

Comparative Evaluation of Niobium Surface Preparation Methods for Electrodeposition

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ABSTRACT

To find a suitable treatment in the preparation of Nb surface for platinum electrodeposition, different methods such as thermal oxidation, anodic oxidation, mechanical roughening, and mechanical roughening with subsequent anodic etching were examined. X-ray photoelectron spectroscopy was used to study the chemical composition of depth analysis of the surface. Moreover, in order to examine the morphology and surface roughness, the samples were analyzed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The results showed that the most appropriate method for niobium surface preparation is mechanical roughening by shot blasting or abrading with emery and then anodic etching at the current density of 200A/m² for 40 min. in a solution containing 95% methanol, 2.5% hydrofluoric acid, and 2.5% hydrochloric acid at the temperature of 35°C.

Introduction

Niobium belongs to the group of refractory metals. Due to its suitable mechanical and electrical properties and especially its high anodic break down potential, Niobium can be an appropriate replacement for Titanium as the substrate in Platinum anodes. The electrical resistance of this metal is (15 $\mu\Omega$ /cm at 20°C), which is much less than titanium (48.2 $\mu\Omega$ /cm at 20°C) [1,2]. Lots of studies have been conducted on the first stage of oxidation of niobium by methods such as X-ray photoelectron spectroscopy [3,4], Ultraviolet photoemission [5], and Auger electron spectroscopy [6,7]. Niobium

resistance to oxidation is low. As a result, it forms a layer of Nb₂O₅ oxide even in low pressure oxygen environments. This oxide layer makes it hard to form a layer with high adhesion because of its high dielectric constant and different structure. Another problem associated with this oxide is the adsorption of hydrogen on it and its emission, which forms a brittle hydride layer on the surface. It has been claimed in the literature that with controlled formation of NbO layer on the surface, one can avoid such a problem and fabricate an adhesive electroplated layer on the surface [8]. However, little is known about surface preparation steps for niobium in

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the literature. There is even no information on its pickling solution to remove the oxides. Nevertheless, some methods have been utilized for surface preparation of metals such as silver, copper, nickel, and chromium [9]. But as the authors' effort to take advantage of those methods for niobium was in vain, in this study, other methods such as thermal oxidation and anodic oxidation have been utilized to change the superficial oxide layer from Nb₂O₅ to NbO to increase the adhesion of the uppermost electroplated layer to the substrate. Also, electrochemical procedures as well as mechanical roughening have been used to increase the adhesion to the surface [8,10,11].

Experimental procedure

Sample preparation

In this study, samples with dimensions of 30×20×3.7 mm were prepared. Degreasing of these specimens was carried out in acetone using an ultrasonic cleaner at the frequency of 20 kHz. To find the best solution for deoxidizing, three different solutions, the compositions of which are shown in **Table 1**, were tested.

Thermal oxidizing treatment

Specimens were pickled in solution No. 1 in **Table 1** and dried. Then, they were oxidized in a furnace at four different temperatures of 300, 400, 500, and 600°C for 10 min. under the flow of Argon gas with flux rate of 1.5 l/min. Gasflow in the furnace was intended to reduce the partial pressure of oxygen in order for NbO to form more easily. **Table 2** shows the preparation and oxidation conditions for the samples. After this step, X-ray photo-electron spectroscopy tests (ThermoFisher, E. Grinstead, UK) were used to find the composition of the samples on the surface and

in depth. The samples were investigated in standard mode and the source of X-ray was monochromatic K α beam of Aluminum. The software controller and analyzer of the device was Advantage.

Anodic oxidation treatment

Anodic oxidation was performed in two oxidizing solutions of sodium hydroxide (10 wt.%) and orthophosphoric acid. The solutions were at ambient temperature and oxidation treatment was done in the range of 2-20 V. For this treatment, samples with dimensions of 50×15×3.7 mm were used and a Platinum plate was picked as the cathode.

Mechanical and electrochemical roughening

Peening and grinding were used for mechanical roughening. Grinding was performed with No. 120 grinding paper. For electrochemical etching, a solution composed of Methanol (oxidizing agent), Hydrofluoric acid (attacking agent) and Hydrochloric acid (conducting agent) at different concentrations was used. To find the best temperature, the etching process was conducted at temperatures of 25, 35, 45, 55, and 65°C. Current densities of 200 and 2000 A/m² were applied to etch the specimens electrochemically.

