes. The nanotubes are randomly selected, and for consistency, three different samples with similar conditions are considered. The tube length ranges from 125 to 180 nm, with an inner diameter of 50 nm and a wall thickness of 10 nm approximately.

Figure 17  Cross-sectional SEM image of 20V 15 mins 50kx tensile sample.  
Figure 18  Cross-sectional SEM image of 20V 30 mins 50kx tensile sample.
I have done the anodization process at 20 V constant voltage for four different times, i.e., 15, 30, 45, and 60 minutes. The increase in the time of anodization process increases the length of the nanotubes formed. When the anodization process is done for more than 60 minutes, the sample becomes weaker in condition and becomes unusable for further dome tests and tensile tests. It is observed that after 75 minutes of the experiment, the sample remains in the same fragile condition.

A uniform structure of thin-walled TiO$_2$ nanotubes is obtained from the anodization process. Table 4 summarizes the quantitative measurements of tube diameter, tube wall thickness, and tube length. For each sample minimum, ten nanotubes are considered, using ImageJ software to calculate the dimensions. From the above observation, tube diameter and wall thickness did not vary with anodization times. These results are consistent with those found by other researchers under similar processing conditions [67]. A small increase in tube diameter and wall thickness is observed with increasing anodization time, but considering the standard deviation of the reported data, this difference becomes insignificant.
Table 4 Dimensions of TiO$_2$ nanotubes through anodic oxidation on Cp-Ti tensile samples

<table>
<thead>
<tr>
<th>Anodization Time (minutes)</th>
<th>Inner tube diameter (nm)</th>
<th>Wall thickness (nm)</th>
<th>Tube length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>48±5</td>
<td>10±2</td>
<td>125±5</td>
</tr>
<tr>
<td>30</td>
<td>50±4</td>
<td>10±2</td>
<td>150±4</td>
</tr>
<tr>
<td>45</td>
<td>51±4</td>
<td>11±2</td>
<td>170±5</td>
</tr>
<tr>
<td>60</td>
<td>53±5</td>
<td>10±3</td>
<td>180±5</td>
</tr>
</tbody>
</table>

2.9 Comparing the Results of Dome Tests

2.9.1 20V 15 Minutes Sample at Room Temperature

For 20V 15 min samples after the dome test at room temperature, the data can be observed in Figure 21. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.9 mm (Figure 22). At 0.95 mm $H_d$, the nanotube layer gets separated after the µLDH test (Figure 23).
Figure 21    Graph for 20V 15 mins at room temperature.

Figure 22    SEM image of 20V 15 mins dome test sample at 0.9 mm $H_d$. 
For 20V 15 min samples after the dome test at 100°C temperature, the data can be observed in Figure 24. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.65 mm (Figure 25). At 0.7 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 26).
Figure 24  Graph for 20V 15 mins samples at 100 °C.

Figure 25  SEM image of 20V 15 mins dome test sample at 0.65 mm H$_d$. 
For 20V 15 min samples after the dome test at 200°C temperature, the data can be observed in Figure 27. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.5 mm (Figure 28). At 0.55 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 29).
Figure 27  Graph for 20V 15 mins at 200 °C.

Figure 28  SEM image of 20V 15 mins dome test sample at 0.5 mm H₂O.
For 20V 30 min samples after the dome test at room temperature, the data can be observed in Figure 30. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.65 mm (Figure 31). At 0.7 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 32).
Figure 30  Graph for 20V 30 mins samples at room temperature.

Figure 31  SEM image of 20V 30 mins dome test sample at 0.65 mm Hₐ.
2.9.5 20V 30 Minutes Sample at 100°C

For 20V 30 mins samples after the dome test at 100°C temperature, the data can be observed in Figure 33. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum \( H_d \) where the nanotube layer is intact is 0.55 mm (Figure 34). At 0.6 mm \( H_d \), the nanotube layer gets separated after the \( \mu \)LDH test (Figure 35).

Figure 32    SEM image of 20V 30 mins dome test sample at 0.7 mm \( H_d \).
Figure 33  Graph for 20V 30 minutes at 100°C.

