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POLISHING METHODS FOR METALLIC AND CERAMIC TRANSMISSION ELECTRON MICROSCOPY SPECIMENS

by

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Contd.)

LIST OF TABLES

POLISHING METHODS FOR METALLIC AND CERAMIC TRANSMISSION ELECTRON MICROSCOPY SPECIMENS

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ABSTRACT

In recent years, the increasing sophistication of transmission electron microscope (TEM) studies of materials has necessitated more exacting methods of specimen preparation. The present report describes improved equipment and techniques for electropolishing and chemically polishing a wide variety of specimens. Many of the specimens used in developing or improving the techniques to be described were irradiated with heavy ions such as nickel or vanadium to study radiation damage. The high cost of these specimens increased the need for reproducible methods of initial preparation, postirradiation processing, and final thinning for TEM examination. A technique was also developed to salvage specimens that had previously been thinned but were unusable for various reasons.

Jet polishing is, in general, the method of choice for surface polishing, sectioning, and thinning. The older beaker electropolishing method is included in this report because it is inexpensive and simple, and gives some insight into how the more recent methods were developed.

I. INTRODUCTION

The purpose of this report is to provide empirical data on chemical polishing and electropolishing techniques used in the preparation of transmission electron microscopy (TEM) specimens for materials studies. It contains results accumulated by the author and other workers over a period of ten years. Three different polishing procedures are addressed:

(a) Surface polishing (smoothing).

(b) Sectioning (the removal of a uniformly thick layer of material from the specimen surface).

(c) Thinning (the removal of material from the specimen surface to create a concavity, the apex of which usually perforates the specimen).

Both the original beaker-bath polishing method and the newer jet polishing method were developed as systems in which conditions could be standardized and used for both surface polishing and sectioning by simply timing the polishing interval accurately. The jet polishing method is more veresatile and, in most cases, more effective than the beaker technique for the reproducible preparation of smooth, dislocation-free surfaces. It lends itself very well to a systems approach because it allows a single piece of equipment to be used for surface polishing, sectioning off of a surface layer, and final thinning to perforation with automatic shutoff. Some of the beaker-polishing data in the present report are included primarily for completeness, as they apply to materials that were no longer under active study in the author's laboratory at the time the newer methods were developed. On the other hand, the beaker method does offer some advantages. The apparatus is relatively inexpensive, and the method can be used for disc specimens larger than 3 mm in diameter as well as for wire specimens. Also, by the use of a timer and relay, the current to the specimen may be turned on for a very short, precise interval, allowing the reproducible removal of a few hundred Å of material from the specimen surface.

II. SURFACE POLISHING

A. Objectives

Foil specimens for TEM require a finish that deviates by less than 50 Å (5 nm) from a true flat plane over a distance of 100 μm. These limits were determined by observing polished specimens in an optical interference microscope with a resolution limit of 5 nm per μm of distance along the surface. Specimens that appear well polished by this criterion have been uniform in thickness and surface finish when observed by TEM. It is permissible for precipitates in TEM specimens to deviate from the surrounding surface by more than these limits, as long as they and the matrix are well polished. However, precipitates can often be polished level with the matrix by adjusting the parameters of the process.

Figure 1 illustrates the effect of current density on the quality of electropolished specimens. Excessive current density leads to pitting, while inadequate density results in etching of the grain boundaries.

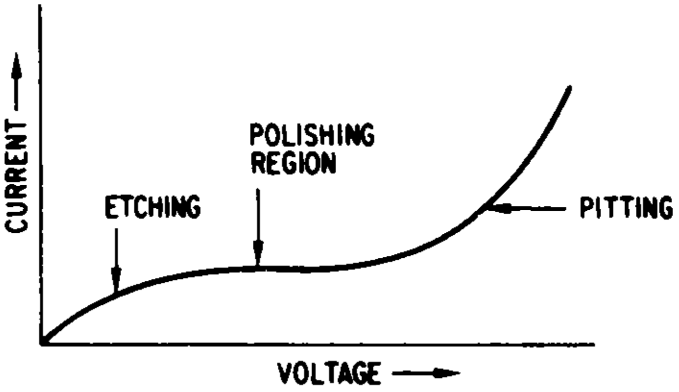

Fig. 1. Variation of Current Density with Voltage During Electropolishing.

B. Methods and Results

1. Surface Polishing by Beaker Method

A typical apparatus for beaker electropolishing is shown in Fig. 2. In most cases, a 250-ml Pyrex beaker containing 200 ml of electrolyte was used. A platinum cathode, 1-3/4 in. x 1/2 in. x 13 mil (44 x 13 x 0.33 mm) in size,

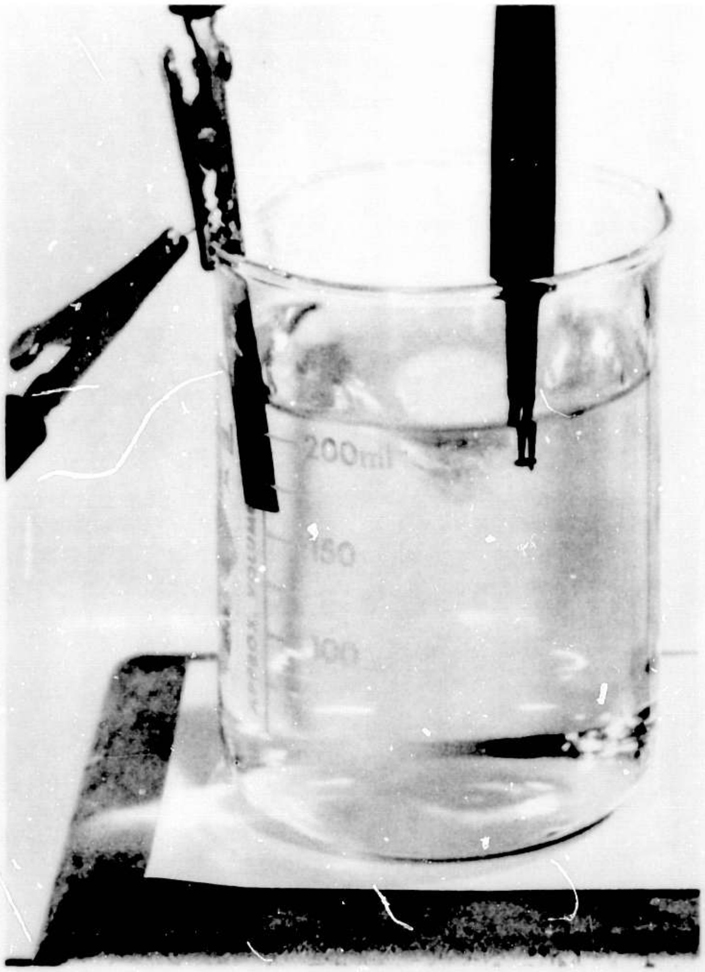

Fig. 2. Apparatus for Beaker Electropolishing. ANL Neg. No. 306-80-232.

was clamped to the inner surface of the beaker with an alligator clip. (Platinum was chosen for its compatibility with all the polishing solutions anticipated, and because it increased the reproducibility of the technique; however, a stainless steel cathode should be adequate for most purposes.) The electrolyte was usually stirred with a 1-1/2-in. (38-mm)-long magnetic stirring bar. Stirring rates were defined by measuring the depth of the vortex below the highest point on the electrolyte surface: "slow", "medium", and "fast" are equivalent to a 1/4-, 1/2-, and 3/4-in. (6-, 12-, and 18-mm)-deep vortex, respectively. With very viscous solutions, a 3/4-in. vortex was not always attainable, but a depth close to 3/4 in. was considered sufficient. A thick piece of cardboard was placed under the beaker to reduce the amount of heat transferred from the magnetic stirring motor to the electrolyte. The cardboard was also used when the beaker was placed in a large crystallizing dish containing a cooling bath.

Disc specimens (3 mm in diameter and nominally 10 mils thick) were usually prepolished on one side with a vibratory polisher through a 0.05-μm alumina slurry. They were then placed crosswise between the tips of a fine-pointed tweezer and secured by means of an O-ring slipped around the tweezer legs; this allowed easy adjustment of the gripping pressure. The tips of the tweezer were occasionally reground on a water-cooled slow-speed metallographic grinder. The specimen was positioned 1/8 in. (3.2 mm) below the electrolyte surface and, in most cases, 3/8 in. (9.5 mm) from the side of the beaker directly opposite the cathode, in one of the six different orientations listed in Table I.

Table I. Specimen Orientations for Beaker Electropolishing

HU	Horizontal, polished side up.
HD	Horizontal, polished side down.
45D	Polished side down, at 45^o to horizontal and facing the electrolyte flow.
30D	Same as 45D but at 30^o to horizontal.
R	Same as 45D but with oscillating rotation of the specimen about the tweezer axis.
V	Vertical, 3/4 in. from cathode, polished side away from cathode.

The HU orientation is necessary in some solutions in which large quantities of gas bubbles are evolved. The disadvantage is that the restriction of solution flow and the ion charge around the tweezer legs sometimes make it difficult to polish the surface of a 3-mm disc uniformly. When large quantities of gas bubbles are not a problem and a viscous electrolyte is used, the HD orientation is preferred because of the freer electrolyte flow it permits. In orientations 45D and 30D the gas bubbles formed by the electrolytic reaction are swept from the specimen surface by the flow of stirred solution. Since the bulky part of the tweezer is above the specimen, very little disturbance to the flow of solution is present at the surface of interest. The rotating orientation R is necessary in certain electrolyte solutions to prevent grooves from forming when gas bubbles are swept across the specimen surface. The vertical orientation V was used to help gas bubbles float upward in a viscous electrolyte.

