



Electropolishing valve metals with a sulfuric acid-methanol electrolyte at low temperature

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ABSTRACT

This study reports the electropolishing of Ti and Nb metals using a fluoride-free electrolyte of sulfuric acid and methanol at low temperature (-70°C) without prior treatment. A fluoride-free electrolyte provides a less hazardous and more environmentally friendly option for electropolishing procedure. Experimental studies are presented on electropolishing with sulfuric acid electrolyte, which provides high quality macro- and micro-smoothing of the metal surfaces. Optimal conditions yielded leveling and brightening of the surface of Ti and Nb metals beyond that by the currently utilized electropolishing procedures with fluoride-containing electrolytes. The root mean square roughness (R_q) from atomic force microscopy analysis was 1.64 and 0.49 nm for Ti and Nb, respectively. Lower temperature experiments led to noticeable kinetic effects, indicated by a dramatic drop in current densities and the expansion of the steady-state current density plateau in anodic polarization curves. In addition, the voltage range of the current plateau expanded with increasing acid concentration. Surface characterization of Ti and Nb metals after polishing provided evidence of salt film formation. In addition, these metals were used as substrates in the formation of nanostructured metal oxides. The overall quality of the electropolishing led to a dramatic improvement in the uniformity of the nanostructures.

1. Introduction

Valve metals such as titanium (Ti) and niobium (Nb) have a variety of applications ranging from biological implants to superconducting wires [1–5]. In many of these devices, it is critical for the metals to have smooth surfaces. Ti medical implants require low surface roughness for better contact, while polished Nb is a vital component of high-field superconducting radio frequency cavities [2,4–8]. Smooth Ti and Nb films also facilitate uniform growth of anodized metal oxide nanostructures, which are used in battery electrodes, gas sensors, electrochromic devices, and photocatalysts [9–13]. Reliable and safe polishing methods are therefore required to fulfill the need for smooth valve metal surfaces.

Mechanical polishing for metals like Ti and Nb can be difficult, time-consuming, and requires abrasives that may deposit impurities at the surface [4,14]. It is also often incapable of reducing surface roughness to the order of nanometers [3,4]. Electropolishing can resolve many of the issues encountered by traditional mechanical polishing techniques. It can yield nanometer-scale finishes, is cost-effective, and successfully polishes irregularly shaped pieces [2–4]. Previous

electropolishing approaches for Ti and Nb have used electrolytes with components such as perchloric acid or hydrofluoric acid (HF) [2,6,15–17]. The use of these electrolytes has resulted in an average surface roughness (R_a) of 2.53 nm and 2.1 nm for Ti and Nb, but the toxic nature of the electrolyte presents harmful operating conditions for laboratory and industrial processing [2,18]. A safer alternative is a sulfuric acid-methanol ($\text{H}_2\text{SO}_4\text{-MeOH}$) solution. The sulfate ions attack the passive oxide film on the metal surface, behaving similarly to the perchlorate or fluoride ions found in other electrolytes [3]. Methanol also plays a role during polishing, as it further destabilizes the oxide film and may form ion complexes with the dissolved metal ions [2,3]. Piotrowski et al. reported a R_a of 33 nm for Ti by electropolishing at -10°C in a 3 M solution of $\text{H}_2\text{SO}_4\text{-MeOH}$. It was also found that higher operating temperatures (e.g. 20°C) led to increased surface heating, resulting in burning and non-uniform etching [3]. This electrolyte is also effective for Nb. Zhao et al. obtained a R_a value of 7.6 nm when the polishing temperature was lowered to -30°C [18]. Although a number of studies have investigated Ti and Nb electropolishing with various concentrations of acidic electrolytes at relatively high temperature conditions, no systematic work has been completed on the effect of

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electropolishing temperatures below -30°C .

Electropolishing mechanisms are based on the limited mass transport of species present in solution. This could be in the form of product diffusion, where a salt film may form, or diffusion of a reactant (acceptor model) [7]. The first model, proposed by Grimm et al., describes how the formation of a compact salt film, which depends on metal ion concentration, effectively polishes the metal surface [19]. The second mechanism involves the transport of the adsorbed intermediates, also known as the acceptor molecules, to the surface of the metal [7,19]. The presence of one of these mechanisms explains how the insoluble metal oxides may be converted to soluble species and removed by dissolution. The participating species therefore play a critical role in controlling the electropolishing rate and overall quality of the polish.

