

## A REVIEW OF METALLOGRAPHIC PREPARATION

### PROCEDURES FOR NIOBIUM AND NIOBIUM ALLOYS

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#### Introduction

Many investigations of niobium and niobium alloys have been conducted with the aim to control and improve the physical properties of the material and to achieve a better understanding of its physical metallurgy. Since metallographic studies are frequently a vital part of these investigations, techniques for the preparation of metallographic specimens must be available, and through the years the development of these techniques has been the subject of study of many metallographers.

A standard metallographic technique has not been universally accepted for niobium and niobium alloys, rather each metallographer appears to have developed a specific technique which "works" well for him. The combination of reported techniques appear to have sufficed for most of the routine and specialized metallographic studies that are made on niobium and niobium alloys, whether utilizing optical microscopy, scanning electron microscopy or transmission electron microscopy.

The purpose of the present paper is to review some of the various techniques that have been used for the metallographic preparation of niobium and to describe these techniques in a form convenient for workers in the field. It is recognized that the preparation of metallographic specimens is still very much in the realm of arts and crafts, and each metallographer often finds that his individual skills enable him to achieve the most satisfactory results with a particular technique, whereas another metallographer may achieve equally satisfactory results with a different technique. Therefore, no attempt will be made to recommend the use of specific techniques in this paper.

Techniques for preparing specimens of niobium and niobium alloys for examination by transmission electron microscopy are included with the techniques for optical metallography because many important contributions to understanding the physical metallurgy of niobium and niobium alloys have been made through the use of transmission electron microscopy. Furthermore, past work has shown that transmission electron microscopy in conjunction with optical and scanning electron microscopy is almost essential when accurate and complete interpretations of the structural features of niobium and niobium alloys are required.

Since most of the preparation techniques that have been developed for optical microscopy normally are amenable to examinations utilizing scanning microscopy (SEM), a separate discussion on SEM metallographic techniques is not included.

Since standard metallographic sectioning and mounting procedures are normally satisfactory for niobium and niobium alloys, and these are adequately described in several references and texts familiar to metallographers, sectioning and mounting procedures will not be described in this paper.

The paper is divided into the following topics:

- (1) Preparation of Specimens for Optical Metallography
  - a. Grinding
  - b. Polishing -- Mechanical, Vibratory, Electrolytic. Chemical
  - c. Macroetching
  - d. Microetching -- Chemical, Electrolytic, Cathodic Vacuum
  - e. Anodic Stain Etching
- (2) Preparation of Specimens for Transmission Electron Microscopy
  - a. Preparation of Specimens from Bulk Material
  - b. Final Thinning Methods -- Electrolytic, Jet Thinning, Ion Beam.

It is the author's belief that this paper represents the first attempt to document the various preparation techniques for metallographic evaluation of niobium and niobium alloys. As such, no doubt many techniques have been omitted that perhaps have certain advantages over those described. The author encourages metallographers to make known these techniques so they will be available for consideration to metallographers involved with niobium and niobium alloys.

### Preparation of Specimens for Optical Microscopy

#### Grinding

Grinding of niobium and niobium alloy specimens for metallographic examination can be done using almost any of the numerous conventional metallographic grinding methods. No special precautions are necessary.

One technique, however, has been described and recommended specifically for niobium (1). This technique involves two steps:

- (1) Coarse grinding on wet 180-grit SiC belts
- (2) Fine grinding on 240-, 400-, and 600-grit wet-or-dry SiC metallographic disks.

The coarse grinding step is to obtain a plane surface and to remove the effects of sectioning. Wet grinding keeps the specimen cool and flushes the belt of loose metal and abrasive particles. Fine grinding is necessary to eliminate any cold-working effects of the coarse grinding and to produce a smoother surface preparatory to polishing. The fine grinding disks are dressed with a stick wax to keep the embedding of abrasive particles in the ground surface to a minimum and for cooling and lubricating. Water also may

be used for cooling and lubricating purposes. The direction of grinding is changed 90 degrees between the use of each grit size to insure the complete elimination of the previous grinding scratches. It is usually best to repeat the grinding on the 600-grit disks two or three times before proceeding to polish.

### Polishing

Several different polishing procedures have been reported for the metallographic preparation of niobium and niobium alloys. These procedures are essentially based on four techniques: (1) conventional mechanical polishing, (2) vibratory polishing, (3) chemical polishing, and (4) electrolytic polishing. These techniques overlay somewhat, especially since conventional mechanical polishing usually is required before either chemical or electrolytic polishing. However, the four techniques are discussed individually below.

Conventional Mechanical Polishing. Polishing of niobium specimens requires great care and much longer times than would be expected from the hardness of the metal. One particular problem is that commercial grades of niobium frequently contain hard particles, e.g., carbides, which can cause excessive relief during polishing.

A number of mechanical polishing procedures have been reported for use with niobium and niobium alloys. One method (2) utilizes three steps. First, rough polishing is done on a dressed wax wheel using a 15- $\mu\text{m}$  levigated alumina as an abrasive. This is followed by intermediate polishing on a microcloth-covered wheel using a 1- $\mu\text{m}$  alumina abrasive. Final polishing is also done on a microcloth-covered wheel, but 0.3- $\mu\text{m}$  alumina is used as the abrasive.

Another method (3) that has been described as being successful involves two steps. Rough polishing is done on a high-speed (1750 rpm), four-inch polishing wheel covered with a low-nap cloth. The abrasive is a slurry made of 15g fine alumina, 35 cc H<sub>2</sub>O, and 5 cc 20 percent chromic acid. Medium to heavy pressure is exerted upon the specimen while, with an eyedropper, the cloth is charged periodically with the aluminachromic acid slurry. Polishing in this manner is continued until the grinding scratches and any embedded abrasive particles are removed. Alternate etching and polishing (etch-polishing) may be done at this time to aid in the removal of any disturbed layer at the surface of the specimen. The etchant recommended is 50 cc lactic acid, 30 cc HNO<sub>3</sub>, and 2 cc HF\* which is best applied by swabbing with a cotton ball.

Final polishing is accomplished using the same slurry as described above on a slow speed (250-500 rpm), 8-inch polishing wheel covered with a low-nap cloth. Medium pressure is used and the cloth is charged periodically using an eye-dropper with the alumina-water slurry. As the polishing progresses the pressure and wheel speed are continually reduced until near the end, a very light pressure and the slowest wheel speed are used.