Figure 34  SEM image of 20V 30 mins dome test sample at 0.55 mm \( H_d \).
For 20V 30 mins samples after the dome test at 200°C temperature, the data can be observed in Figure 36. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.35 mm (Figure 37). At 0.4 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 38).
Figure 36  Graph for 20V 30 minutes at 200°C.

Figure 37  SEM image of 20V 30 mins dome test sample at 0.35 mm Hg.
For 20V 45 mins samples after the dome test at room temperature, the data can be observed in Figure 39. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.4 mm (Figure 40). At 0.45 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 41).
Figure 39  Graph for 20V 45 mins samples at room temperature.

Figure 40  SEM image of 20V 45 mins dome test sample at 0.4 mm $H_d$. 
2.9.8 20V 45 Minutes Sample at 100°C

For 20V 45 mins samples after the dome test at 100°C temperature, the data can be observed in Figure 42. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.35 mm (Figure 43). At 0.4 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 44).
Figure 42  Graph for 20V 45 minutes at 100°C

Figure 43  SEM image of 20V 45 mins dome test sample at 0.35 mm $H_d$. 
2.9.9 20V 45 Minutes Sample at 200°C

For 20V 45 mins samples after the dome test at 200°C temperature, the data can be observed in Figure 45. The circles with red fill represent the samples where the nanotube layer is separated, and green fill represents the samples where the nanotube layer is intact. From the graph, we can determine that the maximum $H_d$ where the nanotube layer is intact is 0.25 mm (Figure 46). At 0.3 mm $H_d$, the nanotube layer gets separated after the $\mu$LDH test (Figure 47).
Figure 45  Graph for 20V 45 minutes at 200°C.

Figure 46  SEM image of 20V 45 mins dome test sample at 0.25 mm H_d.
2.10 Analysis of the Results from Dome Tests

2.10.1 Analyzing Results for Dome Tests of the Intact Nanotube layer

Figure 48 shows the data taken from dome tests compared with the increase in temperature. The value of the punch travel distance shown is the maximum value observed where the nanotube layer does not get damaged or separated. The different temperatures considered for the dome tests are 25 °C, 100 °C, and 200 °C. Therefore, by an increase in temperature, the punch travel distance for a particular condition decreases.
From the graphical analysis, predicted trendlines are as follows:

1. \( y = -0.2x + 1.0833 \) for 20V 15mins samples
2. \( y = -0.15x + 0.8167 \) for 20V 30mins samples
3. \( y = -0.075x + 0.4833 \) for 20V 45mins samples

From this analysis, we can determine that irrespective of the temperature conditions the dome tests are performed in, the increase in the sample’s anodization time decreases the punch travel distance. This analysis directly represents that the material properties of the sample with nanotubes get affected.
From calculating the dimensions of nanotubes, we have observed that by increasing time of the anodization process by keeping the voltage constant, the length of the nanotubes increases. A previous study shows a similar behavior of an increase in the length of nanotubes [67]. From this, it is determined that the structure of the nanotube is changing concerning the anodization process. Also, the friction coefficient increases because of the change in nanotubes properties, which is studied. The previous study shows that the decrease in the friction coefficient of the nanotube layer is possible by utilizing acetylene treatment [74].

Previously we have stated that the reason for not experimenting on the dome test samples of anodization times of more than 60 minutes is that they become more fragile. The decreasing trendlines prove the fact that the integrity of the sample with the nanotube layer decreases with an increase in anodization time [75].

The decreasing trendline is similar for elevated temperatures, which shows that the sample is not yet transitioned into the rutile phase from the anatase phase. Because of this, the performance of the samples is not varied with respect to temperature differences [76].

We can expect this trendline to continue until 450°C, which is the approximate value where the TiO₂ nanotubes transition from anatase to rutile [77]. In the anatase phase, the nanotube layer is not strong compared to the rutile phase and also the mechanical properties differ a lot when there is a phase transition. The samples should be annealed before performing the dome tests.