We report a systematic study on the electropolishing of Ti and Nb substrates using H_2SO_4 -MeOH electrolytes at low temperatures. The influences of the applied potential, acid concentration, and temperature, were investigated. Anodic polarization curves were obtained to determine the ideal electropolishing voltage range. The temperature was dropped to -70°C to investigate its effect on polishing. Acid concentrations and voltages were subsequently varied to obtain the optimal polishing parameters. The quality of the surface was examined via scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, the polished foils were used to investigate the formation and ordering of nanostructured metal oxides. We demonstrate that the optimal electropolishing conditions for Ti and Nb are achieved at a temperature of -70°C using an applied potential of 15 V and 25 V in a solution of 2 M H_2SO_4 . The polished substrates can be subjected to anodic conditions to form more uniform nanostructured metal oxides when compared to unpolished samples.

2. Materials and methods

2.1. Electrolyte preparation

Electrolytes were prepared in various concentrations in the range of 1 to 3 M of H_2SO_4 (Fisher Scientific, 95–98%) in methanol (Fisher Scientific, 99.9%) solutions. The sulfuric acid was gradually added to the methanol and stirred for 30 min at 200 rpm before being used for electropolishing.

2.2. Electropolishing

Pieces of Ti foil ($40 \times 45 \times 0.127$ mm, Strem Chemicals, 99.7%) and Nb foil ($35 \times 40 \times 0.127$ mm, Alfa Aesar, 99.8%) were cut and sonicated in acetone, isopropanol, and deionized water for 5 min each and then blow-dried with air. To prevent uneven current distribution, the back of each piece was masked using tape. The top edge of the foil was left exposed to ensure good electrical contact. Electropolishing was done in a two-electrode cell with the Ti or Nb foil as the working electrode and a Pt mesh as the counter electrode. Samples were electropolished at constant voltage with various values (11–25 V) using a BK9206 power supply. During electropolishing, the electrolyte was cooled to various temperatures (20°C to -70°C). A Buchi bath chiller was used to maintain temperatures above -10°C . A cold bath with dry ice and appropriate solvent (acetonitrile and acetone) was utilized to obtain temperatures below -10°C . The solution was stirred at a rate of about 350 rpm. Each piece of Ti or Nb was subsequently polished under these conditions for 2 h. To conclude the polishing process, the foils were removed from solution and washed in deionized water. After washing, the foils were sonicated for 5 min in deionized water.

2.3. Anodization

Polished and unpolished pieces of Ti and Nb were sonicated in acetone, isopropanol, and deionized water for 5 min each. The foils were then blow-dried with air. The Ti pieces were backed with packing

tape, and the top edge of each sample was left exposed to ensure good electrical contact. The Ti samples were then anodized in 0.27 M NH_4F in formamide at 15 V for 30 min, with Pt mesh as the counter electrode. After anodization, the Ti samples were dipped in deionized water and then sonicated in isopropanol and deionized water for 5 s each. The Ti samples were then put to dry overnight in a vacuum oven at about 80°C . Nb was anodized in a hot glycerol bath (180°C) containing 10% dibasic potassium phosphate (K_2HPO_4) at 25 V for 10 min. After anodization, the Nb samples were soaked in water overnight and subsequently sonicated for 1 min. Samples were then dipped in IPA and dried via nitrogen.

2.4. Surface characterizations

Surface topography of the polished Nb and Ti was analyzed using a Bruker Dimension FastScan AFM. The AFM was operated in PeakForce Tapping Mode using a Bruker ScanAsyst Air-HR (2 nm nominal radius of curvature) probe. Three $5 \times 5 \mu\text{m}$ images were obtained from each sample at 1024 points per line to yield ~ 2.5 nm lateral resolution. Raw topographical data from the samples was processed and analyzed in Nanoscope Analysis version 1.80. A first order plane fit was used to account for sample tilt, and a first order flatten was applied to correct small line to line offsets in the z piezos. Average and root mean squared (R_q) surface roughness data were then acquired and recorded for comparison. Scanning electron microscopy (SEM) images were recorded at 5 kV and energy-dispersive X-ray spectroscopy (EDS) were recorded at 7 kV using an FEI Teneo FESEM.

3. Results and discussion

3.1. Polarization behavior

Previous Nb and Ti electropolishing attempts using H_2SO_4 -MeOH electrolytes have been performed in temperature ranges from 25°C to -30°C [3,5,18]. Although the reduced temperature led to smoother surfaces, the reported surface roughness values were higher than those obtained with fluoride- or perchlorate-containing electrolytes [5,16,18]. It was hypothesized that lowering the temperature below that of previous studies would decrease the surface roughness even further. Lower temperatures could further reduce surface heating, which would allow the polishing to proceed at appropriate rates across the entire surface, hence mitigating uneven etching. Anodic polarization curves were subsequently used to determine the best parameters for electropolishing. Polarization experiments were conducted in H_2SO_4 -MeOH electrolytes at different acid concentrations and temperatures (Fig. 1). The voltage was swept from 0 to 30 V at a scan rate of 0.5 V/s with H_2SO_4 concentrations of 1, 2, and 3 M at 20, -10 , -40 , and -70°C to demonstrate the important roles that these conditions play on the limiting current plateaus.