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\* Hydrofluoric acid is frequently an ingredient of etchants or polishing solutions used for niobium and niobium alloys. It is very dangerous in that it can cause severe burns if it contacts skin. Therefore, extreme care must be used in using it.

A similar two-step polishing method has been described by Dillinger (4). Initial polishing is accomplished using a slurry of 0.5- $\mu\text{m}$  alpha alumina and water, to which 2 or 3 ml of 10 percent chromic acid is added. A fast wheel (1450 rpm) covered with a napless cloth, such as a "lintless cloth" or nylon, is used. In lieu of chromic acid, a few drops of 10 percent oxalic acid can be added to the polishing wheel. Dillinger reports satisfactory final polishing results can be obtained in several ways: (1) using 0.05 $\mu\text{m}$  gamma alumina on a napless cloth with a fast-speed wheel to which small additions of 10 percent oxalic acid have been made, or (2) using 0.05- $\mu\text{m}$  gamma alumina in water on a microcloth-covered fast wheel.

For niobium-titanium alloys, Dillinger reports that a slurry consisting of ferric oxide in 10 percent chromic acid seems to be preferable, both for intermediate and final polishing.

Finally, polishing techniques utilizing diamond abrasive have been described by Nelson (5) and Petzow (6). Nelson's technique consists of two steps. Intermediate polishing uses 6- $\mu\text{m}$  diamond abrasive on a duck cloth. Kerosene is used as a lubricant. Polishing is carried out only long enough to remove the scratches and damaged layers from the grinding step. Over-polishing on this step is reported to cause relief effects which will be made worse by the finishing step. Final polishing is done on microcloth using an alumina-chromic acid slurry. As polishing proceeds the slurry is flushed from the polishing wheel.

Nelson points out that when an acidified slurry on a bronze polishing wheel is used for polishing, copper from the wheel may be deposited onto the specimen. This can be prevented by using a stainless steel wheel or by protecting the surface of the wheel with a thin plastic film placed under the cloth.

Petzow's polishing technique involves the use of diamond paste on a polishing wheel with a hardwood cover. He reports that for most materials attack-polishing with 900 ml  $\text{H}_2\text{SO}_4$  and 10 ml HF (electrolytic) is of advantage.

Vibratory Polishing. Kallfass and Horz (7) investigated several polishing procedures for niobium specimens doped with nitrogen, oxygen, or carbon and concluded that vibratory polishing produced the best results. They used 10 to 20 hour polishing times with fine alumina abrasive on a microcloth. With very low contents of nitrogen, oxygen, or carbon even longer times were required.

Electrolytic Polishing. A number of electrolytic polishing methods have been described for niobium and niobium alloys. These methods can be carried out using a number of conventional electropolishing devices. One such device which is known to work particularly well is shown schematically in Fig. 1. In this device the electrolyte is pumped over the surface of the specimen which tends to produce uniform polishing.

Numerous electropolishing solutions have been reported for use on niobium and niobium alloys. Several of these are listed in Table I.

Chemical Polishing. Chemical polishing has been reported as a useful method for preparing metallographic specimens of niobium and niobium alloys. In using this method a finely ground or rough mechanically polished specimen is prepared and then simply immersed in the chosen chemical solution. This chemical solution attacks the surface, thereby removing the grinding and

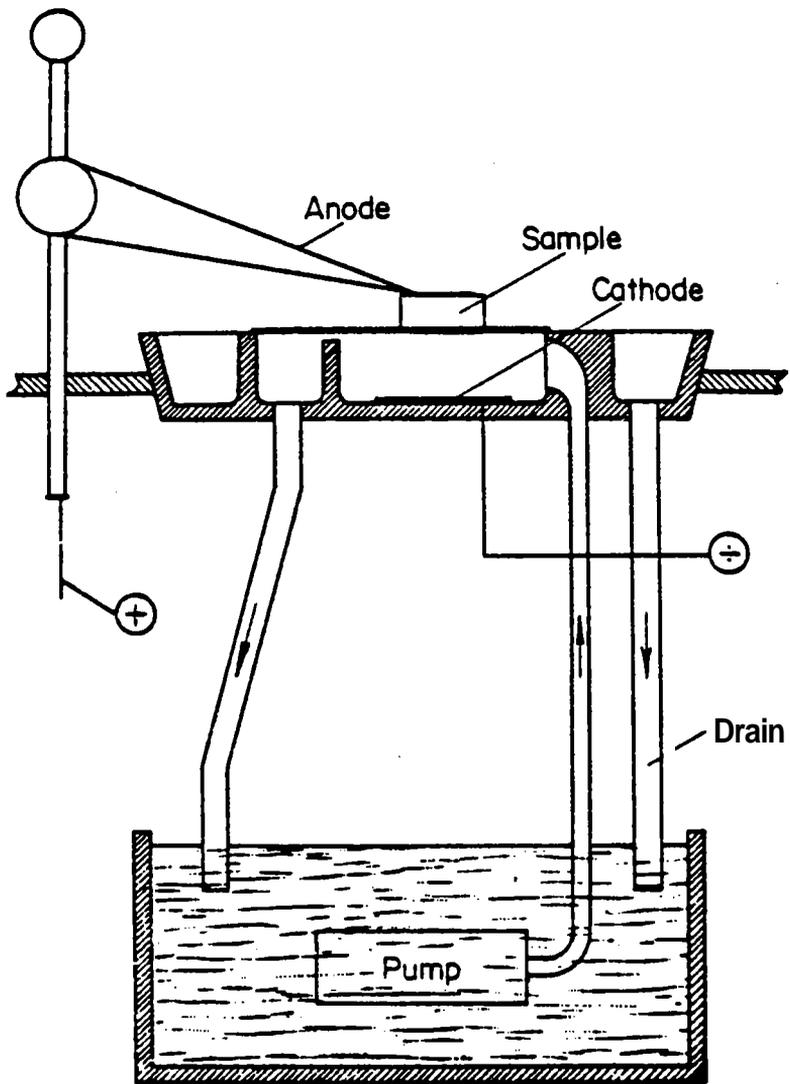


Figure 1. Schematic diagram of commercially available electropolishing device(s).

Table I. Electropolishing techniques for niobium and niobium alloys.