Microscopic observations

To evaluate the morphology and surface roughening, scanning electron microscope (SEM- Philips XL-30) and atomic force microscope (AFM- DME DS95-200E) were used. Dual Scope/ Raster Scope Ver.2.1.1.2 DME was used as the image processing software.

Table 1. Composition of different deoxidizer solutions and immersion time of niobium in them.

Immersion time (min)	Solution composition	Number
20	85% Sulfuric acid+10% Hydrofluoric acid+ 5% Distilled water	1
1	50% Sulfuric acid+25% Hydrofluoric acid+25% Nitric Acid	2
2	26% Hydrofluoric acid+36% Nitric acid+38% Distilled water	3

Table 2. Samples preparation and oxidation conditions.

Temperature (°C)	Primary preparation	Sample
300	Shotpeening + Ultrasonic degreasing + etching in 85% Sulfuric acid +10% Hydrofluoric acid (60%) + 5% distilled water for 20min. + washing in distilled water + Drying by hot air blast	A
400		B
500		C
600		D

Table 3. Chemical composition of solutions used for electrochemical etching of samples.

Solution composition	Number
80% Methanol+10% Hydrofluoric acid(48%)+ 10% Hydrochloric acid(46%)	1
90% Methanol+5% Hydrofluoric acid(48%)+5% Hydrochloric acid(46%)	2
95% Methanol+2.5% Hydrofluoric acid(48%)+2.5% Hydrochloric acid(46%)	3

Table 4. Oxidation states of niobium and their peak positions (eV is the unit of numbers) [12].

Oxidation state	Boundary energy(eV)3d ³	Boundary energy(eV)3d ⁵
Nb ⁺⁵	210	207.3
Nb ⁺⁴	208.8	206
Nb ⁺²	206.8	204
Nb ⁰	205	202.2

Results and Discussion

Acid pickling process

The most appropriate solution for the acid pickling from the three solutions showed in **Table 1** was the solution No. 3. The first solution did not have any visible influence on the Nb surface even after 20 min. of immersion. Acid pickling in this solution takes a long time due to the low corrosion rate of Nb and the oxides cannot be removed completely. However, the second solution attacks to Nb surface very fast and forms a very rough surface after 1min. On the contrary, the third solution had a moderate effect on the surface of Nb and the surface was uniformly roughened and became bright after acid pickling in this solution. Finally, the solution with 26% HCl, 36% HNO₃ and 38% H₂O was preferred to the other solutions for acid pickling of Nb.

Thermal oxidation process

Oxidation states and peak positions of Nb that were obtained by X-ray photoelectron spectroscopy (XPS) are shown in **Table 4**. The relative peak positions can be seen in **Fig.1**. Pure Nb XPS spectra for single crystal and polished states are depicted in **Fig. 2** for

comparison [13]. It can be seen that the major compound of the surface at both states is Nb₂O₅.

XPS spectra of sample A and Oxygen are shown in the **Fig. 3**. Considering Oxygen peaks and the conformity of the positions of these peaks with Nb⁺⁵, it can be claimed that Nb₂O₅ is present on the surface. XPS analysis of the samples B, C and D also showed similar results for the presence of Nb₂O₅ on the samples surface.

Since there is no evidence for the presence of Nb or its other oxides and when the penetration depth of XPS spectrum (~100 nm) is considered, it can be said that the thickness of Nb₂O₅ is more than 100 nm. Therefore, sputtering and subsequent composition analysis at different intervals were conducted

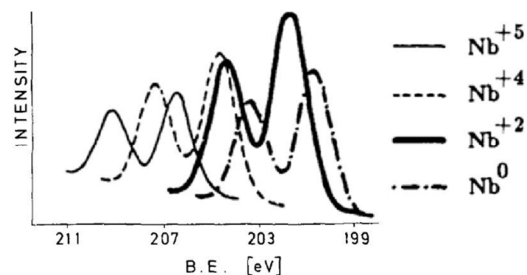


Fig. 1. The relative positions of 3d³ and 3d⁵ cation states of Nb in spectra obtained in the XPS method [12].