Polarization curves are commonly divided into three key regions that describe the phenomena taking place at a given potential. At lower potentials, the first region is where the sample actively forms the localized oxides [2,14,20]. This is known as the pitting area, and ranges from ~ 0 –10 V in the Ti and Nb system. In the second region, a passive surface layer forms while a current plateau is reached [14]. This plateau exists in a range of potentials which varies greatly depending on the sample and electropolishing conditions [2,6,20]. A clear example of a plateau in Fig. 1 exhibits for the 2 M H_2SO_4 -MeOH in Ti system at -10°C and a voltage range of 10–20 V. Current is a function of the electrochemical reaction kinetics occurring between the electrolyte and the electrode. When these reactions take place too rapidly the surface experiences no overall smoothing. Therefore, controlling the kinetics of the electropolishing process is key to surface leveling of the metal. The voltages that lie within this plateau region are ideal for electropolishing, as the passive layer is stabilized and the system is subjected to mass transport control [2,14]. As the voltage continues to increase,

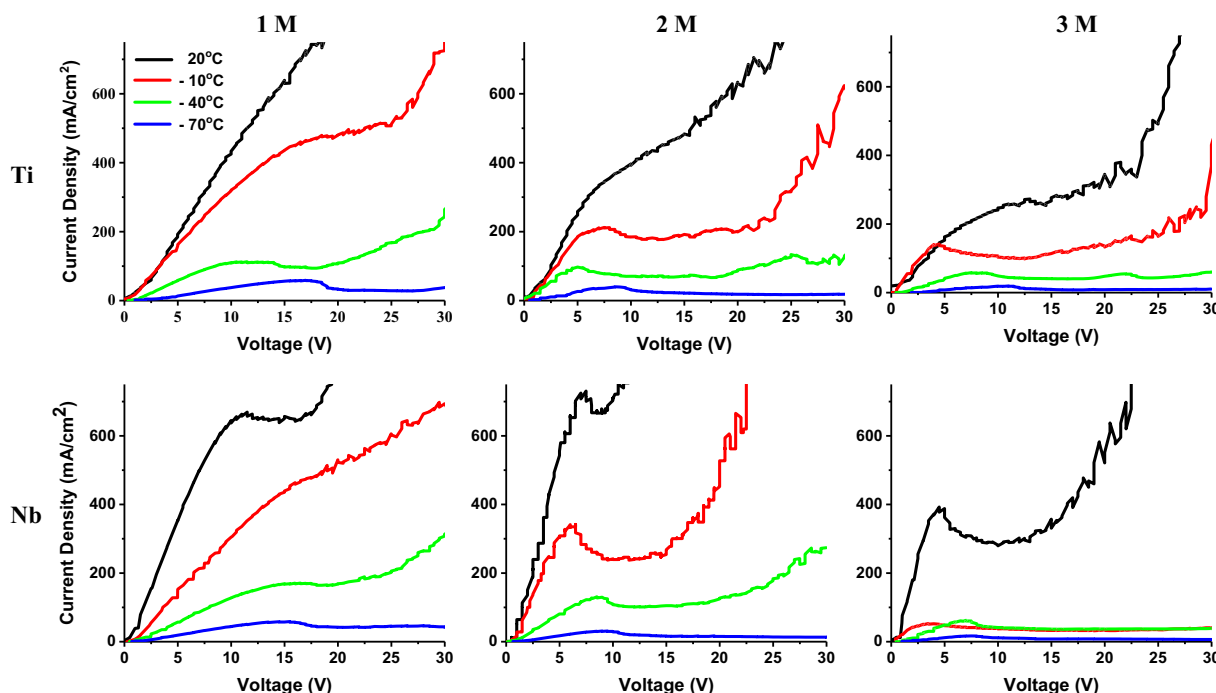


Fig. 1. Ti and Nb polarization curves measured in 1, 2, and 3 M H_2SO_4 -MeOH electrolytes at 20, -10 , -40 , and -70 °C. Scan rate was 0.5 V/s.

the system enters the final region where the current density sharply spikes. In this transpassive region, the passive layer breaks down. Oxygen bubbles may evolve and get trapped on the surface, resulting in significant pitting [2,14].

In both the Ti and Nb metals, a decreasing current density is observed when the concentration of the acid increases. A small plateau in the I - V curves at high temperature (20 °C) was noted only when the acid concentration is above 2 M. This diminishing plateau is consistent with a decreasing solubility of metal ions in the electrolyte, although there could be an effect from a higher water content [18]. Decreasing the temperature played a dramatic role in reducing the current density as well. For each concentration the current density dropped and the width of the plateau expanded as temperature was decreased. Testing various operating voltages within the current plateaus at -70 °C was completed to obtain an optimal condition for electropolishing.