<u>Composition</u>	<u>Technique</u>	<u>Remarks</u>
1 ml Perchloric Acid 99 ml Methanol	-76 C. Cathode-Stainless Steel. Determine voltage/current density curve for each material. Allow specimen to cool in the electrolyte before polishing. Remove specimen from electrolyte with current on.	Use dry ice/acetone cooling bath. Rinse specimen in ethanol then air dry (9).
90 ml H <sub>2</sub> SO <sub>4</sub> 10 ml HF	100-200 Ma/cm <sup>2</sup> . 12-20V. 35-45 C. 5-10 minutes. Cathode-graphite or platinum.	Mix slowly in chemical hood (10).
5 ml H <sub>2</sub> SO <sub>4</sub> 1.25 ml HF 93 ml Methanol	4.5-5.4 A/cm <sup>2</sup> . Medium fast flow rate. <20 C.	50-60V, 10-20 sec (11).

polishing scratches and the disturbed surface layer. An alternative to immersion is to use a cotton swab to rub the solution on the surface. In general, it has been found that swabbing provides better results on niobium specimens because etching is avoided and more uniform polishing occurs.

One chemical polish that has been used successfully for niobium specimens has been described by Titterington and Simpson (12) and consists of:

200 ml H<sub>2</sub>SO<sub>4</sub>  
200 ml HNO<sub>3</sub>  
100 ml HF

They report the rate of attack can be regulated by the temperature of the solution, with a "warm" solution providing the best results.

Another chemical polish, reported by Buchheit, Brady, and Wheeler, (1) consists of:

50 cc lactic acid  
30 cc HNO<sub>3</sub>  
2 cc HF

This solution is applied by swabbing the surface of the specimen for one minute or more with a cotton ball soaked with the polishing solution. This solution also has been used effectively for etch-polishing, i.e. alternate chemical and mechanical polishing.

### Macroetching

Macroetching involves the development of the structure of a specimen for viewing with the unaided eye, or under lens magnification up to 35X (50X in Europe). A method reported (13) for doing this on niobium and niobium alloys involves grinding the specimen to 600 grit on silicon carbide abrasive papers followed by immersion in a solution consisting of:

30 ml HCl  
15 ml HNO<sub>3</sub>  
30 ml HF

Etching is reported to require several (10-20) minutes.

## Microetching

A number of satisfactory and reproducible etching procedures have been developed to reveal the microstructure of niobium and niobium alloys for microscopic examination. In general, these procedures fall into three categories; chemical etching, electrolytic etching, and cathodic vacuum etching.

Chemical Etching. Chemical etching of niobium and niobium alloy metallographic specimens can be performed either by immersion or by swabbing, however, best results are generally obtained by swabbing. Table II lists several chemical etchants which reportedly have yielded satisfactory results. In general the etchants consist of mixtures of various acids, most containing hydrofluoric acid. The many variations in etchants for niobium vividly demonstrates the difficulties that are encountered in establishing standard metallographic techniques for a given material. This indicates what could be a universal law for metallographers: "If it doesn't work, change something, and if it still doesn't work, change something else", on ad infinitum. (8)

Table II. Chemical Microetches for Niobium and Niobium Alloys

<u>Etchant</u>	<u>Remarks</u>	<u>Reference</u>
30cc lactic acid 10cc HNO <sub>3</sub> 10cc HF	Swab with cotton about five seconds and inspect for degree of etching. Repeat for intervals of five seconds each if heavier etching is desired. The pressure of swabbing affects the degree of etching. The HF is the attacking ingredient and may be varied accordingly to give more or less etching. Rinse in water, then alcohol, and dry in air.	(1)
6g FeCl <sub>3</sub> 30 ml HCl 120 ml H <sub>2</sub> O 16 ml HF	Use at 20 C. Etching time about two minutes	(14)
30 ml H <sub>2</sub> O 30 ml HNO <sub>3</sub> 30 ml HCl 15 ml HF	Use at 20 C	(15)
50 ml lactic acid 30 ml HNO <sub>3</sub> 20 ml HF	Etch by swabbing	(4)
20 ml HNO <sub>3</sub> 60 ml HF	Etch approximately 10 seconds	(6)
50 ml H <sub>2</sub> O 50 ml HNO <sub>3</sub> 50 ml HF	Requires seconds to minutes	(6)

Table II. Chemical Microetches for Niobium and Niobium Alloys ... Continued

<u>Etchant</u>	<u>Remarks</u>	<u>Reference</u>
10 ml HF 10 ml HNO <sub>3</sub>		
30 ml lactic acid	15-20 seconds. Etchant must be made fresh each time	(6), (16)
10 ml glycerol	Requires up to five minutes	(6)
10 ml HF 10 ml HNO <sub>3</sub>		
50 ml H <sub>2</sub> O	Requires seconds to minutes	(6)
20 ml HF 10 ml HNO <sub>3</sub>		
15 ml H <sub>2</sub> SO <sub>4</sub>		
90 ml HF 5 ml H <sub>2</sub> O 5 ml HNO <sub>3</sub>	Reveals general microstructure	(17)
30 ml HF 15 ml HNO <sub>3</sub> 30 ml HCl	Swab 3-10 seconds or immerse two minutes	(18)
10 ml HF 10 ml HNO <sub>3</sub> 20 ml glycerin	Swab 5-15 seconds	(18)
5 ml HF 20 ml HNO <sub>3</sub> 50 ml acetic acid	Swab 10-30 seconds	(18)
50 ml HNO <sub>3</sub> 30g ammonium bifluoride 20 ml H <sub>2</sub> O	Swab 3-10 seconds	(18)
HF Ammonium fluoride	Various mixed solutions can be used for etching	(19)
30 ml H <sub>2</sub> SO <sub>4</sub>	--	
30 ml HF 3-5 drops H <sub>2</sub> O <sub>2</sub> (30%) 30 ml H <sub>2</sub> O		(2)
36 ml HNO <sub>3</sub> 10 ml C <sub>2</sub> H <sub>8</sub> O <sub>3</sub> 4 ml HF	For Nb-N, Nb-O, Nb-C alloys. Etching times of 0.5 to 3 minutes. Following etching, specimen must be neutralized in 25 percent NaOH solution and washed with hot water	(7)

Electrolytic Etching. Electrolytic etching also has been used successfully for niobium and niobium alloys and two such etchants are listed in Table III. These etchants can be applied using a simple electrolytic cell that can be constructed easily using a variable d.c. power source or batteries, or using any one of a number of commercial electrolytic etching devices.