Wire specimens represent a special case of surface polishing. Since it does not hold the gas bubbles as tightly by surface tension as a flat-surfaced specimen would, a wire can often be polished most effectively by hanging it in the electropolishing bath vertically and leaving the electolyte solution unstirred.

Two different power supplies were used. Power supply "A" was a Fluke Model 407D, 0-500 mA/0-600 V dc unit with a voltage-regulated, filtered output. Power supply "B" was built in-house and had a 5-A/300-V unregulated filtered output. The large size of power supply B enabled the voltage to remain fairly constant up to 1 A output. Thus, variations in total current due to variations in the tweezer and specimen surface area exposed to the electrolyte did not significantly affect the quality of the electropolishing.

Some solutions polish best with the current on continuously, while others work best on an intermittent schedule. Intermittent current facilitates escape of gas bubbles from the specimen surface; also, the repeated formation and removal of the polishing film or boundary layer at the specimen surface speeds removal of material by bringing fresh chemicals into contact with the specimen. These chemicals tend to attack the highest features first, which aids the smoothing effect.

The viscosity of the polishing film may also be an important parameter. Solutions that are highly viscous at room temperature must often be heated to obtain good electropolishing results; those of moderate viscosity work well at room temperature, while low-viscosity solutions work well at about -60°C. This is illustrated in Table II, which gives the relative viscosities of three common electrolytes at room temperature and at the normal operating temperature for each. Note that the viscosities of the three solutions are similar at the operating temperatures, although they differ at room temperature. The existence of an optimal viscosity for the polishing film would explain these observations. This viscosity could be achieved by the addition of appropriate wetting or thickening agents, as well as temperature adjustment. A detailed study of film viscosities would be of interest in this regard.

Table II. Relative Viscosities of Some Common Electrolytes

Solution	Normal Operating Temp. (°C)	Relative Viscosity at Room Temp.	Relative Viscosity at Operating Temp.
60% phosphoric acid, 40% sulfuric acid	50	Thick	Moderately Thin
20% sulfuric acid, 80% methanol	20	Moderately Thin	Moderately Thin
10% perchloric acid, 90% ethanol	-60	Very Thin	Medium

When a strong leveling or smoothing effect is desired and several solutions are known to polish the material satisfactorily, the one with the highest viscosity at the polishing temperature will usually give the smoothest surface. Often, it will "bridge across" features such as grain boundaries or electroplated interfaces rather than preferentially attacking them. Perhaps the high viscosity prevents movement of fresh electrolyte into tiny areas lower than the average surface, causing passivation and resultant slow polishing of those areas. This effect can be enhanced by adding a thickening agent such as butyl cellosolve to the electrolyte.

The specific surface polishing conditions used for a variety of foil specimens are given in Table III.

2. Surface Polishing by Jet Method

Jet electropolishing of metal is accomplished by pumping a stream of negatively charged electrolyte against the surface of a positively charged

Table III. Electrolytes and Conditions Used for Surface Polishing of Foil Specimens[a] by Beaker Method

Material	Electrolyte	Temp., °C	Orientation[b]	Stir Rate	Volts	Current, mA	Length of Power Cycles, s	Comments
A286 (annealed)	20% H_2SO_4, 80% methanol	5	HD	Medium	As reqd.	170-250	5	Do not stir fast enough to cause bubbles.
A286 (aged or cold worked)	10% $HClO_4$, 90% ethanol	5	30D	Fast	As reqd.	400-450	4	
Aluminum								
(1)	20% $HClO_4$, 80% ethanol	-50	30D	Fast	150	400		Remove oxide (250 V, 450 mA, 4 s) prior to polishing.
(2)	10% $HClO_4$, 90% ethanol	-60	30D	Medium	90-120	450	3 on, 2 off	Rinse in alcohol at least once per s.
Al-1Cu	10% $HClO_4$, 90% ethanol	-50	30D	Fast	30	10	60 on, ~5 off	
Al-0.25Ge, Al-1.5Ge	20% $HClO_4$, 80% ethanol	-50	30D	Fast	150	400		Remove oxide (250 V, 450 mA, 4 s) prior to polishing.
Al-1Mg	10% $HClO_4$, 90% ethanol	-50	30D	Fast	90	90	3 on, 2 off	
Al-0.25Si, Al-1.5Si	20% $HClO_4$, 80% ethanol	-50	30D	Fast	150	400		Remove oxide (250 V, 450 mA, 4 s) prior to polishing.
Al-1Zn	10% $HClO_4$, 90% ethanol	-50	30D	Fast	105	100	3 on, 2 off	
Copper (pure)	300 ml H_3PO_4, 2 ml CrO_3, 200 ml H_2O, 20 g $CuCO_3 \cdot Cu(OH)_3$	20	30D	Medium	2	130+30		
Copper, Cu-7Ge, Cu-9Si	33% HNO_3, 67% methanol	-50	30D	Medium	25	150		

D979 (annealed)	20% H_2SO_4, 80% methanol	5	30D	Slow	8	75-100	4	
D979 (annealed and either aged or 20% cold worked)	10% $HClO_4$, 90% ethanol	-60	V	Medium	As reqd.	aged:450 cw:400	4	
D979 (cold worked and aged)	20% H_2SO_4, 80% methanol	5	30D	Medium	10	300	6	Grain boundaries slightly etched.
Gold	465 ml acetic acid, 87.5 g CrO_3, 25 ml water	0	HD	Fast	35	200	No cycling	Some material precipitates out when electrolyte is chilled to 0°C.
Incoloy 800 (annealed)	20% H_2SO_4, 80% methanol	5	30D	Medium	As reqd.	200-250	4	
Incoloy 901 (annealed or aged)	20% H_2SO_4, 80% methanol	0	30D	Slow	9	100	annealed: 4 aged: 2	
Incoloy 901 (cold worked and aged)	20% H_2SO_4, 80% methanol	5	30D	Medium	23	200-250	6	
Inconel 625 (annealed or 25% cold worked)	20% H_2SO_4, 80% methanol	5	30D	Slow	11	100	annealed: 3 cold worked: 2	Removes scratches but does not improve flatness.
Inconel 718 (annealed)	10% $HClO_4$, 90% ethanol	-60	30D	Medium	As reqd.	275	5	
Inconel 722 (annealed)	20% H_2SO_4, 80% methanol	5	30D	Medium	As reqd.	200-250	4	
Inconel 722 (annealed and aged)	20% H_2So_4, 80% methanol	5	30D	Medium	As reqd.	600	1	Short treatment minimizes grain-boundary attack.
Inconel 722X (annealed)	10% $HClO_4$, 90% ethanol	-60	V	No stirring	As reqd.	275	5 on, 2 off	
Inconel X750 (annealed or aged)	10% $HClO_4$, 90% ethanol	5	45D	Medium	As reqd.	550	4	

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[a] Specimens were 3-mm discs except where noted.

[b] As defined in Table I.

Table III. Electrolytes and Conditions Used for Surface Polishing of Foil Specimens[a] by Beaker Method (Contd.)

Material	Electrolyte	Temp., °C	Orientation[b]	Stir Rate	Volts	Current, mA	Length of Power Cycles, s	Comments
Inconel 901 (aged and cold worked)	10% $HClO_4$, 90% ethanol	5	30D	Medium	As reqd.	150-200	5	
Fe-0.55Al (UHV annealed 850°C, 7 h)	20 ml $HClO_4$, 180 ml methanol, 120 ml butyl cellosolve	-60	30D	Medium	50	100	1 on, 1 off (~ 10 cycles)	Rinse in methanol.
Fe-2.3Cu, Fe-1.46Ge (UHV annealed)	10% $HClO_4$, 90% ethanol	0	30D	Slow	60→40	800		Matrix polished; many fine precipitates in grains.
Fe-20Ni-15Cr	20% H_2SO_4, 80% methanol	20	30D	Slow	10	300→150		
Fe-0.57Si (UHV annealed 850°C, 7 h)	20 ml $HClO_4$, 180 ml methanol, 120 ml butyl cellosolve	-60	30D	Medium	70	200	2 on, 2 off	Rinse in methanol.
Nickel (pure, annealed)	40% H_2SO_4, 60% methanol	30	HD	Slow	19 (open circuit)	200→100	>5	Grain boundaries barely visible.
Nickel (specimen shapes and sizes vary)	40% H_3PO_4, 60% glycerol	20	30D	Slow	15	Varies with specimen size		Very viscous electrolyte; does not preferentially attack grain boundaries or electroplated interfaces.
Ni-1Al (annealed)	40% H_2SO_4, 60% methanol	32	HU	Slow	19	200→100		Adjust voltage to give indicated current drop if bath temp. changes slightly.
Ni-6.35Al (annealed)								
(1)	20% $HClO_4$, 80% ethanol	-10	R	Medium	60	800	3 on, 5 off	Grain boundaries smooth well.
(2)	20% $HClO_4$, 80% ethanol	-50	30D	Medium	95	200	0.25 on, 2 off (20 cyles)	Rotate specimen 90° after 5th, 10th, and 15th cycle.