3.2. Effect of temperature

From Fig. 1, it is evident that decreasing temperature resulted in a sharp decrease of current density for both Ti and Nb polarization curves. In addition, the plateau region and its preceding hump broaden at lower temperatures. The transpassive region begins at higher voltages as temperature decreases, and is completely absent at -70 °C even at a potential of 30 V. These trends are consistent with previous reports of decreasing electropolishing temperatures [3,15,18]. The temperature of the electrolyte is directly related to the mass transport of the electropolishing process. Sulfuric acid provides the SO_4^{2-} ion, which acts as the acceptor species in the electropolishing system. The SO_4^{2-} ion coordinates with the Ti or Nb ion, and carries it away from the metal surface [3,14]. Lower temperatures subsequently cause slower diffusion of Nb or Ti ions away from the surface and SO_4^{2-} ions towards the surface. The low temperature also reduces the metal ion solubility in solution, which would have an additional effect on reducing the current density [18]. Furthermore, the lower temperatures extend the voltage range at which the passive layer is stable. Attempts to electropolish at temperatures above -40 °C resulted in rapid etching on the surface of the Ti and Nb foils.

3.3. Effect of sulfuric acid concentration

Fig. 1 also displays the effect of the acid concentration on the current density and limiting current plateau. The 1 M solutions do not exhibit a distinct passive plateau region at higher polishing temperatures for both metals. It only becomes well-defined when the concentration is increased to 2 M, and it slightly broadens for the 3 M solution. As seen in Fig. 2, the plateau is present in the 1 M solution at -70 °C. As the concentration increases, the plateau widens and shifts the onset of the passivation region to lower voltages.

The limiting current density also decreased with increasing H_2SO_4 concentration for both Ti and Nb, which is consistent with other electropolishing procedures that have used H_2SO_4 -MeOH solutions [2,3,18]. The decrease of current density with increasing acid concentration indicates that the SO_4^{2-} ion does not play a critical role in limiting mass transport. This would lead to the hypothesis that electropolishing in both systems is limited by the transport of metal ions rather than acceptor ions, and thus follows the salt film mechanism [3]. The current density decrease and plateau broadening due to increased acid concentration can also be attributed to decreasing metal ion solubility [3,18]. As it becomes more difficult for the metal ions to dissolve in solution, the stability of the salt film increases, which results in the broadening of the plateau region and current density drop. It must be noted that the decrease in current density may also be a consequence of increasing water content inherently present in the H_2SO_4 [3,18,21].

Due to the similarities in the polarization curves at -70 °C, Ti and Nb samples were subsequently electropolished in solutions with increasing acid concentration to determine the ideal molarity. These electropolishing experiments were run at a potential of 15 V. The surface roughness measurements are presented in Table 1 and reflect an overall smoothing of the metal surfaces. The best results were obtained with a 2 M electrolyte for both the Ti and Nb samples and the final polishing piece can be seen in Fig. 3. The 3 M solution causes the poorest finish for both metals, which suggests that the current density could be too low for effective and practical polishing.

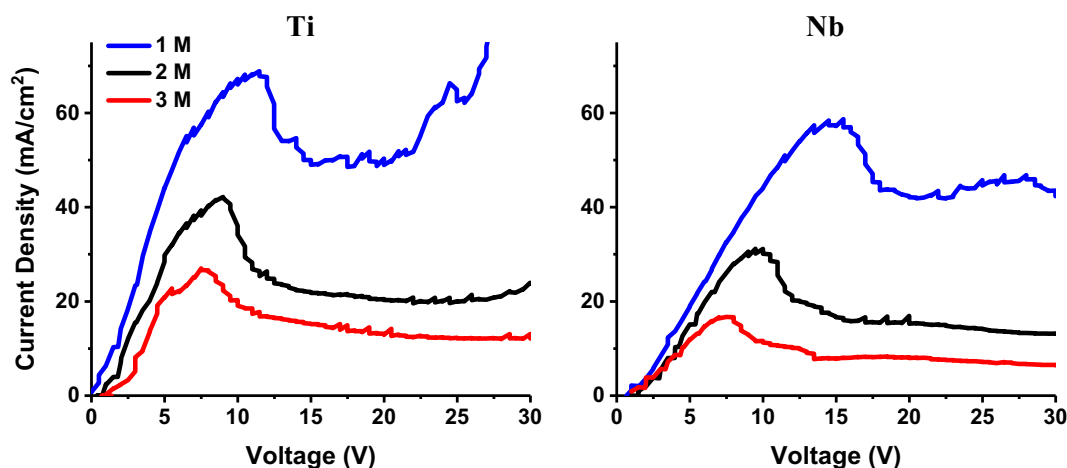


Fig. 2. Polarization curves for Ti and Nb at -70°C with increasing H_2SO_4 concentration.