Schluter, Honecker, and Elssner (21) have applied the technique of potentiostatic etching to reveal certain microstructural features of niobium and niobium alloys. This is an advanced form of etching which is reported to produce the ultimate etching contrast through highly controlled conditions. The potential of the specimen, which usually changes with changes in electrolyte concentration, is maintained at a fixed level through the use of a potentiostat and suitable reference standards. In this way, pronounced contrast usually can be obtained.

The authors also investigated the effect of electrolyte flow rate on the etching behavior of niobium and showed that the current density voltage curve exhibits a good plateau region at low flow rates (5 cm/sec), whereas at higher flow rates (30 cm/sec) the curve almost follows Ohm's law.

Table III. Electrolytic Microetches for Niobium and Niobium Alloys

<u>Etchant</u>	<u>Remarks</u>	<u>Reference</u>
90 ml H <sub>2</sub> SO <sub>4</sub>	60 Ma/cm <sup>2</sup> ■ Time about 1-2 minutes. Use a carbon or platinum cathode. Use at room temperature. <b>Mix</b> acids slowly in a chemical hood.	(20)
65 ml H <sub>2</sub> O 17 ml HNO <sub>3</sub> 17 ml HF <sup>3</sup>	12-30 V dc. Use a platinum cathode	(6)
5g Mg(ClO <sub>4</sub> ) <sub>2</sub> 1000cc Methanol	Electrolyte flow of 5cm/sec	(21)

Cathodic Vacuum Etching. Armstrong, et al, (22) have described a cathodic vacuum etching method which has been used successfully for niobium and niobium alloys. Although not widely used, cathodic vacuum etching, also referred to as ion etching, can be an effective method for delineating the structure of specimens. Etching takes place by the selective removal of atoms from the surface of the specimen by positive ion bombardment in a glow discharge environment. The atoms are removed at various rates, depending on the microstructural details such as crystal orientation of the individual grains, grain boundaries, etc. The glow discharge is initiated by applying a high DC. voltage between the water-cooled specimen support and the anode in a partial vacuum, as shown in Fig. 2.

To etch a specimen by this method it must be broken out of its mount and placed on the specimen support. The system is evacuated to about 10<sub>u</sub>m pressure, followed by the introduction of an inert gas, argon, by means of a controlled leak. The high voltage is applied to the electrodes and, after a short induction period, etching commences.

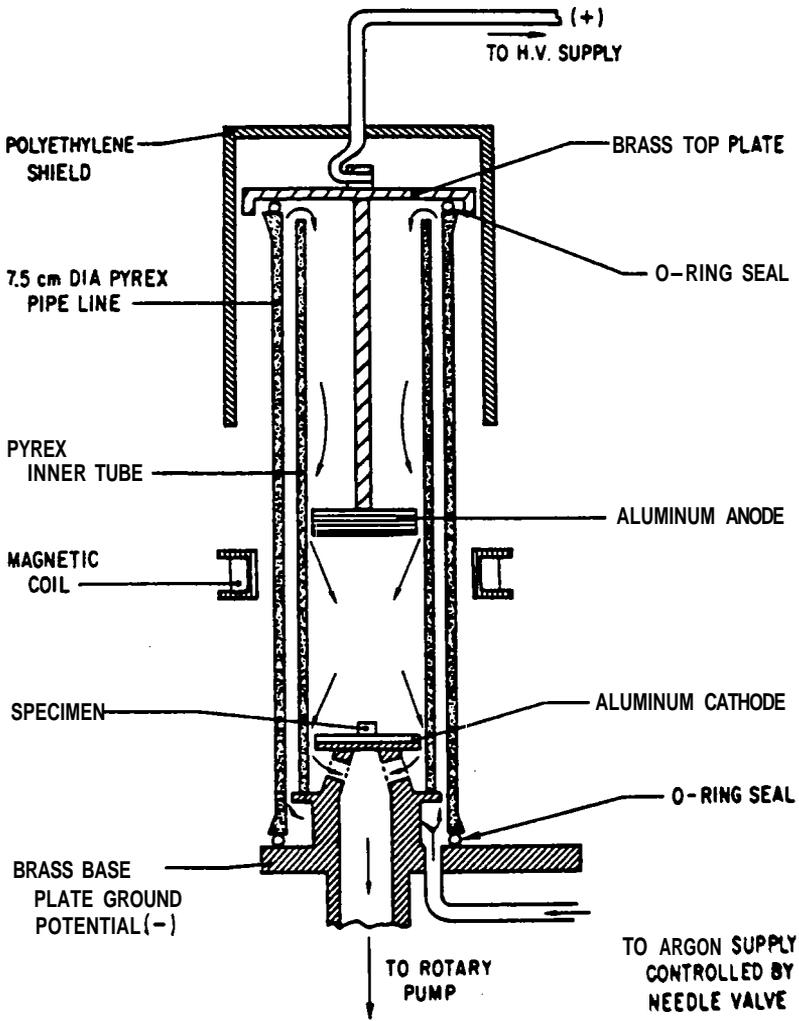


Figure 2. Schematic of a cathodic vacuum etching device.

For etching niobium, the following conditions have been found to be successful (22).

Ionizing gas:	argon
Pressure:	30 $\mu$ m
Voltage:	4.5 kV
Current:	0.5-0.8 Ma/cm <sup>2</sup>
Induction time:	3 minutes
Etching time:	10 minutes
Magnetic field:	100 oersteds

Anodic Stain Etching. An anodic stain etching method has been described by Crouse (24) for the identification of various carbide, nitride, and oxide phases in niobium and niobium alloys. The method is based on the principle that an anodic oxide film formed on niobium produces interference colors. The colors produced are characteristic of the anodic oxide thicknesses which, in turn, depend upon the compositions of the underlying phases.

The anodic films are produced on a polished metallographic specimen in an electrolytic cell using a set-up of the type shown in Fig. 3. To produce anodic films on niobium and niobium alloys, Crouse used a complex electrolyte consisting mainly of organic acids in alcohol. The specific composition of the electrolyte was:

5 g oxalic acid
5 g citric acid
5 ml orthophosphoric acid
35 ml distilled water
60 ml ethyl alcohol

This electrolyte produced satisfactory results at room temperature with a stainless steel cathode and an open circuit potential of 19V.