This trendline contradicts the previous study, which shows that the formability of the dome test samples increases with an increase in temperature. For our study of dome test samples with nanotube layer, there is a decrease in the punch travel distance when the temperature is increased.
2.10.2 Analyzing Results for Dome Tests in Nanotubes Distribution

Figure 49 shows the data for the sample condition 20V 15 mins when performed in dome tests at different temperatures. Blue trendline represents the performance of the sample at 200°C, the yellow trend line represents the tests at 100°C, and the green trendline represents the tests at room temperature. The graph is plotted between punch travel distance and the number of nanotubes. The trendlines show the decline in the quality of the nanotube layer when the punch travel distance is increased. The decreasing trendlines follow the equations:

1. \( y = -48.229x + 64.338 \) at 200°C
2. \( y = -41.473x + 67.586 \) at 100°C
3. \( y = -18.342x + 57.734 \) at room temperature

The decreasing trendlines for 20V 30 mins sample are (Figure 50):

1. \( y = -28.811x + 51.486 \) at 200°C
2. \( y = -28.557x + 56.999 \) at 100°C
3. \( y = -23.428x + 56.724 \) at room temperature

The decreasing trendlines for 20V 45 mins sample are (Figure 51):

1. \( y = -49.011x + 52.918 \) at 200°C
2. \( y = -33.338x + 52.585 \) at 100°C
3. \( y = -23.719x + 51.251 \) at room temperature
Figure 49  Graphical analysis of 20V 15 mins sample dome tests.

Figure 50  Graphical analysis of 20V 30 mins sample dome tests.
Figure 51  
Graphical analysis of 20V 45 mins sample dome tests.

The decreasing trendlines for each of the sample conditions prove that the increase in the punch travel distance damages the nanotube layer, and the decreasing trendline is consistently shown for other sample conditions and temperatures.

Another observation from the analysis is that by the increase in temperature, the punch travel distance for a particular sample is decreased. The possible explanation for the said analysis is the structure of nanotubes is amorphous and stays in the anatase phase instead of transitioning into the rutile phase [76,77].
2.11 Discussion of Dome Tests

From the dome tests, we determined the punch travel distance for each condition where the nanotube layer is intact. The results summarized in Table 5 indicate that with the increase in temperature, the punch travel distance decreases for dome tests decreases. The reason punch travel distance is considered is explained further.

<table>
<thead>
<tr>
<th>Dome test sample condition for anodization process</th>
<th>The temperature where dome tests are performed</th>
<th>Maximum punch travel distance (mm) where there is no damage in nanotube layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>20V 15mins</td>
<td>room temperature</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.50</td>
</tr>
<tr>
<td>20V 30mins</td>
<td>room temperature</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.35</td>
</tr>
<tr>
<td>20V 45mins</td>
<td>room temperature</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.25</td>
</tr>
</tbody>
</table>
For dome tests, a strain is calculated by observing data from SEM studying the deformed microgrids etched on the sample. This grid marking is done by optical lithography and etching process [78]. Then while doing SEM, care must be taken to tilt the base where the sample is kept and capture the image where the highest strain is induced. This is because of the biaxial strain created in the sample.

Another process of doing dome tests and calculating strain is performing bulge testing using a rubber pad to achieve different strain models [79]. These are a few models that are not considered for our study because of the nanotubes present in the samples. Nanotubes will be compromised if etched or when it contacts rubber pad. Because of this consideration, the calculation of strain for dome tests was not done for this study. Instead, punch travel distance (~dome height of the sample) is taken as an alternative variable to compare the data acquired.

A previous study [80] was done on the same material to calculate the maximum strain at which the sample fails (cracks), and comparing the following variables: temperature, strain rate, and physical size. They concluded from their study that the formability of Cp-Ti is increased with an increase in temperature. The formability was increased by 25%, 80%, and 95% at temperatures 100°C, 200°C, and 300°C, respectively.

From this inspiration, we have conducted dome tests at three different temperatures (25°C, 100°C, and 200°C) on three different samples of anodization times (15mins, 30 mins, and 45 mins). Then SEM images of the deformed samples are captured, and ImageJ software is used to compute the number of nanotubes in a particular area. This data is shown in detail in previous pages with tables and figures and then analyzed.
From the inspiration of previous studies, we expected when there is an increase in temperature for the tests, the punch travel distance should increase. But after analyzing data, we found that there is a decreasing trend for any type of sample when the temperature is increased. The reason is explained in a previous study stating that the sample is in the anatase phase until annealed for about 450°C to 650°C [81-85] and will transition into the rutile phase, which is more stable and can withstand high pressures. Rutile TiO$_2$ is more stable, has high melting and boiling point, and is harder (Mohr hardness for rutile is 6 to 6.5 and for anatase is 5.5 to 6) than anatase TiO$_2$.