Table 1

R_a and R_q determined by AFM on Ti and Nb electropolished for 2 h at -70°C and a potential of 15 V under various H_2SO_4 concentrations.

	Ti, 1 M	Ti, 2 M	Ti, 3 M	Nb, 1 M	Nb, 2 M	Nb, 3 M
R_a (nm)	1.39	1.27	2.26	2.77	1.57	5.65
R_q (nm)	2.23	1.64	2.89	4.02	2.19	9.98

3.4. Effect of voltage

It is evident from the aforementioned results that better electropolishing occurs when an electrolyte with a concentration of 2 M H_2SO_4 and a temperature of -70°C is used. Due to the broadness of the passive plateau region, a large range of voltages may be suitable for polishing. As a consequence, several voltages in this region were tested to determine which would create the smoothest surface finish. Using Fig. 2, target voltages were selected from the onset of the current plateau at 11 V, as well as throughout the rest of the plateau (15–25 V). The resulting R_a and R_q values are listed in Table 2.

The Ti samples began to show surface brightening at 11 V, indicating lower surface roughness, but small areas of pitting were also created. When the voltage was increased to 15 V, the Ti surface had an

almost perfect mirror finish with no pitting and its R_q value decreased by over 50%. Polishing at 20 V worsened the quality of the surface, as there were large areas of pitting and significant burning. AFM measurements confirmed these qualitative observations, as the 20 V sample had the largest surface roughness values. In the case of Nb, the 11 V sample only had limited spots of polishing, with the rest of the foil covered by large pitted regions; this poor quality was reflected by its roughness value in Table 2. As the voltages were increased, R_q began to decrease and a near mirror finish on the metal with angstrom-scale surface roughness was obtained at 25 V.

The poor finishes of Ti and Nb at 11 V are most likely a consequence of incomplete passivation of the metal surface. Since the voltage precedes the plateau region, especially in the case of Nb, the passivation layer has not fully formed. This would cause uneven etching and result in the rough surfaces that were obtained. Yet the continued improvement of Nb with increasing voltage contradicts the behavior observed for Ti, even though both metals exhibit similar polarization curves. Polishing at potentials above 15 V ruins the Ti surface finish, but continues to smooth the Nb surface. This result is somewhat surprising for Ti, as the higher voltages are still within its passive plateau region. One possibility for this difference is local surface heating. The higher voltage and resulting increase in current density cause the temperature of the

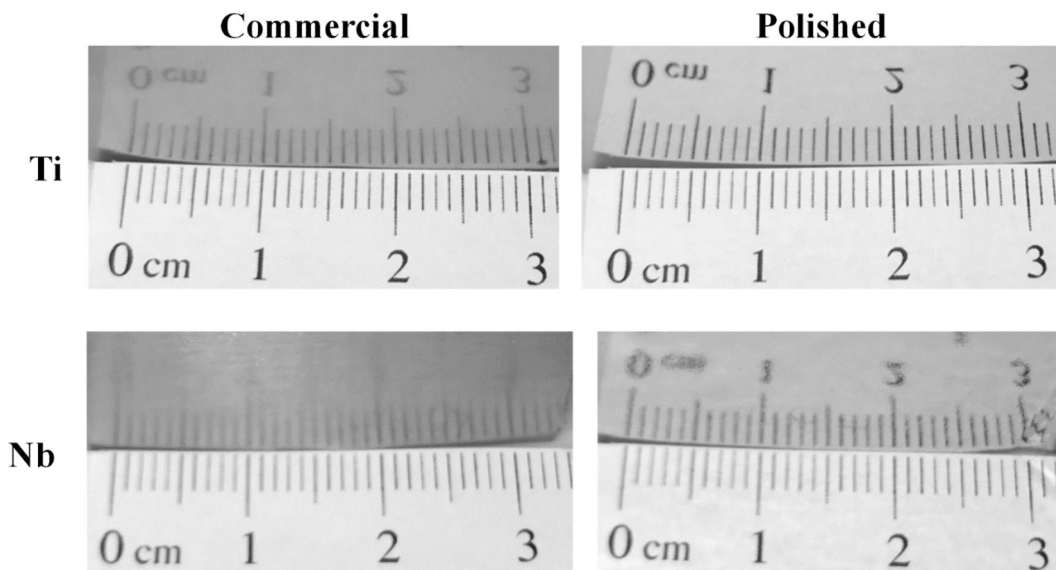


Fig. 3. Reflective properties of the commercial Ti and Nb in comparison to polished metal. Films were electropolished at 15 V with a -70°C 2 M H_2SO_4 -MeOH electrolyte for 2 h.