Results of anodic stain etching are shown in Figs. 4, 5, and 6 for niobium carbides, niobium nitrides, and niobium oxides, respectively.

According to Crouse, the identifying colors for various phases in niobium after anodizing are as listed in Table IV.

Table IV. Colors of Various Nb-N, Nb-C and Nb-O Phases  
When Anodic Stain Etched (24)

Nb	Pale Aqua Blue
Nb <sub>2</sub> N	Cherry Rose
NbN	Butter Yellow
Nb <sub>2</sub> C	Peach
NbC	Light Maize
NbO	Light Turquoise Green
NbO <sub>2</sub>	Light Beige
Nb <sub>2</sub> O <sub>5</sub>	Light Tan

Dillinger (4) has reported that somewhat similar results can be achieved by electrolytic etching of niobium-carbon alloys in a solution of 10 percent oxalic acid. Etching is carried out for ten to twenty seconds using 10 volts. He reports that Nb<sub>2</sub>C is stained canary yellow and the niobium matrix a blue.

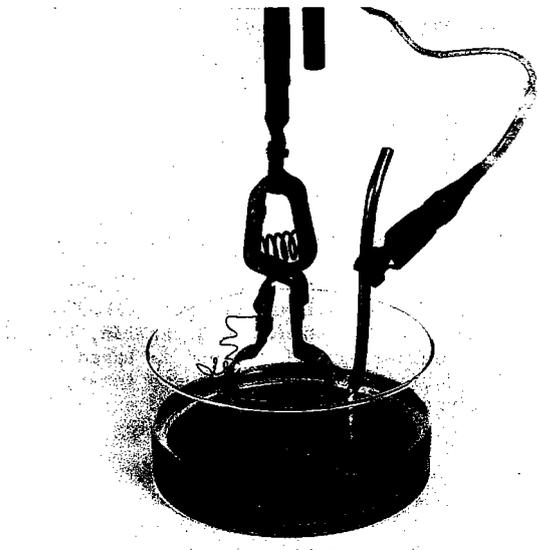


Figure 3. A typical electrolytic polishing and etching setup used for anodic stain etching of niobium specimens. Electrical contact is made through the back of the specimen (24).

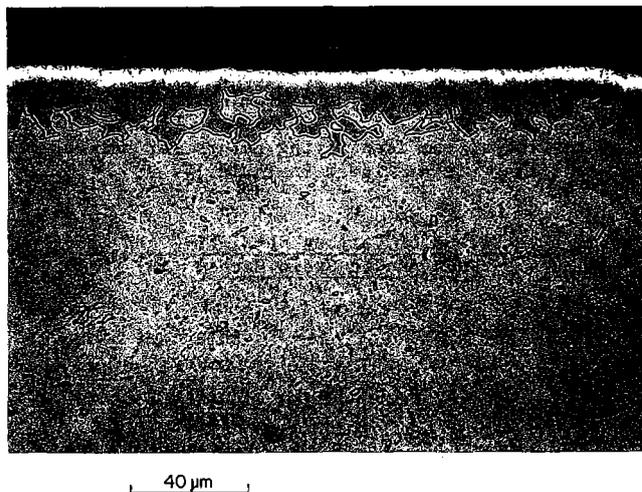


Figure 4. Anodic stain etched Nb-1% Zr specimen held in hydrogen plus benzene at 1200 C for 65 hours. The  $\text{Nb}_2\text{C}$  precipitate and massive phase is stained peach. The NbC surface layer is light maize. The base metal is pale aqua blue (24).

... niobium specimen oxidized in air  
and 850 C. Three oxides are present:  
pale green, NbO<sub>2</sub> is light beige, and  
The base metal, niobium, is pale



... niobium specimen exposed to  
for 1365 hours. The Nb<sub>2</sub>N pre-  
layer is stained cherry rose.  
er is butter yellow. The  
is pale aqua blue (24).



Preparation of Niobium Specimens for  
Transmission Electron Microscopy

The preparation of samples for transmission electron microscopy (TEM) usually involves two major steps; preparation of specimens from bulk material and final thinning. Methods that have been used successfully for accomplishing these steps for niobium and niobium alloys are described below.

Preparation of Specimens from Bulk Material

Niobium, particularly in its pure state, is soft and ductile and therefore small specimens can experience a large amount of cold work (microstructural damage) if not handled properly. This is particularly important in the initial preparation of niobium specimens for T.E.M. from bulk material.

Usually samples for T.E.M. are obtained from either thin sheet material or from bulk material, e.g., rods or tensile specimens. Perhaps the simplest and quickest method for obtaining a small specimen from either form is by mechanical sectioning using a saw or cut-off wheel. However, since the depth of surface damage that can occur in a niobium specimen by such a method can be quite severe (easily extending greater than  $200\text{-}\mu\text{m}$  below the surface) it is important to avoid cutting too thin a specimen. Since all the damaged surface layer must be removed in subsequent preparation steps, "gentle" sectioning techniques must be employed. For instance, it has been shown that sectioning using a jeweler's saw produces about five times less damage than that resulting from a conventional cut-off wheel (25). Even less damage has been shown to occur using a "string saw", utilizing an acid with or without an abrasive. One such saw is shown in Fig. 7. Several variations of this type of saw have been described (26-31).

For niobium and niobium alloys the following solutions have been used with a string saw:

<u>Solution</u>	<u>Comments</u>
30% HF, 70% HNO <sub>3</sub>	-
34% H <sub>3</sub> PO <sub>4</sub> , 33 HF, 33 HNO <sub>3</sub>	Additional H <sub>3</sub> PO <sub>4</sub> can be added to slow down the cutting rate

To either of these solutions can be added an abrasive, such as alumina, to speed up the sectioning process.

Once a conveniently-sized specimen has been produced it is usually necessary to remove the surface damage. This can be accomplished rather rapidly on niobium and niobium alloys using either an electro-polishing method or a chemical polishing method. Although both can effectively produce a strain-free surface, chemical polishing is usually used since it is more rapid. This can be done by simple immersion or by swabbing. Another method, called chemical planning or chemical jet machining (Fig. 8), has been found to be particularly effective because flat, parallel surfaces, which are desirable for final thinning, can be produced.