The second reason for the above analysis is that as the titanium material is used to form nanotubes, the substrate is the same material as the nanotube layer. Therefore, the two layers have different phase transition parameters and are often with weaker adhesion if not prepared properly. So, the sample must be either annealed or treated with an acetylene-like compound before proceeding into doing experimentation.

The study also demonstrates a correlation between the anodization process time of a sample and punch travel distance. It shows that for different samples, the increase in anodization time for a sample decreases the maximum punch travel distance (H$_d$). This analysis proves that the anodization process has a time limit and cannot be extended to hours expecting to produce lengthier nanotubes. As the length of nanotubes [67] increases to a certain point as the time of the anodization process increases, there is a higher friction coefficient for longer nanotubes. Due to this, the punch coming in contact with the sample is damaging the sample while applying pressure. The sample has a nanotube layer on both sides, which is the reason for the decrease in punch travel distance.
The second reason for the behavior of the sample increasing the punch travel distance is that there is an increase in the surface area where the punch encounters. Because of that, a small increase in friction coefficient induces more strain on the sample [76].

The final reason observed to be is that the nanotube layer has pores, ridges, and walls, which act as a place for higher stress concentration factors leading to the lower punch travel distance for increasing anodization times [86].

The importance of this analysis is to understand the nanotubes’ behavior with the surface of the substrate under dome tests. The nanotube layer is being damaged with less strain in the sample, which shows that the process should be optimized further so that the samples can withstand more strain and also follow the formability curve for future applications.
Chapter 3 TENSILE TESTS

3.1 Sample Preparation for Tensile Tests

For tensile tests, the specimens which were purchased from Arnold Magnetic Technologies in Marengo, Illinois, are prepared using standard ASTM dimensions, as shown in Figure 52 below. These samples are cut using water jet machining and then appropriately cleaned using water and then distilled water to remove the impurities carried from the machining process.

![Tensile sample with dimensions in inches.](image)

Figure 52 Tensile sample with dimensions in inches.

The same process as done for dome test samples is followed to prepare samples for the anodization process. But the tensile samples are cleaned twice thoroughly to remove the impurities and dust from samples as much as possible. For electrochemical anodization, a bigger beaker is taken and filled with 1000 ml of distilled water and then added 10 ml of H.F., which is 1% of weight volume. A magnetic stirrer starts to mix the solution with the help of a small magnet in the solution, as shown in Figure 53. Only a slight difference from the dome test samples' process is
that the tensile sample is suspended into the solution in such a way that one side of the sample leans to the inner walls of the beaker. This method is done to prevent the sample from repeatedly moving because of the stirring motion. In this way, even though the sample is thin and long, the nanotubes are formed very well on the other side, which is faced by the platinum electrode.

Figure 53  Setup for electrochemical anodization.

Then the anodization process is done the same way as before. The solution is stirred at low speed and performed at a constant voltage of 20V for about 45 minutes. The combination of 20V and 45 minutes is the best setup to get the nanotubes formed on the Ti foil sample. For tensile samples, I have performed a similar "trial and error" anodization process. Combinations of different voltages, different times of experimenting, and different concentrations of electrolyte solutions are considered to get nanotubes: voltages at 5V, 10V, 15V, and 20V; times at 15 mins, 30 mins, 45 mins, 60 mins, and 75 mins. Also, 0.5%, 1%, and 1.5% H.F. electrolyte solutions were
used for anodizing the Ti samples before taken to scanning electron microscope (SEM) for the tensile test.