Table 2

R_a and R_q determined by AFM on Ti and Nb electropolished for 2 h in a $-70\text{ }^{\circ}\text{C}$ 2 M $\text{H}_2\text{SO}_4\text{-MeOH}$ electrolyte under various potentials.

	Ti, 11 V	Ti, 15 V	Ti, 20 V	Nb, 11 V	Nb, 15 V	Nb, 20 V	Nb, 25 V
R_a (nm)	2.51	1.27	4.10	9.70	1.57	1.05	0.36
R_q (nm)	3.98	1.64	5.75	12.17	2.19	1.58	0.49

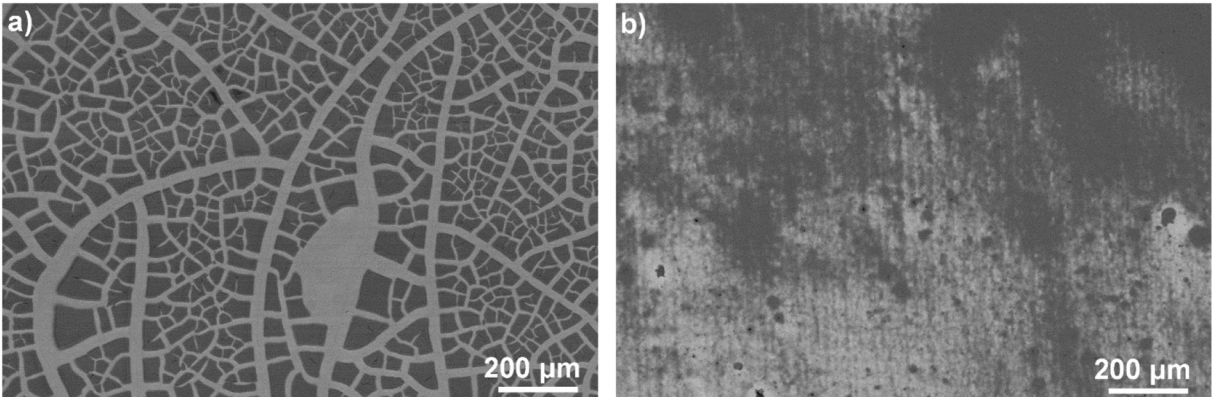


Fig. 4. SEM images of the salt film after drying on electropolished a) Nb and b) Ti.