Chemical polishing solutions that have been used for niobium are listed in Table V.

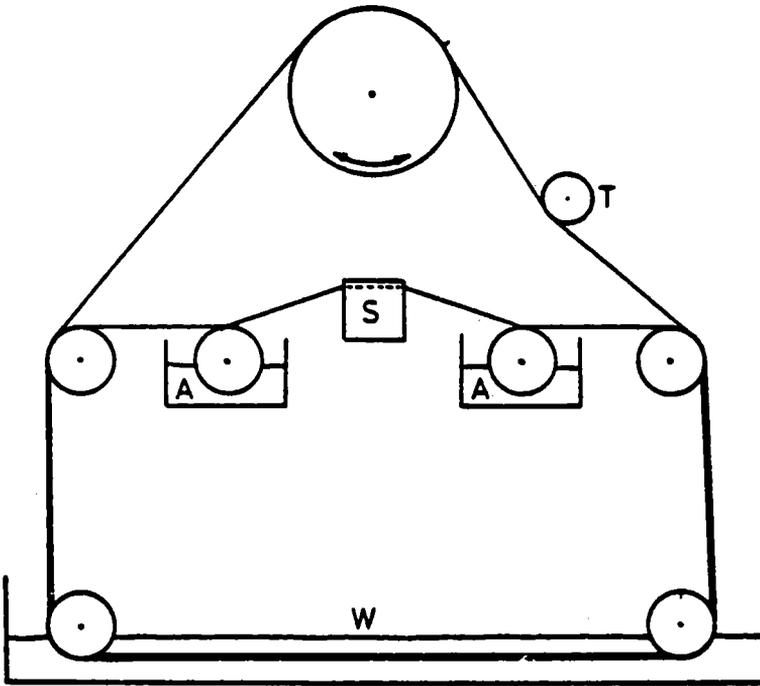


Figure 7. Schematic of a "string saw" used for cutting specimens for TEM. A: Acid baths, S: Specimen, T: Tensioning Wheel, W: Wash bath (25).

Table V. Chemical Polishing Solutions for Niobium and Niobium Alloys

<u>Solution</u>	<u>Reference</u>
30% HF, 70% HNO <sub>3</sub>	(33)
34% H <sub>3</sub> PO <sub>4</sub> , 33% HF, 33% HNO <sub>3</sub>	(34)
12% HNO <sub>3</sub> , 11% HF, 27% H <sub>2</sub> SO <sub>4</sub> , 50% H <sub>2</sub> O	(35)

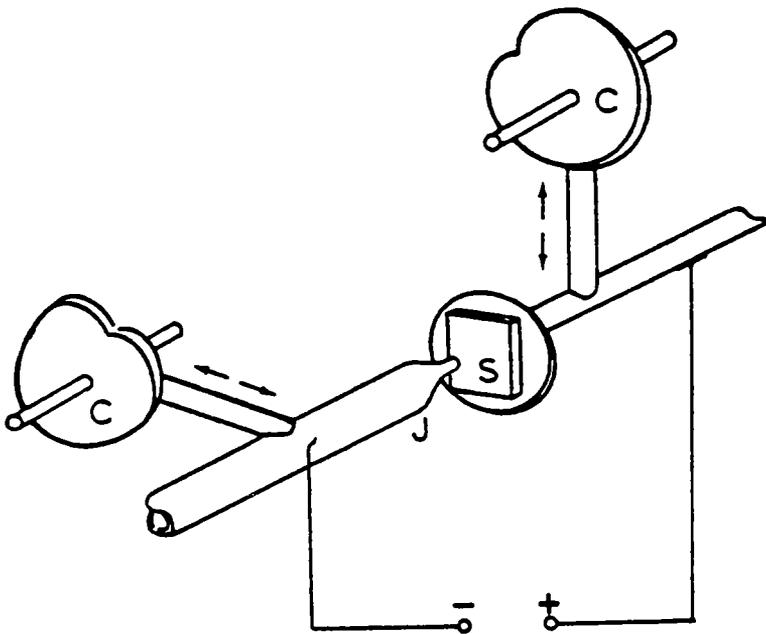


Figure 8. Schematic of scanning jet machining device.  
 C: Drive cams, J: Electrolytic jet, S:  
 Specimen (32).

### Final Thinning Methods

Electrolytic Techniques. Thin sheet specimens of niobium and niobium alloys frequently are thinned electrolytically for TEM. using the "window technique" originally described by Tomlinson (36). The steps involved are shown schematically in Fig. 9. First, a small specimen is cut and a "frame" of lacquer is painted around its periphery. The "window" within the frame is polished electrolytically until perforation occurs, usually occurring at the top edge nearest the electrolyte surface. To assist in determining the optimum electropolishing conditions it is advisable to establish a current-potential curve as described by Goodhew (37). If pitting occurs during thinning the cell voltage should be lowered, whereas, if etching occurs the cell voltage should be raised. As soon as the first perforation occurs the specimen is removed, washed, and dried. Additional lacquer is painted on the seal of the perforated edge. It is generally beneficial to invert the specimen at this stage. Polishing is then restarted until a second perforation occurs. This process is repeated until the edge of a perforation appears very jagged, indicating the specimen is locally very thin. Small specimens are cut from the thin areas for examination in the electron micro-

scope.

Many variants of this basic window technique have been employed successfully. One technique, described by Brandon and Nutting, (38) is a "figure-of-eight" technique which is intended to guarantee perforation at a particular point and to produce larger thinned areas. Briefly, the technique involves painting lacquer on the specimen in a figure-of-eight pattern such that initial perforation will occur at the middle of the eight.