	(3) 20% $HClO_4$, 80% ethanol	-35	HU	Medium	80	480	1 on, 2 off	Electrolyte flows better at -35 than at -50°C (method #2).
	(4) 20% H_2SO_4, 80% methanol	20	30D	Medium	70 (open circuit)	450		
	(5) 20% $HClO_4$, 80% ethanol	-50	30D	Fast	42	100→60		Wide polishing plateau, removes ~50 nm per 2-s burst.
Ni-6.35Al (aged)	20% H_2SO_4, 80% methanol	20	30D	Medium	70 (open circuit)	450		
Ni-9Al (annealed)	20% $HClO_4$, 80% ethanol	-50	30D	Fast	42	100→60		Contains γ′ phase.
Ni-9Al (annealed and aged)	20% $HClO_4$, 80% ethanol	-50	30D	Medium	95	200	0.25 on, 2 off	Rotate specimen frequently as in orientation R.
Ni-14Al (annealed)	20% $HClO_4$, 80% ethanol	-10	30D	Medium	60	800	3 on, 5 off	Rotate specimen frequently as in orientation R.
Ni-14Al with γ′ phase	20% $HClO_4$, 80% ethanol	-50	30D	Medium	95	200	0.25 on, 2 off	Rotate specimen after every 5th cycle.
Ni-0.01Be, (annealed)	10% $HClO_4$, 90% ethanol	-20	30D	Very Slow	As reqd.	500-550	4 on, 2 off	
Ni-0.1Be, Ni-0.3Be (annealed)	40% H_2SO_4, 60% methanol	30[c]	R	Slow to medium	19	150→100	15 on, 15 off	Above 32°C, some grains are polished preferentially
Ni-0.7Be (annealed)								
	(1) 10% $HClO_4$, 90% ethanol	-20	30D	Very slow	As reqd.	500-550	4 on, 2 off	
	(2) 20% H_2SO_4, 80% methanol	0	30D	Medium	20	250		

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[a] Specimens were 3-mm discs except where noted.

[b] As defined in Table I.

[c] Do not exceed 32°C.

Table III. Electrolytes and Conditions Used for Surface Polishing of Foil Specimens^{a} by Beaker Method (Contd.)

Material	Electrolyte	Temp., °C	Orientation^{b}	Stir Rate	Volts	Current, mA	Length of Power Cycles, s	Comments
Ni-10Ge (annealed 1000°C, 6 h; water quenched)	20% $HClO_4$, 80% ethanol	-60	V	Fast	70	700	1 on 5 off (10 cycles)	Move specimen briskly to help remove bubbles from surface.
Ni-1Au (annealed)								
(1)	40% H_2SO_4, 60% methanol	32	HU	Slow	19	200→100		Adjust voltage to give indicated current drop if bath temp. changes slightly.
(2)	20% $HClO_4$, 80% ethanol	-10	30D	Fast	95	700		Long power bursts prevent etching. Change orientation frequently.
Ni-1Mo	20% H_2SO_4, 80% methanol	0	HD	Medium	25	180		
Ni-1Mo (annealed)	40% H_2SO_4, 60% methanol	23	30D	Medium	23	400		
Ni-1Pt	20% $HClO_4$, 80% ethanol	-60	R	Fast	80	200	0.5 on, 2 off	
Ni-1Si	40% H_2SO_4, 60% methanol	32	HU	Slow	19	200→100		Adjust voltage to give indicated current drop if bath temp. changes slightly.
Ni-2Si	40% H_2SO_4, 60% methanol	32	HU	Slow	19	200→10		Adjust voltage to give indicated current drop if bath temp. changes slightly.
Ni-2Si (annealed, 1 in. by 3/16 in. by 10 mils)	40% H_2SO_4, 60% methand	30	30D	Medium	95	1800		Use 32°C water bath to give large heat sink.
Ni-4Si	13% HCl, 87% methanol	-60	30D	Medium	80	400		If specimen surface has a "bumpy" texture, try a different bath temp.

Ni-6Si (annealed)	30 ml $HClO_4$, 175 ml butyl cellosolve, 295 ml methanol	-40	30D	Medium	25	75	≥ 0.25	0.25-s polish removes 50 nm.
Ni-6.5Si (annealed)	13% HCl, 87% methanol	-60	30D	Medium	80	400		If specimen surface has a "bumpy" texture, try a different bath temp.
Ni-6.5Si (annealed and aged)	13% HCl, 87% methanol	-60	HD	Very fast	80	375	2 on, 5 off	Change specimen orientation often. Grain boundaries somewhat visible.
Ni-1Ti (annealed)	40% H_2SO_4, 60% methanol	23	30D	Medium	23	400		
Ni-8.75Ti (annealed)	40% H_2SO_4, 60% methanol	30	30D	Slow	21	450		Treatment smooths grain boundaries but leaves fine Ti precipitates visible at 500X.
Ni-8.75Ti (annealed and aged)	20% $HClO_4$, 80% ethanol	-50	HD	Medium	90	300	0.5	Short power bursts minimize preferential polishing of needle-shaped precipitates.
Ni-0.5Ti-1Si (annealed)								
	(1) 40% H_2SO_4, 60% methanol	23	30D	Medium	23	400		
	(2) 20% $HClO_4$, 80% ethanol	-10	R	Fast	80+40	700		Long power bursts reduce etching.
Niobium (annealed; specimen sizes vary)	250 ml HNO_3, 75 ml HF	10	30D	Medium	2	Varies with specimen size		Very slow removal rate.
PE-16 (annealed or aged)								
	(1) 10% $HClO_4$, 90% ethanol	-60	HD	Medium	200	450		
	(2) 20% $HClO_4$, 80% ethanol	-50	HD	Medium	80	125+110	1 on, 3 off	Precipitates remain slightly higher than specimen surface.

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[a] Specimens were 3-mm discs except where noted.

[b] As defined in Table I.

Table III. Electrolytes and Conditions Used for Surface Polishing of Foil Specimens[a] by Beaker Method (Contd.)

Material	Electrolyte	Temp., °C	Orientation[b]	Stir Rate	Volts	Current, mA	Length or Power Cycles, s	Comments
	(3) 20% H_2SO_4, 80% methanol	0	HD	Slow	25	400		
PE-16 (cold worked)	10% $HClO_4$, 90% ethanol	-60	HD	Medium	200	450		
18-8SS (annealed)	H_3PO_4 saturated with CrO_3	20	HD	Medium	As reqd.	100		
18-8 SS-1Cu, 18-8 SS-1Mn (annealed)	10% $HClO_4$, 90% ethanol	20	HD	Medium	As reqd.	300		
18-8 SS-1Mo, 18-8 SS-1Pt, 18-8 SS-1Si (annealed)	10% $HClO_4$, 90% ethanol	5	HD	Fast	As reqd.	500		High current reduces etching.
304 SS (annealed; specimen sizes vary)	60% H_3PO_4, 40% H_2SO_4	50	HD	Medium	10	Varies with specimen size		Solution is hygroscopic and will overflow if left in open beaker too long.
316 SS (annealed)								
	(1) 20% H_2SO_4, 80% methanol	20	30D	Medium	20	200		Also works well for larger specimens, at 25°C and proportionately higher current, with frequent changes in orientation.
	(2) 10% $HClO_4$, 90% ethanol	5	45D	Fast	As reqd.	450		

321 SS (annealed or cold worked)	10% $HClO_4$, 90% ethanol	-60	30D	Medium	As reqd.	400		
T16-25-6 (annealed)	10% $HClO_4$, 90% ethanol	-60	V	Medium	As reqd.	450		
Titanium (pure, annealed; specimen sizes vary)	30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	HD	Medium	30	Varies with specimen size		
Ti-6Al-4V (annealed)	10% $HClO_4$, 90% methanol	-60	HD	Medium	65	400		Two-phase alloy shows some difference in polishing rate between the phases.
Ti-8Al-1Mo-1V (annealed)	20 ml $HClO_4$, 180 ml methanol, 120 ml butyl cellosolve	-60	HD	Medium	80	200	2 on, 2 off	Second phase polished but still visible.
Ti-15V-3Cr-3Al-3Sn (annealed)	20 ml $HClO_4$, 180 ml methanol, 120 ml butyl cellosolve	-60	HD	Medium	80	200		Two-phase material.
Vanadium (pure; 10-mil-dia wire)	20% H_2SO_4, 80% methanol	20	(c)	No stirring	19	400	30 (2 cycles)	After first cycle, rinse in alcohol and suspend by opposite end.
Vanadium, V-0.4C (annealed)	20% H_2SO_4, 80% methanol	21	HD	Fast	19	420		
V-15Cr (annealed), V-1N, V-1O	20% H_2SO_4, 80% methanol	21	HD	Fast	19	420		

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[a] Specimens were 3-mm discs except where noted.
[b] As defined in Table I.

Table III. Electrolytes and Conditions Used for Surface Polishing of Foil Specimens[a] by Beaker Method (Contd.)