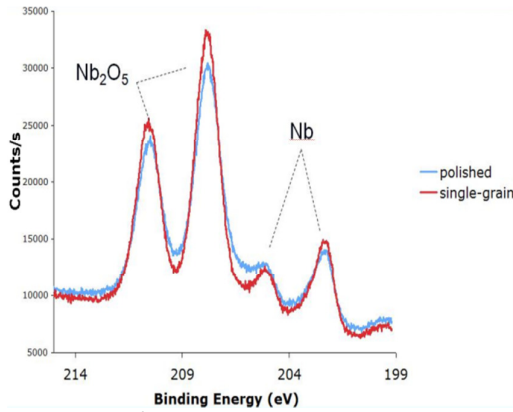


Fig. 2. XPS of pure niobium [13].

to estimate the depth of oxide layers and determine their type.

Fig. 4 shows XPS spectra of the sample A at the sputtering time interval of 20s. It can be observed that after sputtering of 20s, some contents of Nb₂O₅ are removed, while sputtering time of 40s can totally remove the oxide layer and only pure Nb can be detected. Longer times of the sputtering have no special effect on the spectra. It seems that NbO oxide layer does not exist in this sample, or it might have been removed completely between 20 and 40s of the sputtering due to its low thickness.

However, some contents of NbO were present

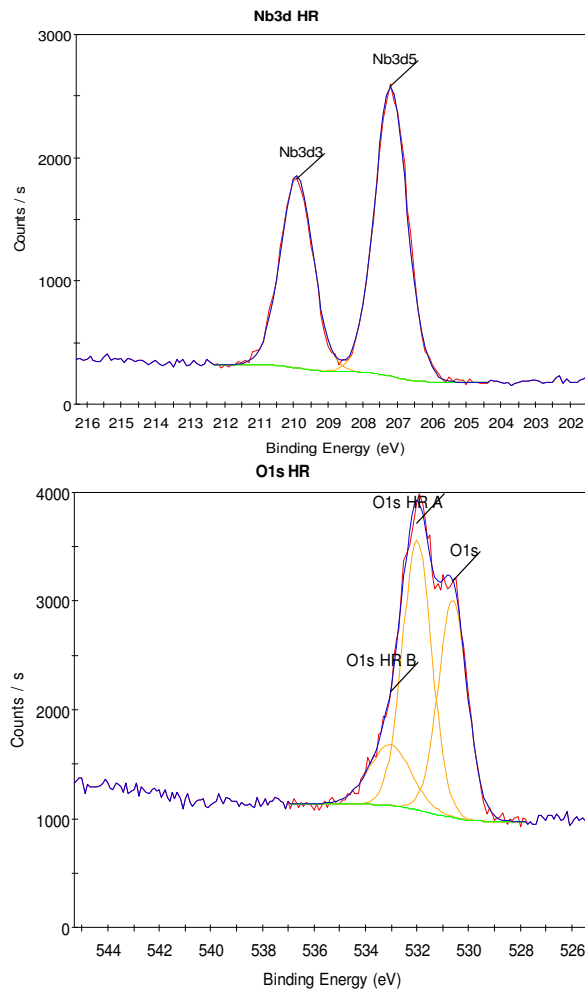


Fig. 3. Niobium and oxygen peaks in XPS of surface of sample A.

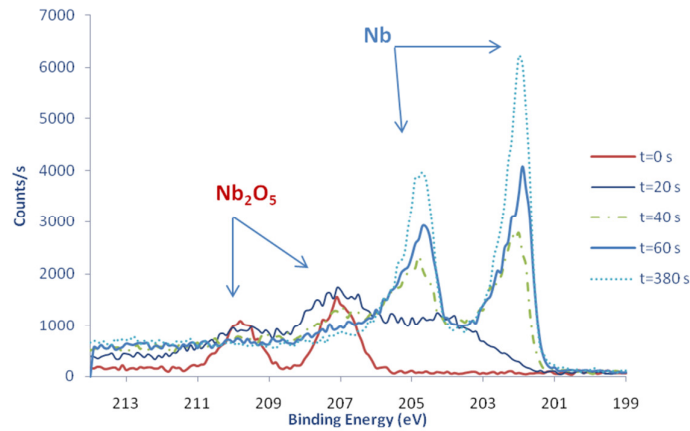


Fig. 4. XPS spectra of the sample A in depth of the sample from the surface and 380s sputtering (a spectrum is taken per 20s, in the interval between 60 to 380s, there is no change in peaks and so, they are not presented).