3.2 Anodization Process on Tensile Test Samples

With 20 constant voltage and submerging the sample in an electrochemical solution of 1% hydrofluoride solution, these samples are formed with titanium nanotubes. For these samples, different conditions are checked to get the nanotube layer. The optimization of the process is done by the "trial and error" method. The first four different constant voltages are used, i.e., 5V, 10V, 15V, and 20V, at different process times, i.e., 15, 30, 45, 60, and 75 minutes. It is observed that the samples prepared from constant 20 voltages facilitated to form nanotube layer and therefore is utilized for further experimentation. The samples that are developed at 60 minutes and 75 minutes anodization process are very thin and fragile, so the experiments done showed inconsistent results. Therefore, for further performing tensile tests, only samples formed from anodization process of 15, 30, and 45 minutes are considered.

3.3 SEM Images of Tensile Test Samples

![Figure 54](image1.png) A tensile test sample prepared at 20V 15 mins taken at 30kx magnification.  
![Figure 55](image2.png) A tensile test sample prepared at 20V 30 mins taken at 30kx magnification.
3.4 Experimental Procedure of Tensile Test

3.4.1 Preparing Samples for Tensile Tests

Tensile samples after being machined using a water jet machine and anodized to form nanotubes are taken and kept in the setup for the tensile test, as shown in Figure 58. Before fixing into the setup, two reflective tapes are held on the tensile sample at the start and end of the region, as shown in Figure 59. This highlighted part is where the crack occurs in the sample due to the tensile test. These tapes on both sides help to read the extensions from the laser extensometer. The laser extensometer used in this setup is shown in the below Figure 60.
Figure 58  Tensile test setup.

Figure 59  Highlighted area of the tensile sample is where SEM images are taken.
3.4.2 Tensile Tests Procedure

After preparing the samples with electrochemical anodization and letting them dry for a day, the samples are taken and kept in the tensile setup with reflective tapes on it. Then laser extensometer is connected to the MTS Test Suite software, which runs the MTS tensile setup. The laser is then pointed to the tensile sample, and then the experiment started with speeds of about 0.0001 mm/s rate. At first, the limit of extension is noted where the sample cracks and then percentage elongations are done accordingly for each sample. In this way, we have done 3%, 2%, 1.5%, and 1% elongations for different samples and then taken for SEM images. The different samples considered are 20V 15 mins, 20V 30 mins, 20V 45 mins, and 20V 60 mins. For each condition, three different samples are done for accurate results.
The following are simple stress and strain equations considered for tensile tests. Stress ($\sigma$) and strain ($\varepsilon$) relations are given below as Equations 3 and 4:

\[
\sigma = \frac{F}{w \times t} \quad (3)
\]

\[
\varepsilon = \frac{\delta}{l} \quad (4)
\]

Where $\sigma$ represents stress:

- $F$ is the force read from the load cell.
- $w$ is the width of the specimen after tensile test.
- $t$ is the thickness of the specimen.
- $\varepsilon$ represents a strain of the sample.
- $\delta$ is the extension read from the extensometer.
- $l$ is the initial length of the specimen.

### 3.5 Precautionary Steps Taken During Tensile Tests

Consider the surfaces of Cp-Ti foil named as side one and side two. Side one is the surface faced away from platinum cathode, and side two faces platinum cathode. Both the surfaces of the Cp-Ti have nanotubes formed, but it is more prominent on the side exposed to the platinum cathode (side two). Side one of the tensile samples is in contact with the inner walls of the beaker while doing the anodization process, therefore not considered for further SEM images. While doing tensile tests, side one has the reflective tape attached to it, and the laser is aligned accordingly.

Then the tensile test is started, and elongation is noted from the reading of the laser extensometer. The testing is done at 0.0001 mm/s rate so that we can quickly stop the tensile at the required elongation. For all the samples, the elongation considered was 1%, 2%, 3%, 4%, and 5%.
After observing the images using SEM, it is determined that most of the samples' nanotube layer gets separated from 3% elongation, which can be identified as the maximum strain the sample can withstand without damaging the nanotube layer. Tensile tests are also done at 200°C temperature using a similar setup, as shown in the dome tests.

### 3.6 Studying the Results from Tensile Tests

Using Hitachi S4500 field emission scanning electron microscope (SEM), images are captured at higher magnification. Analysis of SEM images for tensile tests is done at different elongations, as mentioned above. One should take special care while getting SEM images for tensile samples because of its bigger size.