Material	Electrolyte	Temp., °C	Orientation[b]	Stir Rate	Volts	Current, mA	Length of Power Cycles, s	Comments
Addendum: polishing procedures documented between mid-1981 and mid-1985								
Aluminum (15 x 20-mm strip)	30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	V[c]	Slow	38	1200	1 on, 5 off	Place specimen "downstream" from cathode, 1/4 of the way around beaker.
Copper, Cu-1Au, Cu-7Be, Cu-40Ni, Cu-9Si (7 x 17-mm strip)	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	-30 to -50 (see comments)	V[c]	Fast	40	1200 typical	1 on, 5 off	Place specimen "downstream" from cathode. Start near cathode but increase distance after a few cycles. Best temperatures are: Cu, -30°C; Cu-40Ni and Cu-1Au, -40°C; Cu-7Be and Cu-9Si, -50°C. Use <u>fresh</u> electrolyte to avoid redepositing residue on specimens.
Gold (5 x 10-mm strip)	250 ml HCl, 175 ml ethanol, 75 ml glycerine	0	V[c]	Fast	42	4000	1 on, 5 off	Lacquer rear surface of specimen to reduce current required.
Ni-4Sb (5 x 15-mm strip)	20% $HClO_4$, 80% ethanol	-60	V[c]	Fast	90	--	1 on, 5 off	Lacquer rear surface of specimen. Place specimen "downstream" from cathode, 1/4 of the way around beaker.

Ni-6Al-6Ge, Ni-8Al-8Ge, Ni-6Si-6Ge (7 x 16-mm strip)	20% $HClO_4$, 80% ethanol	-60	V[c]	Fast	70	400 • 200	1 on, 5 off	Lacquer rear surface of specimen "downstream" from cathode, 1/4 of the way around beaker.
Ni-12.7Si (7 x 17-mm strip)	130 ml HCl, 870 ml methanol, 60 ml butyl cellosolve	-50	V[d]	Medium	90	800	1 on, 5 off	Place specimen "downstream" from cathode 1/4 of the way around beaker and nearly parallel to liquid flow.
Niobium (7.5 x 15-mm strip)								
	(1) 20 ml methanol saturated with NH_4F, 180 ml methanol, 40 ml ethylene glycol, 5 ml H_2SO_4	-40	V[c]	Fast	82	800	2 on, 5 off	Lacquer rear surface of specimen. Place specimen "downstream" from cathode, 1/4 of the way around beaker.
	(2) 90 ml H_2SO_4, 30 ml HF, 500 ml methanol, 100 ml butyl cellosolve	-50	V[e]	Medium	50	600	10 to 18 steady	Lacquer rear surface of specimen. Place specimen "downstream" from cathode, 1/4 of the way around beaker. Polishing longer than 20 s leaves bumps on surface; possibly hydrides.
Zirconium (10 x 200-mm strip)	5.3 g LiCl, 11.16 g $Mg(ClO_4)_2$ 500 ml methanol, 100 ml butyl cellosolve	-50	V	Medium to Fast	250	300	2 on, 5 off	Lacquer rear surface of specimen. Place specimen "downstream" from cathode, 1/4 of the way around beaker.

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[a] Specimens were 3-mm discs except where noted.
[b] As defined in Table I.
[c] Polished side toward cathode.
[d] Polished side toward center of beaker.
[e] Polished side 45° toward cathode.

specimen. In general, this process is used to create a dished or dimpled area, and is continued until perforation of the specimen occurs (see Section III.A). However, a variation of the standard jet polishing technique can also be used to smooth the surface of specimens. The jet method offers several advantages over the beaker method for surface polishing: The flow of electrolyte over the specimen can be varied from slow to very fast, so that the electropolishing film can be more closely regulated than in a stirred bath. Also, gas bubbles can be swept away from the specimen surface rapidly enough to prevent pitting, and grooves on the specimen surface (which result from the slow, unidirectional electrolyte flow in a stirred bath) are avoided.

The discs were first glued with Microshield lacquer (Michigan Chrome and Chemical Co., Tolber Division, Pyramid Plastics, Inc., 220 West 5th Street, Hope, Arkansas 71801) to the end of a stainless steel block made to fit rotary polishing equipment. Nylon cloths lubricated with lapping oil and charged with 6, 3, and 1-μm diamond paste were used consecutively to polish and flatten the specimen surface. Final mechanical polishing was done for 15 min. on a vibratory polishing machine with 0.05-μm alumina and Microcloth. The lacquer was dissolved with acetone and the discs were cleaned well.

Surface polishing was performed with a Model 550 B Jet Thinning Instrument (South Bay Technology, Inc., 5209 Tyler Avenue, Temple City, California 91780). The instrument (shown in Fig. 3) consists of two main parts, the jet head assembly and a control cabinet. Figure 4 shows a close-up of the jet head assembly and specimen holder. Controls are provided for changing the electrolyte pump speed, jet-to-specimen distance, voltage, and specimen polarity. (Polarity reversal is sometimes helpful during initial polishing of a slightly oxidized specimen.)

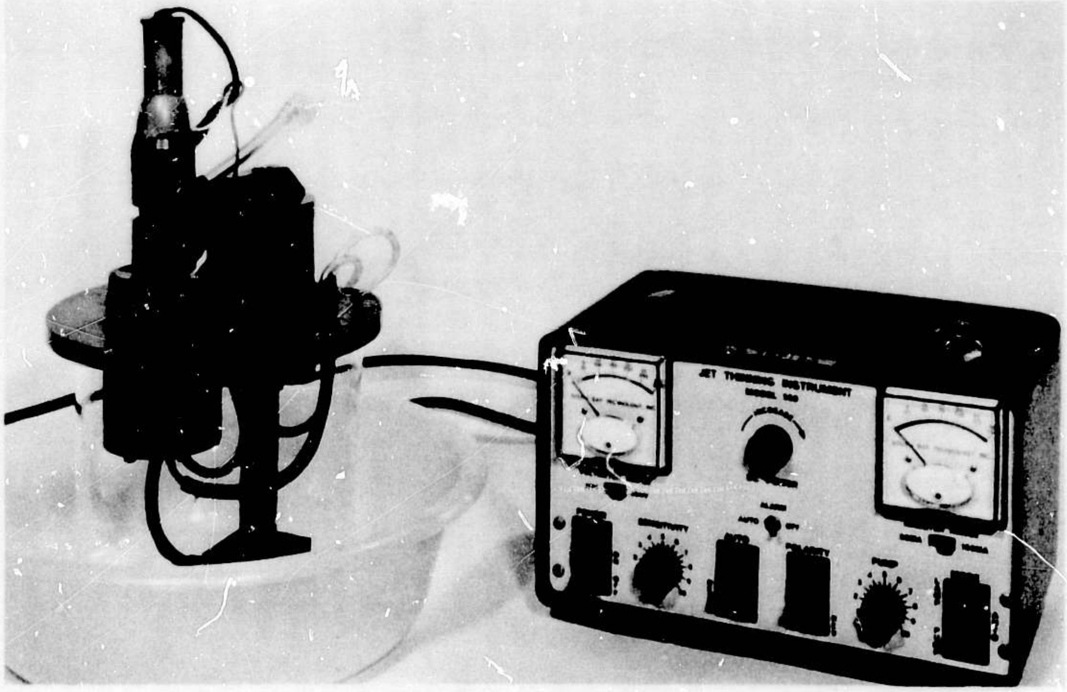

Fig. 3. Apparatus for Jet Electropolishing. ANL Neg. No. 306-80-234.

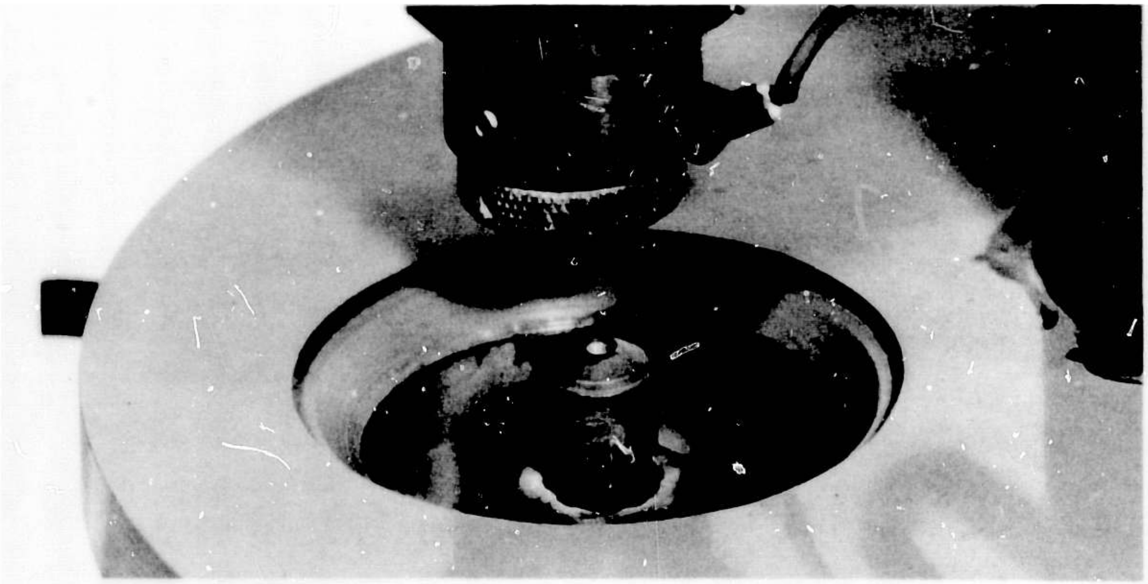

Fig. 4. Closeup of Jet Head Assembly and Specimen Holder. ANL Neg. No. 306-80-230.