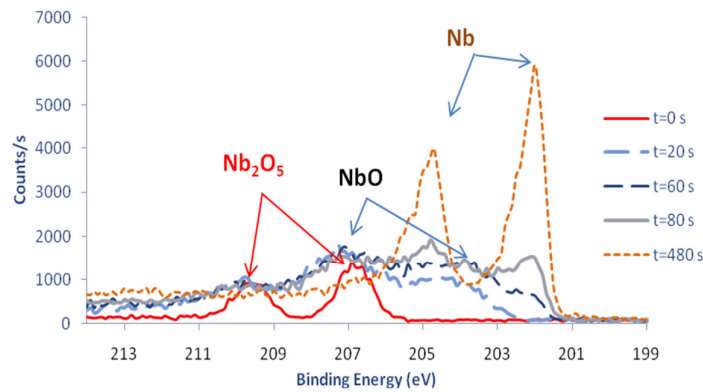


Fig. 5. XPS spectra of the sample B in depth of the sample from the surface and 480s sputtering (a spectrum is taken per 20s).

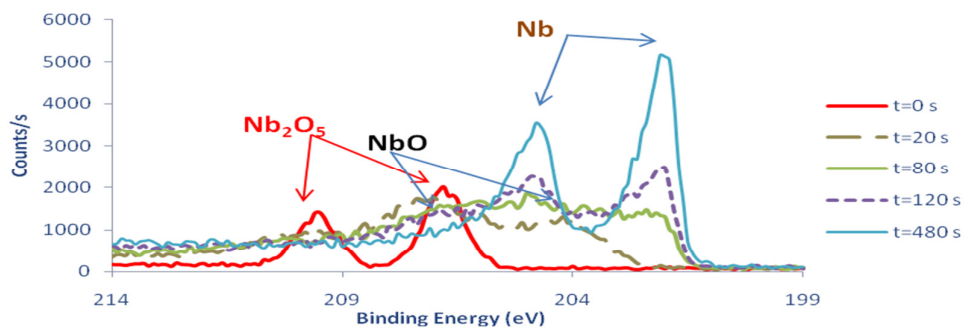


Fig. 6. XPS spectra of the sample C in depth of the sample from the surface and 480s sputtering (a spectrum is taken per 20s).

in the sample B that can be seen in **Fig. 5**. Obviously, NbO is present after 20, 40 and 60s of the sputtering; while by increasing the time to 80s, no NbO or other oxides can be found on the surface and the majority of the composition contains pure Nb.

Similarly, the thickness of NbO has been increased in the sample C. As can be seen in XPS spectra of this sample (**Fig. 6**), the spectra of 20, 40, 60, 80 and 100s contain NbO, but only Nb is detected after 120s of the sputtering.

Nevertheless, XPS spectra of sample D are completely different (Fig. 7). It can be obviously seen that the NbO thickness is much higher than three other specimens

because there is almost no trace of pure Nb even after the sputtering time of 480s. Considering XPS results of all samples, it can be concluded that Nb₂O₅ oxide layer with the thickness of about 100nm is always present

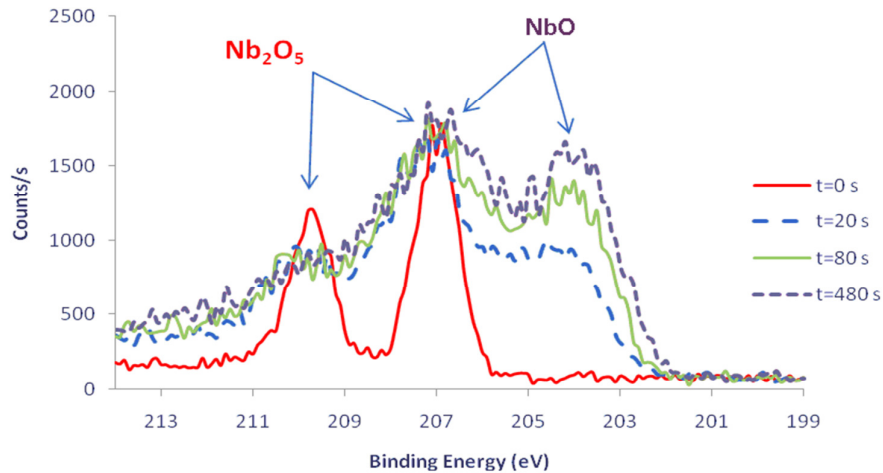


Fig. 7. XPS spectra of the sample D in depth of the sample from the surface and 480s sputtering (a spectrum is taken per 20s).