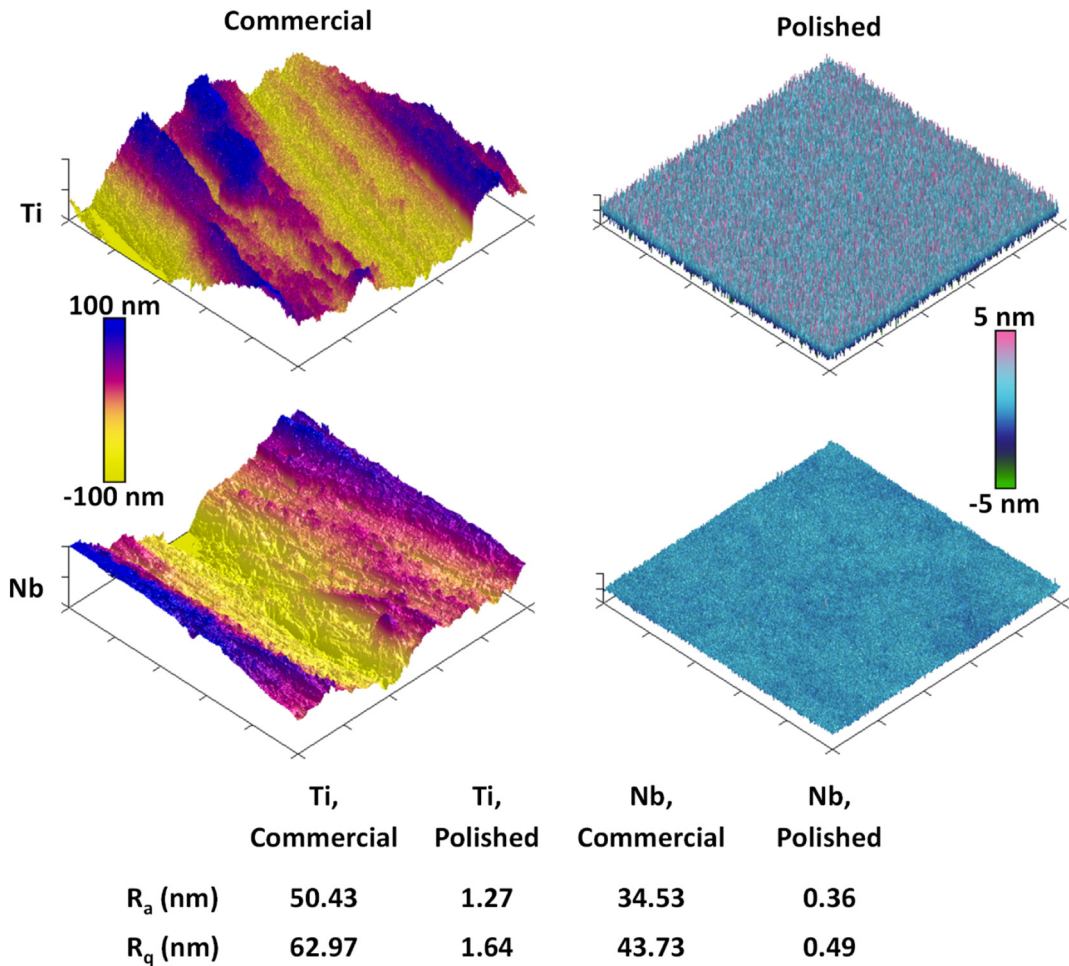


Fig. 5. AFM $5 \times 5\text{ }\mu\text{m}$ topographical images and surface roughness data of commercial and polished Ti and Nb.

foil to increase, leading to tarnishing and uneven etching [5,21]. Nb may be less susceptible to this heating due to the nature of the passive layer that forms on its surface; this layer was particularly noticeable after electropolishing (Fig. 4a). Upon removal of the Nb sample

from the electrolyte, a white film was present on the metal surface, which had not been seen in samples polished at higher temperatures. The sample was not sonicated and allowed to dry. The film was then characterized via SEM (Fig. 4a) and the resulting images show a

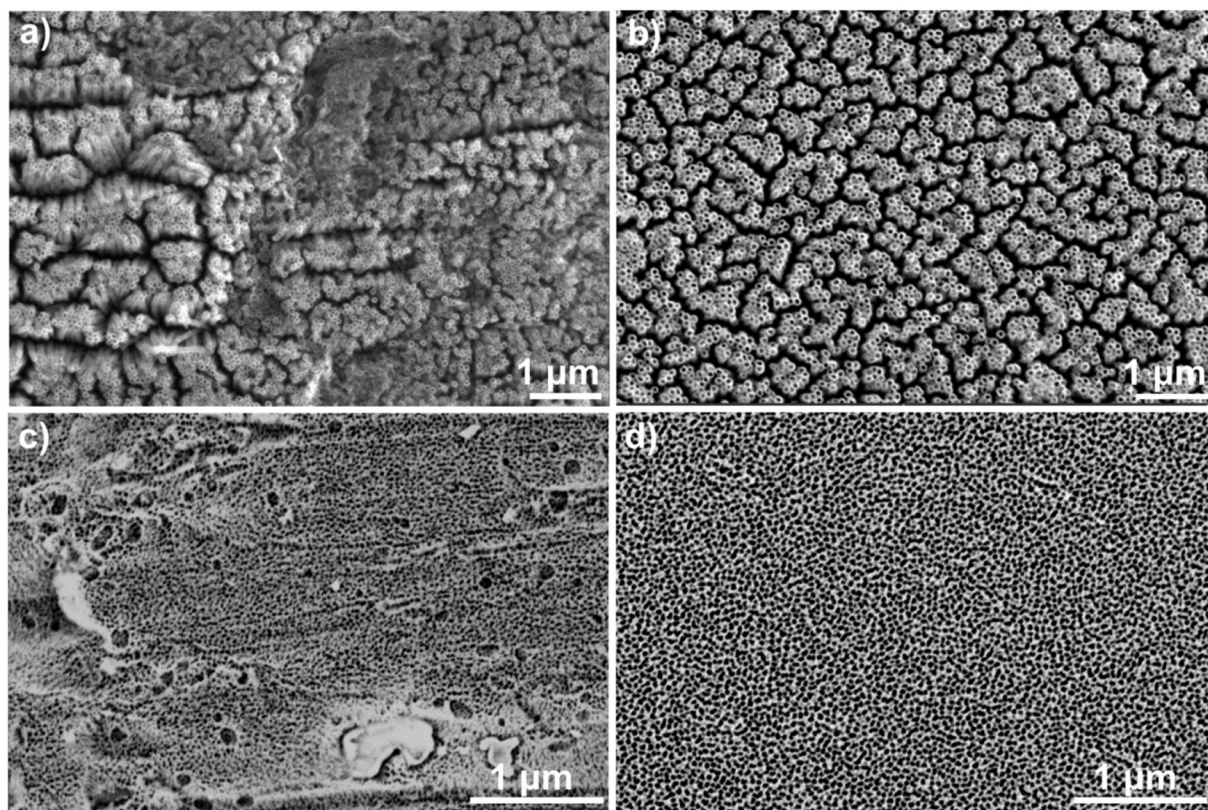


Fig. 6. SEM images of a) unpolished anodized Ti, b) polished anodized Ti, c) unpolished anodized Nb, d) polished anodized Nb.