All specimens were 3 mm in diameter and nominally 10 mils (0.3 mm) thick. (A small portion of a larger specimen may be jet polished by positioning it under the jet, with the specimen connected to the positively charged mount post by a platinum wire.) A stainless steel jet nozzle was modified by boring out the 1.5-mm-diameter hole to 3 mm, allowing a stream of electrolyte of the same diameter as the specimen to be pumped onto the specimen surface from above. The light-pipe centering device was removed from the nozzle to ensure that a uniform flow of electrolyte would impinge on the specimen surface. Thus, on striking the specimen, the electrolyte stream spreads out evenly in all radial directions, as shown in Fig. 5.

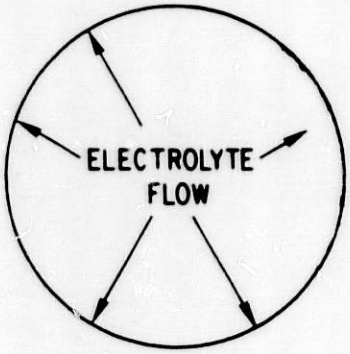

Fig. 5. Schematic Top View of Specimen During Jet Sectioning.

A platinum-tipped pedestal was used to support the specimen. A side view of the specimen and holder is shown in Fig. 6. The polyethylene diaphragm normally used to retain the specimen on the pedestal was removed; the force of the electrolyte flow was sufficient to hold the specimen in place on the pedestal mount when the PVC specimen retainer was adjusted level with the top of the specimen.

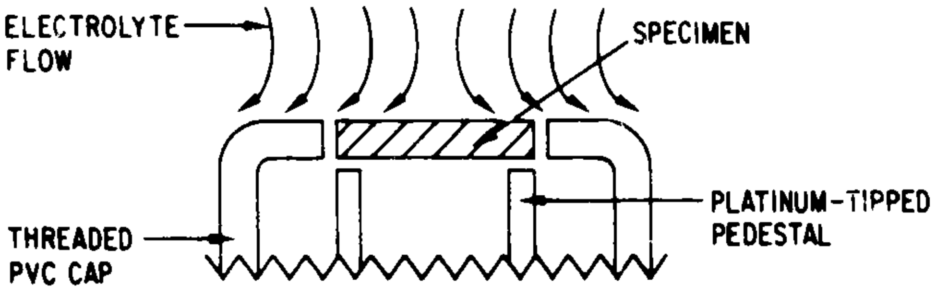

Fig. 6. Arrangement of Specimen on Pedestal During Jet Surface Polishing.

Gas bubbles evolved during polishing may cause the specimen to rise off the supporting pedestal. To provide an escape path for these bubbles, a 0.25-mm-thick diamond saw blade was used to cut two slots in the top of the PVC cap, at 90° to each other, extending about halfway to its bottom. The circular diaphragm retaining ring was then slipped over the cap. Gas bubbles flow out through the slots. This makes possible the use of slower pumping of the electrolyte when necessary to get a good electropolishing film. If a specimen does float off its pedestal mount, it is usually caught on the top of the retaining ring, from where it can be readily retrieved.

When the jet-to-specimen distance and electrolyte flow velocity are adjusted properly, a surface which is flat over a distance of at least 100 μm can be produced. Even if gradual variations from true flatness occur over longer distances (e.g., 1 mm), the specimen will still be adequate for applications such as heavy-ion or neutron bombardment studies. The specific jet surface polishing conditions used for a variety of foil specimens are given in Table IV.

III. SECTIONING AND THINNING

A. Objectives

Sectioning is defined as the removal of a uniformly thick layer of metal by electropolishing for a given amount of time in an appropriate electrolyte, using a specified set of parameters. The amount of metal removed is determined by the length of time that current is allowed to flow through the cell while the other parameters are held constant. Sectioning is used in a variety of applications where information is sought on the structure of a material at some distance below the surface. These include studies of radiation damage, oxidation, and ion implantation of doping elements.

Sectioning works well on small specimens (i.e., 3-mm discs) for removal of a surface layer 500 to 8,000 Å (50 to 800 nm) thick. If less than 500 Å (50 nm) of material is removed, the polishing time required is usually too short to establish a good electropolishing film, and etching or pitting of the specimen occurs. At depths greater than 10,000 Å (1 μm), the difference between removal rates at the center and edge of the disc becomes noticeable. The specimen surface may also become uneven, owing to electrolyte and bubble flow and to the different rates at which grains of different orientations are sometimes polished. Fortunately, the depth range specified for effective use of the technique is adequate for most applications. Ion milling gives a more controllable removal of material but has been found to introduce damage into the microstructure, which makes identifying defects or other features of interest a very difficult task.

Thinning is defined as the removal of material to produce a concavity or "dimple", the apex of which eventually perforates the specimen. As discussed in Section III.D below, it may be accomplished either electrolytically or chemically.

The preparation of radiation-damage specimens for TEM provides a good illustration of the relationship between sectioning and thinning. When a specimen is bombarded with heavy ions to simulate radiation damage, the distribution of damage with respect to depth from the specimen surface varies in the general way shown in Fig. 7. The exact shape of the curve and position of the peak damage will vary depending on the elemental ion used, accelerating voltage, and specimen composition, but the curve usually has a sharper drop-off after the peak damage depth than before it. The peak damage depth can be calculated from the above-mentioned parameters.

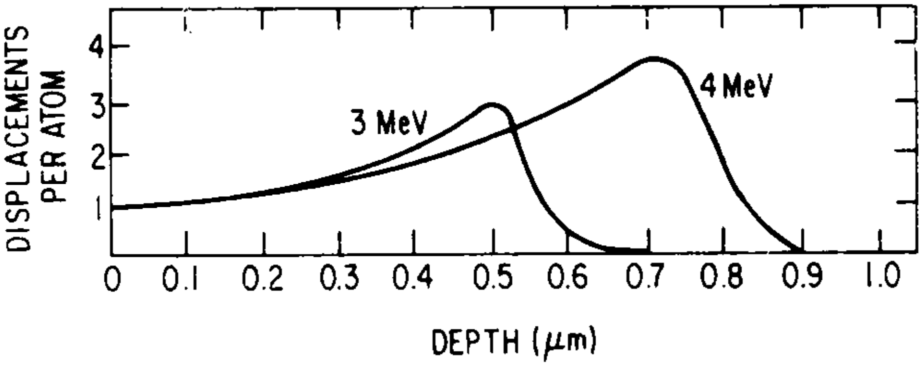

Fig. 7. Typical Damage Curves in a Metal After Bombardment with Heavy Ions in Two Different Energy Ranges.

Consider the damage curve shown in Fig. 8 for a stainless steel specimen bombarded with Ni ions. The goal of the microscopist is to prepare a TEM foil that contains the peak damage zone, between depths A and B (shaded). The first step is to remove material from the surface of the specimen to depth B by sectioning. The new surface is coated with lacquer and the specimen is back-thinned; i.e., material is removed from the surface opposite the ion-bombarded surface so as to produce a wedge-shaped specimen, shown schematically in Fig. 9. The shaded part of Fig. 9 represents the region of peak ion damage; only the part of the specimen to the left of the dashed line is thin enough to transmit the electron beam. Thus, the back-thinning step creates a surface ("S" in Fig. 9) that spans the entire region of interest, while the sectioning step is needed to make the specimen thin enough to transmit the electron beam.

Table IV. Electrolytes and Conditions Used for Surface Polishing of 3-mm-dia Foil Specimen by Jet Method

Material	Electrolyte	Temp., °C	Flow Rate[a]	Volts	Current, mA	Comments
Cu_3Au, Cu-25Au	5% $HClO_4$, 95% ethanol	-60	Medium	170	50	
Cu-40Ni (UHV annealed 875°C, 2 h)	30% HNO_3, 70% methanol	-60	Fast	40	100	
Cu-7Si, Cu-9Si (annealed)	30% HNO_3, 70% methanol	-60	Medium	20	70-100	
Au-50Cu	20% $HClO_4$, 80% ethanol	-40	Fast	50	75	Run pump 3-4 min to remove brown film.
Fe-Cr-Ni	20% $HClO_4$, 80% ethanol	-40	Fast	70	125	Matrix well polished, with some pits left by precipitates that fell out.
Fe-15Cr-20Ni (UHV annealed 1020°C, 1/2 h; He quenched)	20% H_2SO_4, 80% methanol	0	Medium	20	80	Swing nozzle slightly to produce flat surface.
Fe-Cr-Ni-Mo	20% $HClO_4$, 80% ethanol	-40	Fast	70	125	Matrix well polished, with some pits left by precipitates that fell out.
Fe-Cr-Ni-Mo-Si	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	Slow	50	140	Good precipitate retention.
Fe-Cr-Ni·Sc	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	Slow	30	85	Good precipitate retention.
Fe-Cr-Ni-Si	20% $HClO_4$, 80% ethanol	-40	Fast	70	125	Matrix well polished, with some pits left by precipitates that fell out.
Fe-Ni-Cr-P-B	20% $HClO_4$, 80% methanol	-40	Medium	30	75	
Nickel (pure, annealed)	20% $HClO_4$, 80% ethanol	-50	Medium	50	30	