I have observed and taken images while checking the entirety of the sample. Then I have studied the images where the width is less, where the stress concentration is higher. Then images that represent the most value are chosen for each sample.

Then for analyzing the SEM images, several circles of diameter 1 inch are drawn at the center of the picture. After calibration, we found out the area covering the circle, which is approximately 0.2172 µm². Counting and marking the number of nanotubes inside the circles of said area are done using ImageJ software. Apart from calculating the engineering strain, number of nanotubes is calculated to analyze the behavior of nanotubes while under strain.
3.7 Comparing the Results of Tensile Tests

3.7.1 20V 15 Minutes Sample at Room Temperature

For 20V 15 mins samples after the tensile test at room temperature, the data can be observed in Figure 61. The circles with red fill represent the samples where the nanotube layer is separated and with green fill represent the samples where the nanotube layer is intact. From the graph, we can determine that the maximum strain where the nanotube layer is intact is 0.02 (Figure 62), and it gets separated at 0.03 (Figure 63).

![Graph for 20V 15 mins tensile sample at room temperature.](image)
Figure 62  SEM image of 20V 15 mins tensile test sample at 2% elongation.

Figure 63  SEM image of 20V 15 mins tensile test sample at 3% elongation.
3.7.2 20V 30 Minutes Tensile Sample at Room Temperature

For 20V 30 mins samples after the tensile test at room temperature, the data can be observed in Figure 64. The circles with red fill represent the samples where the nanotube layer is separated and with green fill represent the samples where the nanotube layer is intact. From the graph, we can determine that the maximum strain where the nanotube layer is intact is 0.02 (Figure 65), and it gets separated at 0.03 (Figure 66).

Figure 64  Graph for 20V 30 mins tensile sample at room temperature.
Figure 65 SEM image of 20V 30 mins tensile test sample at 2% elongation.

Figure 66 SEM image of 20V 30 mins tensile test sample at 3% elongation.
3.7.3 20V 45 Minutes Tensile Sample at Room Temperature

For 20V 45 mins samples after the tensile test at room temperature, the data can be observed in Figure 67. The circles with red fill represent the samples where the nanotube layer is separated and with green fill represent the samples where the nanotube layer is intact. From the graph, we can determine that the maximum strain where the nanotube layer is intact is 0.02 (Figure 68), and it gets separated at 0.03 (Figure 69).

![Graph for 20V 45 mins tensile sample at room temperature.](image.png)
Figure 68  SEM image of 20V 45 mins tensile test sample at 2% elongation.

Figure 69  SEM image of 20V 45 mins tensile test sample at 3% elongation.
3.7.4 20V 60 Minutes Tensile Sample at Room Temperature

For 20V 60 mins samples after the tensile test at room temperature, the data can be observed in Figure 70. The circles with red fill represent the samples where the nanotube layer is separated and with green fill represent the samples where the nanotube layer is intact. From the graph, we can determine that the maximum strain where the nanotube layer is intact is 0.015 (Figure 71), and it gets separated at 0.02 (Figure 72).

Figure 70  Graph for 20V 60 mins tensile sample at room temperature.
Figure 71  SEM image of 20V 60 mins tensile test sample at 1.5% elongation.

Figure 72  SEM image of 20V 60 mins tensile test sample at 2% elongation.
3.7.5 Tensile Tests at 200°C Temperature

Two or three samples for each condition are tensile tested at 200°C temperature to check the behavior of the nanotube layer even though the previous study from dome tests did not provide better results. Figures 73-76 show the SEM images for different samples at respective elongation where the nanotube layer is intact.

Figure 73 20V 15 mins at 200°C at 2% elongation.

Figure 74 20V 30 mins at 200°C at 2% elongation.

Figure 75 20V 45 mins at 200°C at 2% elongation.