cracked layer on top of the Nb metal with a thickness of over 5 μm . Subsequent energy dispersive spectroscopy (EDS) analysis indicated that the film contained niobium, oxygen, and sulfur (Fig. S1, Supporting Information). A salt film (Fig. S2, Supporting Information) was also present at the surface of Ti after electropolishing, although it was considerably thinner and much more difficult to observe; EDS showed the presence of titanium, oxygen, and sulfur in the film. The variation in salt film thickness helps explain the difference in surface finish between Ti and Nb at potentials above 15 V. Because the Nb salt film is so thick, it may remain robust enough at higher potentials where it can continue to act as a barrier against local surface heating. In the case of Ti, the salt film is already quite thin at 15 V and increasing the voltage only serves to reduce its thickness further and make it more unstable. This is further reinforced by Fig. 4b, as only sections of the metal contain a noticeable film residue. The resulting film is too thin to be a suitable barrier against local heating, thus causing tarnishing and poor finishes.

The effect of the salt film thickness on the surface roughness led to the final determination of the optimal polishing conditions. Both metals must be polished at -70°C in a 2 M H_2SO_4 -MeOH solution, with Ti and Nb requiring potentials of 15 and 25 V, respectively. The dramatic smoothing of the metal surfaces after polishing under ideal conditions can be seen in the AFM images (Fig. 5). EDS measurements were conducted at the electropolished Ti and Nb after salt removal and it was evident that both metals are free of impurities (Figs. S3–4, Supporting Information). The surface roughness of the polished metals improved by an order of magnitude compared to commercial pieces. The unpolished Ti and Nb pieces contained peaks and troughs that span over 200 nm in vertical distance, which were eliminated once the samples completed electropolishing. Smaller features that were present on the commercial material are also erased from the surface. This combined leveling led to much smaller values of R_q , which to the authors' knowledge are the best to date for the H_2SO_4 -MeOH electrolyte.

3.5. Application of polished foils for oxide growth

The smooth metal surfaces obtained via the optimal polishing conditions facilitated an investigation into the formation of well-ordered metal oxide nanostructures (Fig. 6). Nanoarchitected oxides have gained increasing attention in recent years due to the unique properties provided by the high surface area and nanoscale features. Transition metal oxides in conjunction with their nanoarchitecture have proven to be useful as intercalation electrodes for Li-ion batteries [22–29]. Consequently, facilitating well-ordered and uniform growth across an electrode is critical to the overall performance of the oxides. Anodically grown nanostructures of TiO_2 and Nb_2O_5 were prepared on commercial and polished metal substrates to elucidate whether the reduced surface roughness would affect the ordered oxide layer formation. The polished samples clearly enabled a dramatic improvement to the overall uniformity and ordering of nanostructures. For both metals, the unpolished surface created clumps of poorly organized and misshapen nanostructures (Fig. 6a, c). When polished Ti was anodized, well-ordered and distinct nanotubes formed; the tubes were more evenly distributed with small size variation (Fig. 6b). Polished Nb metal resulted in uniform and even nanopore distribution across the surface of the substrate (Fig. 6d). Both results indicate that the substrate surface roughness must be on the order of a few nanometers for well-ordered nanostructures to be grown via anodization.

4. Conclusion

A safe and effective way to electropolish Ti and Nb with a R_q below 2 nm has been developed from a H_2SO_4 -MeOH electrolyte. The optimally electropolished conditions for Ti and Nb were with an electrolyte of 2 M H_2SO_4 , constant voltages of 15 V and 25 V, respectively, and a temperature of -70°C for 2 h. This polishing technique is capable of creating mirror finishes on both metals with R_q values of 1.64 nm for Ti and 0.49 nm for Nb. Polarization experiments were performed to

determine the potentials at which passivation occurred. The current plateaus decreased in value and the voltage range expanded when the acid concentration was increased or the temperature was lowered. This behavior is explained by a polishing process that operates according to the salt film mechanism. Further evidence for this mechanism was discovered once the temperature of the electrolyte was dropped to -70°C . A visible salt film which developed at this temperature on the surface of the metal was found to contain oxygen and sulfur, along with the respective metal species. After polishing at optimal conditions, the metal had noticeable macro- and microscopic surface leveling. The smooth finishes were also beneficial to the production of well-ordered metal oxide nanostructures grown via anodization. These results suggest that the electropolishing procedure established herein may be effective for other valve metals, such as vanadium, zirconium, hafnium, and tantalum.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.surfcoat.2018.04.082>.

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