Ni-1Al, Ni-1Mo (annealed)	20% $HClO_4$, 80% ethanol	-40	Slow	30	70	Adjust voltage to maintain indicated current.
Ni-12.7Al (annealed)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	0	Medium	40	125	Surface smooth and flat with precipitates retained.
Ni-6Al-6Si (annealed)	30% HNO_3, 70% methanol	-60	Fast	40	60	Grain boundaries smooth.
Ni-8Al-8Si	13% HCl, 87% methanol	-60	Medium	30	50	Use 3.2-mm jet-to-specimen distance.
Ni-12Al-12Si (annealed)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	-60	Fast	70	20	
Ni-40Nb (amorphous)	20% $HClO_4$, 80% methanol	-40	Slow	40	125	
Ni-1Pt (annealed)						
	(1) 30% HNO_3, 70% methanol	-60	Medium	45	120	Flat, evently polished surface; no grain-boundary attack.
	(2) 13% HCl, 87% methanol	-50	Medium	45	75	Grain boundaries smooth and visually undetectable up to 2 min of polishing time.
Ni-0.1Sc (annealed)	20% $HClO_4$, 80% ethanol	-60	Fast	80	70	Reduce current density by using longer nozzle-to-specimen distance, up to 5/16 in. (8 mm); swing nozzle slightly to produce flat surface.
Ni-1Si, Ni-2Si (annealed)	20% $HClO_4$, 80% ethanol	-40	Slow	50	45	
Ni-4Si (annealed)	30% HNO_3, 70% methanol	-60	Medium	20	75-100	Adjust voltage to maintain indicated current. Store used electrolyte in vented bottle.
Ni-6Si (annealed)						
	(1) 30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	Medium	30	75	Grains not polished to different heights.

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[a] Pump settings 2-4 = slow, 5-7 = medium, 8-10 = fast.

Table IV. Electrolytes and Conditions Used for Surface Polishing of 3-mm-dia Foil Specimen by Jet Method (Contd.)

Material	Electrolyte	Temp., °C	Flow Rate[a]	Volts	Current, mA	Comments
	(2) 30% HNO_3, 70% methanol	-60	Medium	20	75-100	Adjust voltage to maintain indicated current. Store used electrolyte in vented bottle.
Ni-6.5Si (annealed)	13% HCl, 87% methanol	-50	Slow	30	30	
Ni-4Si-.01Sc (annealed)	20% $HClO_4$, 80% ethanol	-40	Fast	70	120	
Ni-1Ti (annealed)	20% $HClO_4$, 80% ethanol	-40	Slow	30	70	Adjust voltage to maintain indicated current.
Pd-18Mo, Pd-18W (annealed)	10% $HClO_4$, 90% acetic acid	20	Slow	23	75	
Pd-18W	10% $HClO_4$, 90% acetic	20	Medium	23	75	
18-8 SS, 18-8 SS-1Si, 18-8 SS-1Ti (annealed)	20% $HClO_4$, 80% ethanol	-40	Medium	30	70	Adjust voltage to maintain indicated current.
316 SS (annealed)	20% H_2SO_4, 80% methanol	0	Initial: Fast Final: Medium	20 10	150 70	Use high current and pump speed at start to break up oxide layer; lower them for smooth final polish. Final current is critical parameter.
316 SS (annealed and aged)	20% $HClO_4$, 80% methanol	-60 (-40)	Medium	70 (30)	70	Values in ( ) give faster polishing. Current is critical parameter.
Ti-0.56Al (annealed), Ti-8.65Al (annealed)	30% HNO_3, 70% methanol	-50 -40	Fast Medium	30 30	100 75	Swing nozzle frequently to produce flat surface. Current is critical.
Ti-14.4Al	13% HCl, 87% methanol	-60	Medium	90	35	
Ti-6Al-4V	13% HCl, 87% methanol	-60	Slow	70	50	Use maximum jet height.
Ti-0.8Mo, Ti-4Nb, Ti-4Ta, Ti-20Zr	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	0	Medium	40	125	Use fresh solution.

Ti-13Sn	130 ml HCl, 100 ml butyl cellosolve, 670 ml methanol	-60	Fast	150	135	
Ti-3V (aged 688°C)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	0	Slow	40	140	Use fresh solution and jet-to-specimen distance of 3.5 mm.
Vanadium (pure, annealed)	20% H_2SO_4, 80% methanol	5	Slow	20	115	Do not reverse polarity of specimen (this would cause hydride formation).
V-15Cr-5Ti (annealed)	20% H_2So_4, 80% methanol	0	Slow	25	100	
Zr-0.2Au (annealed)	25 ml HCl, 425 ml methanol, 50 ml butyl cellosolve	-60	Fast	150	100	Increase voltage rapidly to avoid brown, anodized surface. Fast flow rate removes reaction products. Polished surface is clean but second phase and grain boundaries are clearly visible.
Zr-2.5Nb (annealed and aged 500°C, 21 days)	600 ml methanol, 15 g $ZnCl_2$, 45 g $AlCl_3$ $6H_2O$, 18 ml dist. water, 15 ml H_2SO_4	-60	Fast	100	75	Increase voltage slowly. Use specimen-to-nozzle distance of 1/16-1/8 in. (1.6-3.2 mm).
Zr-12.5Nb (annealed and aged 900°C, 30 min, + 450°C, 30 min)	20% $HClO_4$, 80% ethanol	-60	Fast	80	65	May also be effective treatment for Zr-2.5Nb.
Zr-11.6Ti	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	-55	Fast	70	35	Increase voltage slowly. A brown film forms, then floats off specimen. Leave voltage and pump on at end of polish cycle and swing nozzle aside to prevent etching. Rinse with methanol.

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[a] Pump settings 2-4 = slow, 5-7 = medium, 8-10 = fast.

Table IV. Electrolytes and Conditions Used for Surface Polishing of 3-mm-dia Foil Specimen by Jet Method (Contd.)

Material	Electrolyte	Temp., °C	Flow Rate[a]	Volts	Current, mA	Comments
Addendum: polishing procedures documented between mid-1981 and mid-1985						
Aluminum	10% $HClO_4$, 90% ethanol	-60	Fast	70	30	Excellent polish. Nozzle may be moved side to side slightly to produce more uniform surface.
Cu-1Au, Cu-7Be, Cu-40Ni, Cu-9Si	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	-50	Medium	40	75	Excellent polish. Sometimes necessary to start with fine scratches on surface rather than a high mechanical polish.
Germanium (polycrystal)	90 ml H_2SO_4, 30 ml HF, 500 ml methanol, 100 ml butyl cellosolve	-50	Fast	150	100	Good polish, but grains are polished at different rates.
Ni-10Al, Ni-0.7Au, Ni-10Cu	20% $HClO_4$, 80% ethanol	-50	Fast	80	75	Excellent polish.
Ni-12.7Al	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	Medium	80	125	Excellent polish. Precipitates appear level with matrix when viewed optically at 500x magnification.
Ni-4Al-4Ge, Ni-8Al-4Ge, Ni-8Al-8Ge	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	Fast	50	125	If etching occurs at edge of disc, increase pump speed and adjust specimen surface until level with top of retaining cap.
Ni-6Al-6Si	30% HNO_3, 70% methanol	-60	Fast	40	60	Excellent polish with smooth grain boundaries.
Ni-8Al-8Si	130 ml HCl, 870 ml methanol, 60 ml butyl cellosolve	-60	Medium	60	50	Two-phase material. Butyl cellosolve causes both phases to be polished at the same rate.

Ni-12Al-12Si	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	-60	Fast	70	20	Excellent polish. Dendritic structure.
Ni-9.5Si	13% HCl, 87% methanol	-60	Medium	80	50	Excessive pump speed results in a "textured" surface on some grains. Addition of 30 ml of butyl cellosolve results in smooth grains but causes them to be polished at different rates.
Niobium	65 ml HCl, 20 ml HF, 435 ml methanol, 25 ml butyl cellosolve	-60	Medium	190	65	Excellent polish without oxide formation on surface.
Silicon <110>	90 ml H_2SO_4, 30 ml HF, 500 ml methanol, 100 ml butyl cellosolve	-60	Fast	80	40	Excellent polish. For material with <111> orientation, use chemical polish of 25% HF, 75% HNO_3 at 20°C.
Tantalum	90 ml H_2SO_4, 30 ml HF, 500 ml methanol, 100 ml butyl cellosolve	-50	Fast	150	100	Excellent polish. Use 5-mm nozzle-to-specimen distance. High voltage-to-current ratio improves result.
V-15Cr-5Ti	100 ml H_2SO_4, 400 ml methanol, 90 ml butyl cellosolve	0	Medium	40	150	Good to excellent polish. Move nozzle side to side slightly to prevent streaks from slower polishing of precipitates.
V-20Ti	10% H_2SO_4, 90% methanol	-40	Medium	30	80	Temp. and current are critical. Polish only 20 to 30 seconds to minimize uneven grain boundaries.

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[a] Pump settings 2-4 = slow, 5-7 = medium, 8-10 = fast.