Figure 76 20V 60 mins at 200°C at 1.5% elongation.
Figures 77-80 show the SEM images for different samples experimented at 200°C temperature at respective elongation where the nanotube layer is separated. For 20V 15 mins, 30 mins, and 45 mins tensile samples experimented at 200°C temperature, the maximum strain without damaging the nanotube layer is 0.02. For 20V 60 mins tensile samples, the maximum strain is 0.015.
3.8 Analysis of the Results from Tensile Tests

3.8.1 Analyzing Results for Tensile Tests to know the Effect of the Anodization Process

Figures 81 and 82 show analysis for the tensile test data experimented on room temperature and 200°C. For both the graphs, the green bar represents an intact nanotube layer, the yellow bar is the separated nanotube layer, and the blue bar represents the average nanotube layer. The average strain is calculated for intact, and the separated nanotube layer represents the expected strain where the nanotube layer gets damaged.

**Figure 81** Graphical analysis showing the data from tensile tests at room temperature
Figure 82  Graphical analysis showing the data from tensile tests at 200°C temperature

The samples performed similarly at both temperatures. They are showing a decreasing trendline with an increase in anodization time. This trend is similar in the dome tests, where the rise in anodization time decreases the properties of the sample [75]. Also, the phase transition to rutile did not take place at this temperature [76,77].

3.8.2 Analyzing Results for Tensile Tests of the Intact Nanotube Layer

Figure 83 shows that the results from both the tests have a similar maximum strain value where the nanotubes are intact. The data is insufficient to create a trendline between the two temperatures. But the results are different from dome tests, where the decrease is shown clearly from the data. When dome tests are observed, there is a definite decrease in the strain value when the temperature is increased, but for the case of tensile tests, it is not, mainly because of the amorphous structure of anatase phase sample does not show the loss because of the surface area
of the sample is high. So, the temperature distributed among the sample dissipates faster, making it cooler and back to normal conditions faster [86].

![Graphical analysis showing the data from tensile tests where nanotubes are intact](image)

**Figure 83**  Graphical analysis showing the data from tensile tests where nanotubes are intact

### 3.8.3 Analyzing Results for Tensile Tests in Nanotubes Distribution

Figures 84-87 show the analysis between nanotubes and the strain developed for different samples. There is a downward trend as the strain increases in a sample. The difference between dome tests and tensile tests is that the temperature has less effect on tensile tests. One of the main reasons is the large surface area of the tensile sample when compared to the dome tests. The second reason is that the structure of the nanotube is amorphous and not highly stable, due to which the nanotube layer is getting damaged at a low strain of 0.02 [77].
Figure 84  Graphical analysis of 20V 15 mins sample tensile tests.

Figure 85  Graphical analysis of 20V 30 mins sample tensile tests.
Figure 86  Graphical analysis of 20V 45 mins sample tensile tests.

Figure 87  Graphical analysis of 20V 60 mins sample tensile tests.
3.9 Discussion of Tensile Tests

Previous studies have performed tensile testing on nanotubes, such as tensile testing on multiwalled carbon nanotubes [11] and micro-tensile testing. For this study, we have performed tensile tests on Cp-Ti having titanium nanotubes. We were unable to calculate the strain induced in the case for dome tests, but we have calculated strain in the case for tensile tests.

After performing tensile tests, the data is acquired by SEM and then analyzed by ImageJ. For each condition, we calculated the maximum strain induced in the sample at which the nanotube layer is not damaged, as shown in Table 6.

Table 6 Results from tensile tests

<table>
<thead>
<tr>
<th>Tensile sample condition after anodization</th>
<th>The temperature where tensile tests are performed</th>
<th>Maximum elongation where there is no damage in nanotube layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>20V 15mins</td>
<td>room temperature</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.02</td>
</tr>
<tr>
<td>20V 30mins</td>
<td>room temperature</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.02</td>
</tr>
<tr>
<td>20V 45mins</td>
<td>room temperature</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.02</td>
</tr>
<tr>
<td>20V 60mins</td>
<td>room temperature</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>0.15</td>
</tr>
</tbody>
</table>
After analyzing the data from tensile tests, we can determine that an increase in the anodization time for a sample decreases the strain it can induce without damaging the nanotube layer, due to the length of nanotubes increasing by anodization time, making the sample more fragile and weaker compared to less time [67].