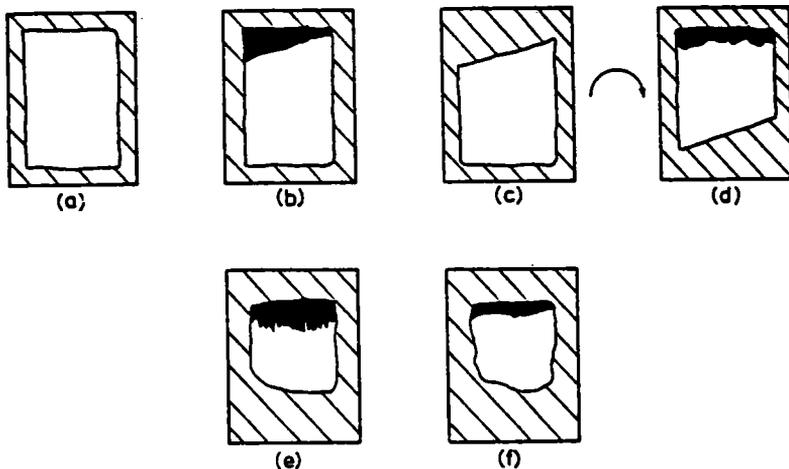


Figure 9. The window technique for preparing specimens for TEM. (a) initial lacquer window, (b) first perforation, (c) relacquered, (d) inverted and polished to second perforation, (e) appearance of an edge which is likely to be thin enough, (f) appearance of a "thick edge" (37).

A widely used procedure is that developed by Bollmann (39) which uses two pointed cathodes as shown in Fig. 10. The cathodes, lacquered except at their very points, are placed very near the specimen to be thinned. After the first perforation occurs, which almost always happens between the cathodes, the cathodes are moved back from the specimen and polishing is continued until a second perforation occurs. The second perforation usually occurs at the edge of the window and excellent foils can be obtained from the neck between the two.

The electrolytes listed in Table VI have been used successfully for electrolytic thinning of niobium and niobium alloy specimens.

Table VI. Electrolytes Used for Electrolytic Thinning  
Niobium and Niobium Alloys for TEM.

<u>Electrolyte</u>	<u>Remarks</u>	<u>Reference</u>
17.5% HF, 17.5% $\text{HNO}_3$ , 65% $\text{H}_2\text{O}$		(40), (41)
90% $\text{H}_2\text{SO}_4$ , 10% HF	14V, Pt Cathode	(42)
19% HF, 34% $\text{H}_2\text{SO}_4$ , 48% Lactic Acid	4.2V	(43)
5% $\text{H}_2\text{SO}_4$ , 2% HF, 93% $\text{CH}_3\text{OH}$	20V, -60 C, Nb-Zr Alloys	(44)
90% $\text{CH}_3\text{OH}$ , 10% $\text{HClO}_4$	-30C, 5.5V	(45)

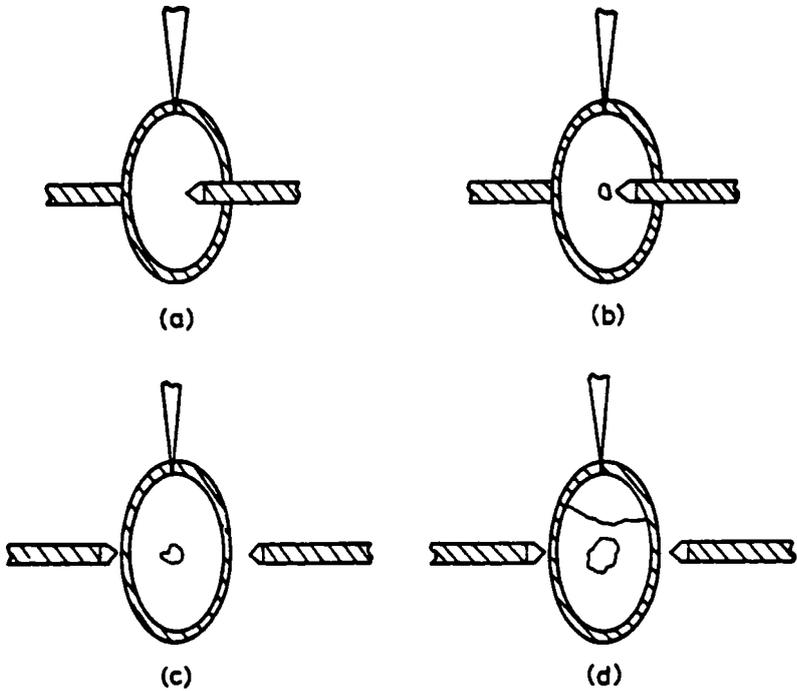


Figure 10. The Bollmann electropolishing technique using pointed electrodes. (a) initial position of specimen and electrodes, (b) first perforation, (c) further thinning with electrodes moved away from specimen, (d) specimens for microscopy are cut from the remaining bridge of specimen (39).

Jet Thinning Techniques. A number of "jetting" techniques have been described for the thinning of disc-shaped specimens for electron microscopy. One such system, described by DuBose and Stiegler, (46) is shown in Fig. 11. The specimen is placed in some type of holder and positioned between the two jets of electrolyte. An electrolytic cell is established between the specimen and a cathode which is located somewhere in the electrolyte stream. In some systems the jets are totally immersed in the electrolyte (47). Usually the thinning is accomplished in two stages; first, the specimen is electrolytically dimpled from each side in such a way that thinned region is produced in the center of the disc-shaped specimen. This specimen is then electrolytically and/or chemically polished until perforation occurs.

Numerous improvements have been made to the jet polishing technique through the years. Perhaps the most notable has been the addition of automatic methods for detecting the onset of perforation and the shutting off of the polishing process when this occurs. One such system, shown schematically in Fig. 12, utilizes "light tubes" which are connected to an electrical circuit that is activated when the light passes through the perforation and strikes a detector (48).

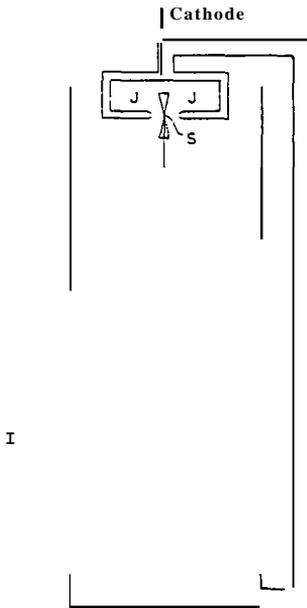


Figure 11. Diagram of an all-glass jet electropolishing cell, S: specimen, J: jets, T: electrolyte return tap (46).