on the Nb surface. In fact, the existence of this oxide layer hinders the electrodeposition of any deposit on Nb surface. It should be mentioned that removing of this layer needs controlled conditions with high vacuums. Even at these conditions, NbO can be converted to Nb₂O₅ in the presence of sufficient amounts of oxygen. Thus, even the electrodeposition in vacuum may not be effective due to the presence of oxygen in the electrolyte (H₂O) and the possibility of the Nb₂O₅ formation on the surface.

Anodic oxidation

Oxidation in NaOH 10%

Using the third solution of the Table 1, surface oxides of the specimens were removed before anodic oxidation. The process of oxidation in this solution within the voltage range of 2-5 V for 40min resulted in a thin and non-uniform oxide layer. Changes in the solution temperature did not cause any considerable effects.

Oxidation in orthophosphoric acid

Similar to the previous anodic oxidation, the samples were first put in solution No. 3. Then, the specimens were oxidized in the orthophosphoric acid with the concentrations of 50% and 100% and voltages of 5, 10 and 20V for different times. The oxidation process in this solution at the voltage of 5V and the times even lower than 1min resulted in the formation of a relatively dense and uniform purple oxide layer. Varying the parameters only changed the color of the oxide layer from gold to pink due to the increase in the layer thickness. When the oxide thickness is increased, the coating formation is restrained due to the increase in Nb surface electrical resistance.

Roughening

Since anodic and thermal oxidations did not result in acceptable outcomes, mechanical and electrochemical roughening was investigated for the formation of a mechanical bonding between the coating and the substrate. Shot

blasting was successful to produce a rough surface in macro scale, but the bonding of the coating to this surface was not satisfactory. Therefore, abrading the specimens with emery was put into use to create micro roughness on the surface. Moreover, electrochemical etching was used to find a better solution for making the surface rough. For this purpose, the sample was put as anode and Pt was taken as anode. In the electrolyte, methanol was the oxidizer, HF was the attacking species, and HCl was the electrical conductive species. Anodic etching on the acid pickled sampled caused a non-uniform roughness. Thus, ground specimens were used for obtaining uniform rough surfaces. In fact, the sites attacked by F^- can be developed equally and uniformly on the surface by abrading. Increasing the current density from 200 to 2000 A/m^2 caused excessive roughness and non-uniformity on the surface. On the other hand, a suitable rough surface could not be obtained at the temperature below 25 °C and the current density was below 100 A/m^2 due to low reactions rate on the surface. As a result, the third solution of the **Table 3** at the temperature of 35 °C with the current density of 200 A/m^2 was used for determining the

appropriate time. **Fig.8** shows SEM micrograph of the etched sample in the solution No. 3 for 40min at the current density of 200 A/m^2 and temperature of 35 °C. It can be seen that the abrading and subsequent electrochemical etching resulted in the formation of micro lines and pores on the surface. These pores can act as grips to increase the binding of the coating to the surface. The grinding lines cause these micro pores to form uniformly on the entire surface. The acceptable binding of the coating to this surface emanated from the following two reasons:

- 1- This surface contains some jagged (or edged) sites that are suitable for crystallization of the deposit due to the local increase of the current density at these regions.
- 2- The rough sites on the surface are often preferred regions of the crystallization.