The declining trend when compared with dome tests is very minimal because in the tensile tests it is pulled by the two ends, so the surface where strain is higher is not in contact with any other surface. Because of this, the slightly higher friction coefficient does not affect the results of the data [76].

When done at 200°C, the value of the engineering strain does not change. This data, when compared to the results from dome tests, is different. In dome tests, when the temperature is increased, the punch travel distance is decreased, but for the case of tensile tests [87], it is almost the same. One of the reasons for this to happen is the size of the sample. Dome tests are performed on 4 mm samples, but the tensile samples are performed on a large sample in comparison. The area covered by nanotubes is much larger when compared to dome tests. This is the main reason why there is a decrease in punch travel distance for dome tests while increasing temperature.

Tensile test samples are also not having a higher value of strain induced without the nanotube layer getting damaged because of the samples not transitioning into the rutile phase. The tests conducted are maximum at 200°C, which is not sufficient for TiO₂ to enter the rutile phase. The range of temperature required for the transition from the anatase phase to rutile phase is 450°C to 650°C [81-85]. Therefore, the weaker anatase phase sample only withstood 2% elongation.
Chapter 4 CONCLUSION

Anodization is the most preferred process among all the methods used for fabricating titanium oxide nanotubes. Moreover, to improve the strength of adhesion to substrates, the coating parameter conditions should be optimized [88,89]. The conventional method is to use the "trial and error" approach, which is very time consuming due to the large number of experiments required. Therefore, a reliable strategy for optimizing coating parameters is needed [90]. In this study, we have optimized the anodization process for both dome test samples and tensile test samples to form a uniform layer of TiO$_2$ nanotubes. At a constant voltage of 20V, four different times of anodization processes of 15, 30, 45, and 60 minutes are performed in a 1% H.F. solution to obtain nanotube layer. The previous study [73] also shows that for similar material, the parameters are very similar. In that research, they obtained titanium oxide nanotubes at 20V at 45 minutes combination.

After performing dome tests and tensile tests, we have calculated the maximum punch travel distance for dome test samples and maximum elongation for tensile test samples without damaging the nanotube layer. We have depended on two variables, i.e., temperature condition for experiments and anodization process times.

From the analysis, we can conclude that by the increase in anodization time for a sample, there is a decrease in the maximum strain a specimen can withstand without damaging the nanotube layer. With increase in the temperature of the experiments, there is a decrease in the maximum strain a sample can withstand without damaging the nanotube layer.
The main objective of this study is to understand the adhesiveness of the nanotube layer under different stress conditions. For dome tests, the stress is applied radially on the titanium oxide nanotubes in two directions. But in tensile tests, the stress is applied radially in one direction. Apart from the radial stress, the bond between the nanotubes and the substrate is weak. For the higher temperature experiments, the samples stay in the heating chamber for approximately two hours. From previous studies, we know that annealing of the titanium samples is done for more than six hours in the temperature range of 450°C to 600°C. In our research, we have worked for less time and lower temperatures for both dome tests and tensile tests. The annealing process is important and should be used for future study so that phase transition occurs, and there are phase changes from anatase to rutile.

Previous studies show the surface modifications of the nanotube layer to know the adhesive ability between the sample and its application. Considering biomedical implants, most of the researches was done to increase the surface modification, and testing was directly on the nanotube layer. But in this study, we are considering the external stress applied to the sample with nanotubes. By optimizing the adhesive ability of the titanium nanotubes, they can be further used in more applications such as fuel cells, storage systems, and sensors.

4.1 Future Work

1. The anodization process should be optimized for other materials, too, like stainless steel, to increase the field of research and applications.

2. The samples prepared after anodization should be annealed. Then the transition of the TiO$_2$ nanotubes from anatase to rutile phase is calculated for getting better strain values.
3. After finding the rutile phase of this particular sample, then studying the formability of the 
Cp-Ti with nanotubes must be done.

4. Consider different materials to work on and find an optimal method for obtaining the 
nanotube layer. Then testing should be done to find its adhesive nature. Tensile tests are 
preferred over dome tests to calculate the strength.

5. Dome tests should be optimized to get strain values for samples having a nanotube layer, 
using a computer model possibly.
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