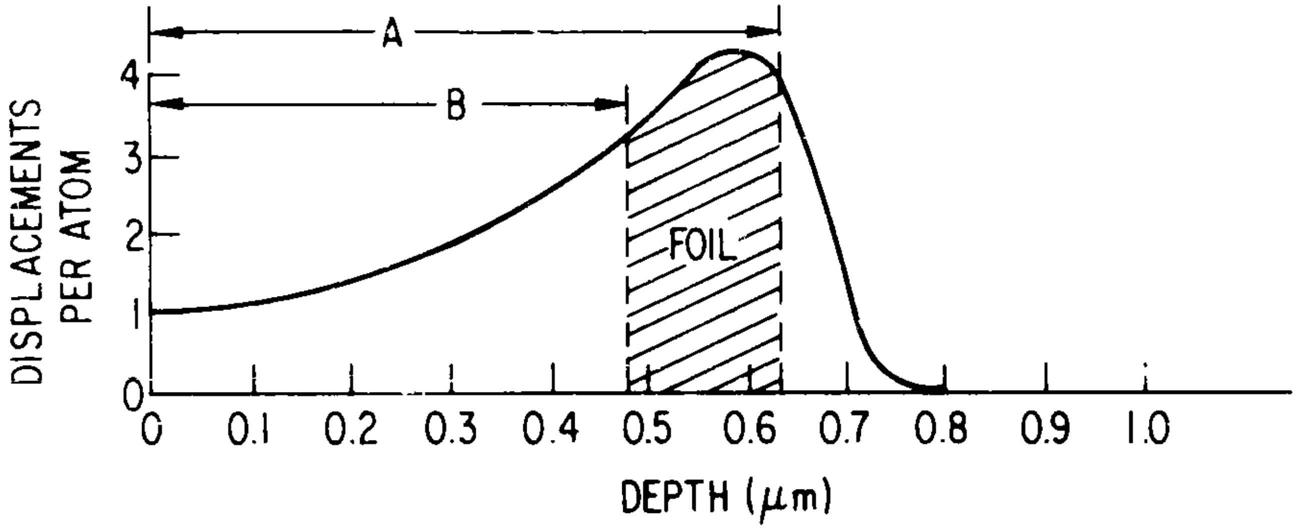


Fig. 8. Portion of Ion-damaged Zone Included in a Typical TEM Foil after Sectioning to Near Peak Damage. Peak damage zone (shaded) lies between depths A and B.

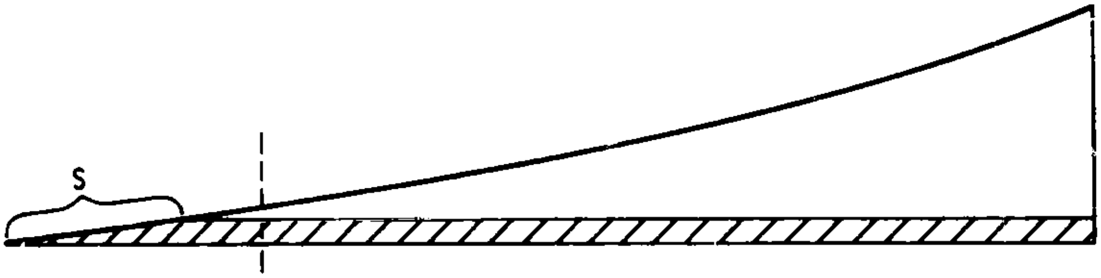


Fig. 9. Schematic Cross Section of Wedge-shaped TEM Foil. Region S of the thinned surface spans the peak damage zone (shaded).

B. Factors Influencing Removal Rate

The removal of metal by electropolishing occurs more rapidly in specimens that contain a large volume fraction of voids caused by radiation or heavy-ion damage. The removal rate will usually be greatest at the peak damage depth in the material. At that depth, the actual metal surface area in contact with the polishing film is reduced. Therefore, the current density per unit of specimen area in contact with the film increases and the overall removal rate increases.

In contrast, a slower than normal removal rate may occur for specimens having a large volume fraction of precipitates. This is because (1) the precipitates are polished at a slower rate than the matrix, and (2) if the precipitates are sufficiently close together, the comparatively thick surface film formed by the electrolyte will tend to bridge across from one precipitate to the next, so that the film cannot make contact with the matrix until the height of the precipitates is reduced. However, proper choice of solutions and other parameters can result in a nearly smooth surface on materials containing precipitates.

When material removal by either the beaker or the jet method is plotted against polishing time, the curve usually shows a faster initial removal rate. For this reason, test runs should be made on the material of interest and the results plotted to determine the polishing time that will remove the desired amount. The slower the polishing rate, the more accurate this calibration will be; when two solutions will polish a specimen equally well, the slower one is the best choice for accurate sectioning, while the faster one may be used for thinning to save time.

Another good way to increase the accuracy of sectioning by either the beaker or the jet method is to use two stages of material removal, with the first stage timed to achieve about half the total removal desired. The amount removed is then determined, and the polishing time for the final stage can be adjusted as necessary. In this way any change of parameters is calibrated directly on the specimen, and rate variations due to the factors discussed above are accounted for.

C. Measurement of Sectioning Depth

Before a 3-mm disc specimen is sectioned, part of the surface is coated with fresh Microshield lacquer, using a #1 artist's brush. The specimen is then placed in a stirred or pumped bath in the orientation shown in Fig. 10, and electropolished as described in Section III.D (below).

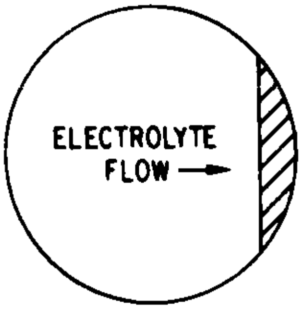


Fig. 10. Schematic of Disc Specimen During Sectioning, Showing Orientation of Interface Between Lacquer-coated (Shaded) and Uncoated Regions.

The relative size of the lacquered area is important. The interface between the protected and unprotected regions must not be too near the center of the disc because perforation of the protected area upon back-thinning would produce a surface containing the wrong information. However, if the interface is too far from the center, the measured removal rate will reflect the rate at the edge of the specimen; this is usually considerably different from the removal rate in the central area, which is of greatest interest. Also, the lacquer film should be thin so that the flow of electrolyte over the leading edge is as unimpeded as possible. This results in better reproducibility and minimizes trapping of gas bubbles, which can cause pitting or etching along the interface.

After electropolishing, the specimen is washed in acetone to dissolve the lacquer, and rinsed three times with ethanol. A small droplet of water is placed on a microscope slide and the specimen is lowered onto it. Surface tension holds the specimen in place. The slide and specimen are then inverted and placed on the stage of a Zeiss two-beam interference microscope equipped with a tungsten light source. This instrument makes non-contact measurements of surface flatness or step heights by measuring the shift of interference fringes reflected from the surface of the specimen. For maximum accuracy with this technique, the unprotected region of the specimen surface must be uniform, flat, and highly polished.

Figure 11 is a schematic representation of the image obtained when the microscope is properly focused and adjusted at a magnification of about 300X. (The image can also be photographed.) The curved line represents a small portion of the interface between the protected and electropolished regions. The horizontal lines represent interference fringes between the specimen and a reference mirror in the microscope. The fringe spacing (distance between adjacent fringes) is one half the wavelength of tungsten light, or about 3,000 Å (300 nm). The line nearest the center of each set of fringes is black, while the others show a rainbow-like array of colors. The amount of material removed by the electropolish is determined from the vertical distance, or fringe shift, between lines of the same color on opposite sides of the interface: a shift of one full fringe spacing indicates a removal of 3,000 Å (300 nm). Thus, the shift shown in Fig. 11 indicates a step height of 1500 Å (150 nm). Other interference microscopes, such as the Model M 307 microinterferometer (Gaertner Scientific Co., 1201 Wrightwood Avenue, Chicago, Illinois), should also be suitable for measuring section depths.

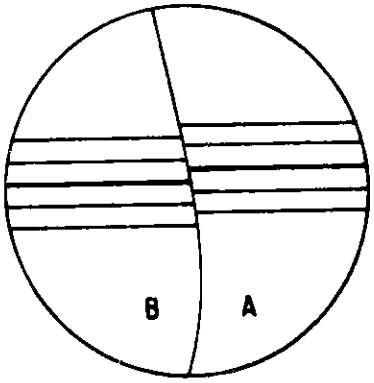


Fig. 11. Interference Fringe Shift at Interface Between Protected (A) and Electropolished (B) Regions of Specimen Surface.

D. Methods and Results

1. Sectioning by Beaker Method

The apparatus described in Section II.B.1 was modified for sectioning by the addition of a timer-operated relay to supply brief pulses (as short as 0.1 s) of current to the specimen. A voltage-regulated power supply with a capacity of at least 1 A was used. Figure 12 is a schematic of the apparatus; sectioning conditions and removal rates for various specimens are shown in Table V. Removal of material to within ±300 Å (30 nm) of the desired depth can be achieved with this method.