AFM was also used for more studies on the effect of electrochemical etching of the ground surface. **Fig.9a** shows the morphology of the surface that has been only ground. The morphology of this ground surface after anodic etching in the solution containing 95% methanol, 2.5% HF and 2.5% HCl for 40 min at the current density of 200 A/m^2 and the

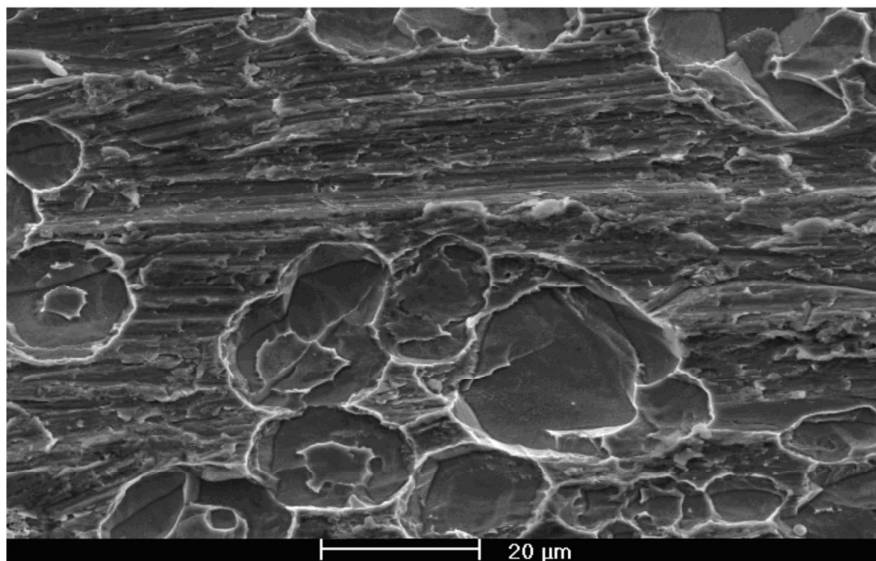


Fig. 8. Scanning electron microscope image of the niobium surface grinded and anodic etched in a solution containing 95% methanol, 2.5% hydrofluoric acid and 2.5% hydrochloric acid at 35°C temperature and 200 A/m^2 current density for 40 min.

Table 5. Roughness obtained from 10×10µm atomic force microscopy image.

Rq(nm)	Roughness calculated from image 10×10 µm ²		Sample
	Rz(µm)	Ra(nm)	
298	1.17	226	A
580	2.61	475	B

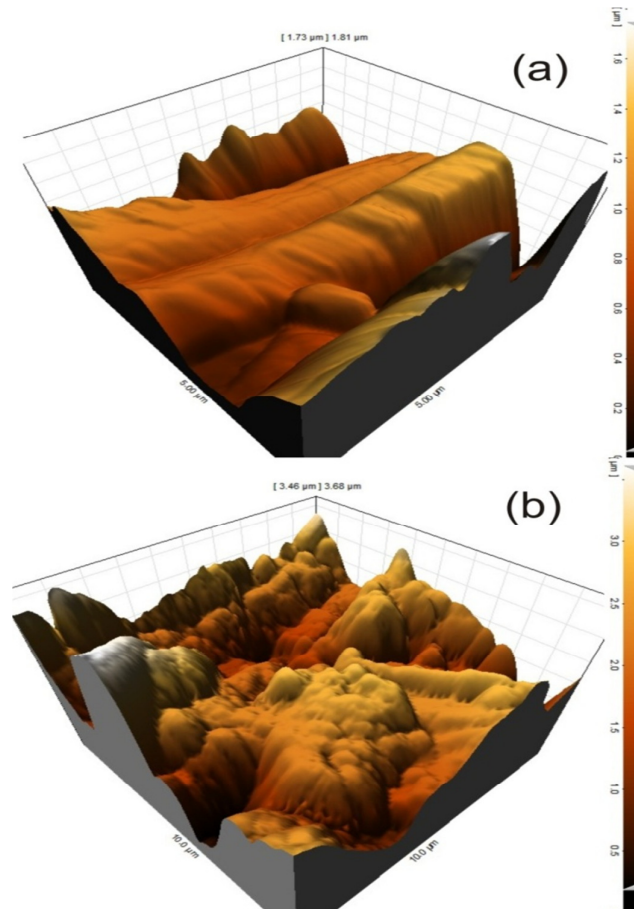


Fig. 9. Atomic force microscopy image: (a) grinded sample and (b) grinded and anodic etched sample in a solution containing 95% methanol, 2.5% hydrofluoric acid and 2.5% hydrochloric acid at 35°C temperature and 200 A/m² current density for 40 min.