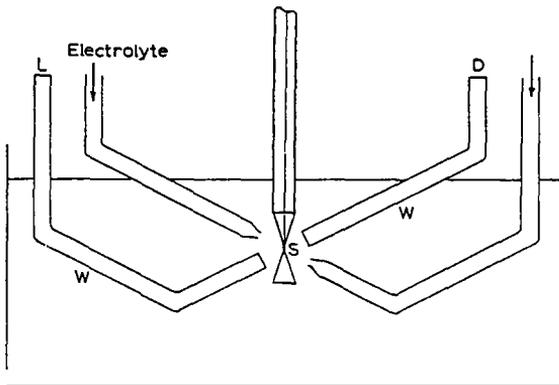


Figure 12. Submerged jet technique using "light wires", W, to illuminate the specimen, S, with a lamp, L. performance is observed by a detector placed at D (48).

Although most of the electrolytes that can be used for electropolishing will work in jet thinning, one electrolyte reportedly used successfully for niobium specimens in an electrolytic jet thinning system is:

<u>Electrolyte</u>	<u>Remarks</u>	<u>Reference</u>
90% H <sub>2</sub> SO <sub>4</sub> , 10% HF	10-20 v	(49)

Jet chemical thinning also has been used to prepare disc-shaped specimens of niobium for TEM. One type of device for doing this is shown in Fig. 13 (50). In this device the jet is held in position by a glass tube which also serves to direct the illumination onto the bottom surface of the specimen. When penetration occurs a bright spot can be observed from the top side of the specimen. Numerous improvements and variations have been made to this basic technique and have been documented in the literature (51-55). One such improvement, shown in Fig. 14, is a totally enclosed system. This type of system is particularly applicable to the thinning of niobium specimens because the very corrosive solutions required, usually containing hydrofluoric acid, are completely contained within the system. Incorporated in the system is a washing facility, allowing the specimen to be flooded rapidly with solvent as soon as the first sign of perforation is observed.

A solution that has been used for jet chemical thinning of niobium and niobium alloys has been reported by Hepfer (52) consisting of:

<u>Solution</u>	<u>Conditions</u>
70% HNO <sub>3</sub> , 30% HF	0°C, Wash in methyl alcohol

Ion Beam Thinning. Thinning of niobium specimens for TEM also can be accomplished by a process called ion beam thinning (sputtering). In this process a beam of ions at an energy of several keV is used to remove material from the surface of a specimen. Although the equipment required to do this is relatively expensive and the thinning time can be extremely long, the technique frequently offers the only method for obtaining truly deformation-free thinning.

Fig. 15 shows a schematic diagram of an ion beam thinning device. This type of device has been used successfully for the thinning of niobium and niobium alloy specimens, including Nb-25% Zr (57). The conditions recommended are:

<u>Initial Angle <math>\phi</math>.</u>	<u>Final Angle <math>\phi</math>.</u>	<u>kV</u>	<u>Gas</u>	<u>Pressure (torr)</u>	<u><math>\mu</math> A</u>	<u>Thinning Rate (<math>\mu</math> m/hr)</u>
20°	4.5	4.5	Argon	$6 \times 10^{-4}$	40	0.5

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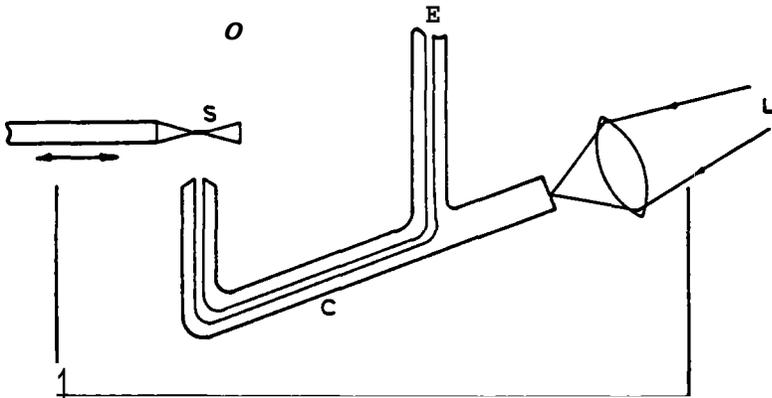


Figure 13. Gravity-fed jet chemical polisher. S: Specimen, L: light source, O: observer, E: electrolyte from header tank, C: 1mm inside diameter capillary tube (50).

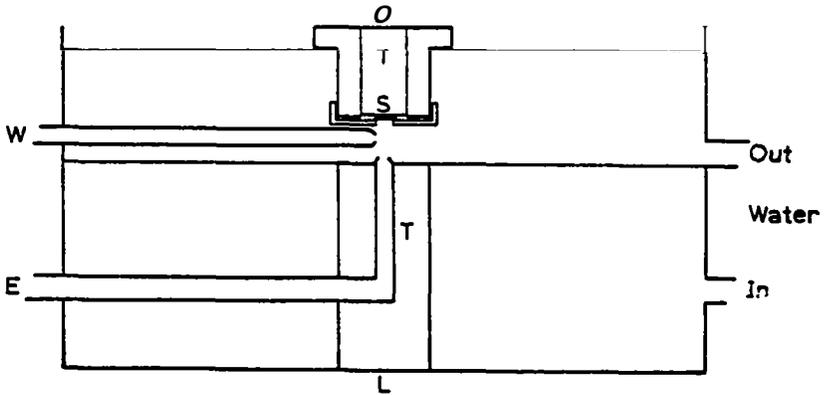


Figure 14. An enclosed cell for polishing with corrosive solutions. E: electrolyte input, W: wash input, T: transparent plastic, O: observer, L: light, S: specimen (55).

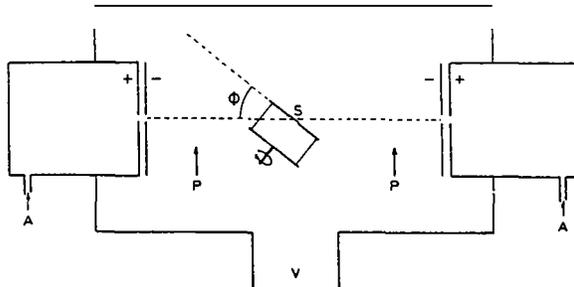


Figure 15. Schematic diagram of an ion beam thinning device. A: argon inlets, S: specimen, W: window for observation, V: vacuum pumps, P: retractable probes for ion beam current measurement,  $\phi$ : angle of incidence (56).

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