temperature of 35 °C can be seen in **Fig.9b**. The developed roughness on this surface makes the coating form easily on the substrate. The obtained roughness parameters from the surface of 10×10µm on each specimen are shown in **Table5**. Apparently, the roughness of the electrochemically etched specimen is almost twice that of just ground sample. Nevertheless, it seems that the morphology of the surface has been influenced more than the roughness factor after anodic etching. Since the roughness factor for the

sand blasted specimen is more than this specimen (**Table 5**), and the coating was not formed on the sand blasted specimen, it can be concluded that the presence of appropriate roughness and morphology simultaneously causes the coating to form on the substrate.

Conclusions

The XPS results of the oxidized samples at different temperatures in the inert gas environment showed that the formation of

NbO layer was not possible with conventional methods. Therefore, mechanical and electrochemical roughening was recognized as the only practical and economical procedure for coating formation on Nb surface.

A solution containing methanol, HF and HCl was used for electrochemical etching. It was found that the content of the acids in the solution should be equal for the best results. Thus, the combination of the solution was optimized at 95% methanol, 2.5% HF and 2.5% HCl. Increasing acidic species caused the solution to be very corrosive and reducing their content to less than 1% considerably decreased corroding characteristics of the solution. In addition, it was found that the most appropriate temperature for the solution was 35 °C. Increasing the temperature more than 35 °C showed similar effects as the increasing in acidic species and less temperature (25 °C) decreased the power of the solution for suitable etching. The current density was another optimized parameter. The best result in the roughness was obtained at 200 A/m² of current density, while more currents corroded the surface selectively and the current densities less than 100 A/m² decreased the reactions rate. Finally, the most appropriate time for anodic etching was found to be 40 min.

It was also found that abrading or sand blasting of the samples before the electrochemical etching process is necessary for achieving a uniformly roughened surface. Neglecting these preliminary processes causes the non-uniformity of the roughness on different regions of the surface.

References

- [1] ASM Hand Book, Vol. 2, 1990.
- [2] L.L. Shreier, "Corrosion", Vol. 1, 3rd Edition, Planta Tree, 1994.
- [3] M. Grundner, J. Halbritter, "On the natural Nb₂O₅ growth on Nb at room temperature", *Surf. Sci.*, Vol. 136, 1984, pp.144–154.
- [4] Z.P. Hu, Y.P. Li, M.R. Ji, J.X. Wu, "The interaction of oxygen with niobium studied by XPS and UPS", *Solid State Communication*, Vol. 71, 1989, pp.849–852.
- [5] I. Lindau, W.E. Spicer, "Oxidation of Nb as studied by the UV-photoemission technique", *J. Appl. Phys.*, Vol. 45, 1974, pp. 3720–3725.
- [6] H.H. Farrell, H.S. Isaacs, M. Strongin, "The interaction of oxygen and nitrogen with the niobium (100) surface: II. Reaction kinetics", *Surf.Sci.*, Vol. 38, 1973, pp. 31–52.
- [7] R. Franchy, T. U. Bartke, P. Gassmann, "The interaction of oxygen with Nb(110) at 300, 80 and 20 K", *Surf. Sci.*, Vol. 366, 1996, pp. 60–70.
- [8] L.A. Mikhailova, E.V. Kasatkin, V.E. Kasatkin and S.G. Prutchenko, "Manufacturing corrosion-resistant electrode materials on the Basis of Ti, Ta, Nb, and W covered with thin electrodeposited platinum layers", *Russian J. Electrochemistry*, Vol. 36, No. 8, 2000, pp. 866-873.
- [9] H. Mix, U.S. Patent 4632734, 1986.
- [10] R.E. Buxbaum, P.C. Hsu, U.S. Patent 5149420, 1992.
- [11] J.W. Dini, "Electrodeposition", Reprint Edition, Noyes, 1993.
- [12] B.R. King, H.C. Patel, D.A. Gulino and B.J. Tatarchuk, "Kinetic measurements of oxygen dissolution into niobium substrates: In situ X-ray photoelectron spectroscopy studies", *Thin Solid Films*, Vol. 192, No. 2, 1990, pp. 351-369.
- [13] <http://www.fnal.gov>, Last check: 06/08/2011.