2. Sectioning by Jet Method

Sectioning by the jet method produces very consistent results because the electrolyte can be pumped onto the specimen at a controlled rate, and bubbles are swept away before they can interfere with electropolishing. The polishing

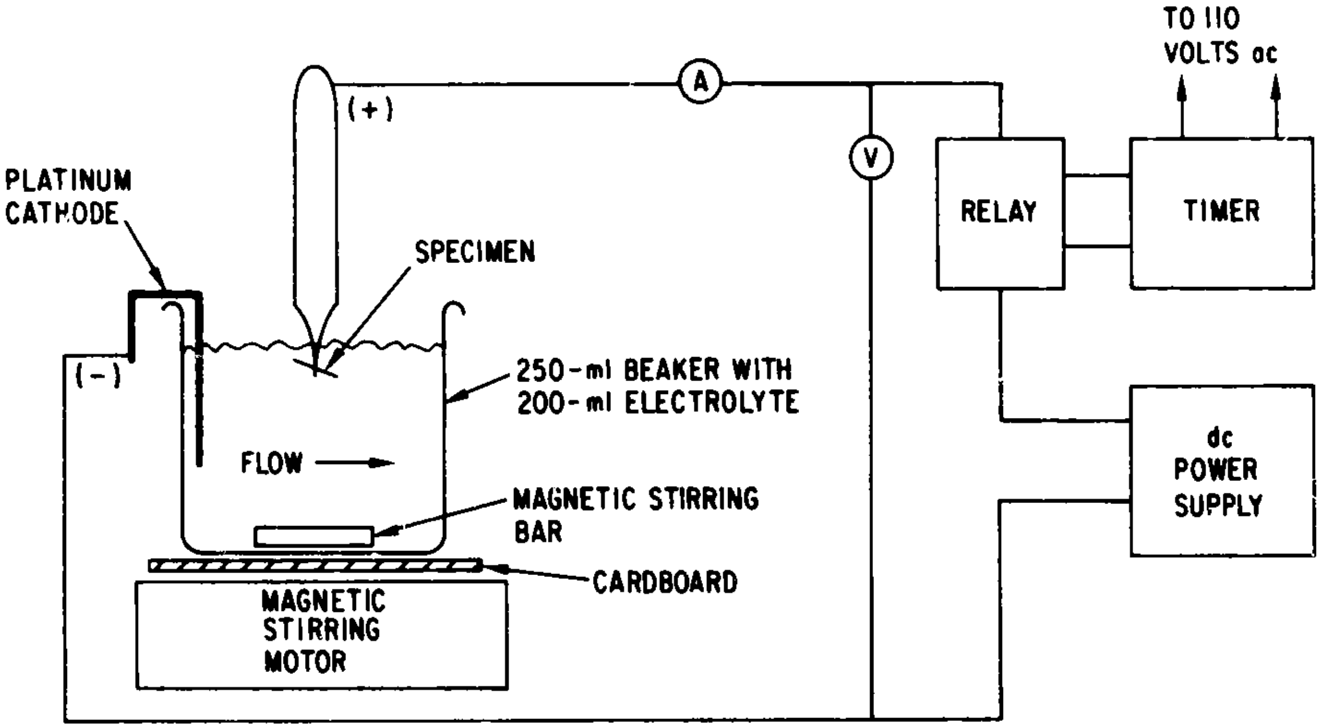


Fig. 12. Schematic of Apparatus for Sectioning by Beaker Method.

time for jet sectioning is usually under two seconds; the slightly greater polishing rate at the center of the specimen is not detectable by interference microscopy of test specimens dotted with lacquer at various positions on the surface. Thus, for practical purposes, the removal rate may be considered uniform across the entire specimen.

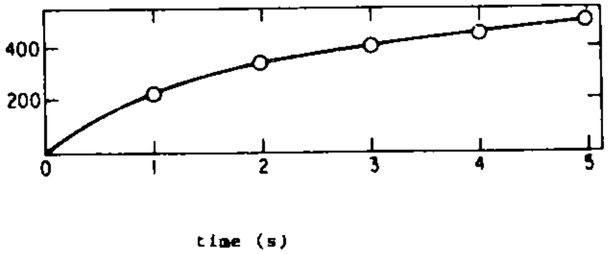
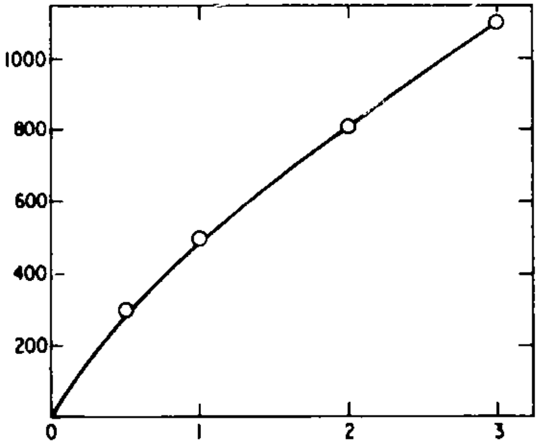
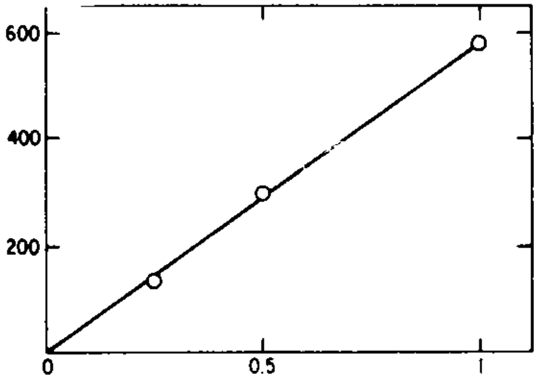
The Model 550 B jet instrument described in Section II can be used for sectioning with only one modification, i.e., the addition of a junction box (shown in Fig. 13) between the jet head assembly and the control box. This allows dc power from an external source to be connected by a timer and relay to the jet head assembly. Only the pump is powered directly by the control cabinet. A schematic of the complete system is shown in Fig. 14.

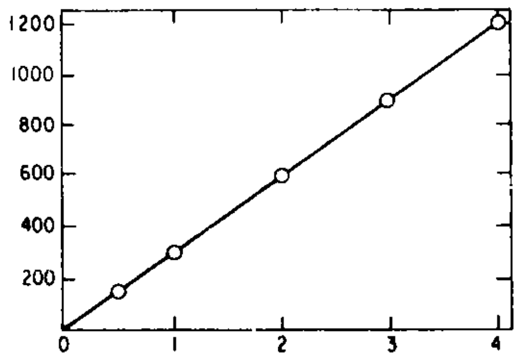
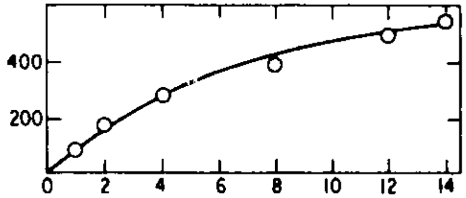
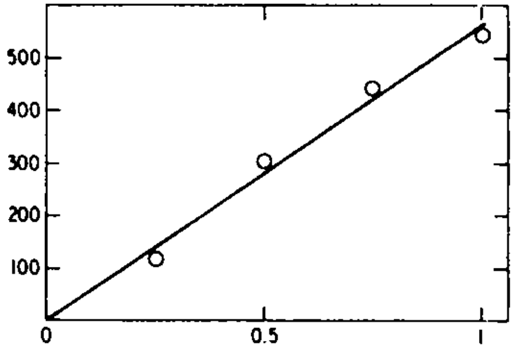
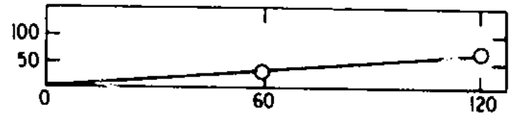
The timer and relay have the same requirements as for beaker sectioning, i.e., the ability to time intervals ranging from 0.1 second to several seconds and a relay capacity of several A to ensure long life and good reproducibility. The specimen is held in the same configuration as for jet surface polishing (Fig. 6), and the 3-mm nozzle described earlier is used.

The jet technique is especially convenient because once optimal surface-polishing conditions are known for a given specimen, sectioning requires only a few test runs to determine the proper timing. In most cases, the specimen can also be jet thinned (see below) with the same electrolyte and voltage used for surface polishing and sectioning.

Table VI gives conditions and removal-rate data for jet sectioning of a variety of 3-mm-diameter specimens.

Table V. Sectioning of 3-mm-dia Foil Specimens by Beaker Method: Electrolytes, Conditions, and Results

Material	Electrolyte	Temp., °C	Orientation[a]	Stir Rate[b]	Volts	Current, mA	Depth of Material Removed (nm) vs Polishing Time (s)
A286 (annealed)	20% H_2SO_4, 80% methanol	5	HD	Medium	As reqd.	200	
A286 (annealed and aged)	10% $HClO_4$, 90% ethanol	0	HD	Medium	As reqd.	475	
A286 (aged and cold worked)	10% $HClO_4$, 90% ethanol	-60	HD	Medium	210 (no load)	400	

Aluminum, Al-3Cu, Al-1Mg, Al-1Zn	10% $HClO_4$, 90% ethanol	-60	V	Medium	As reqd.	425	
D979 (annealed)	20% H_2SO_4, 80% methanol	0	HD	Medium	10	100	
D979 (cold worked)	10% $HClO_4$, 90% ethanol	-60	HD	Medium	235 (no load)	350	
Gold (pure)	465 ml acetic acid, 87.5 g CrO_3, 25 ml dist. H_2O	10	HD	Fast	30	50	

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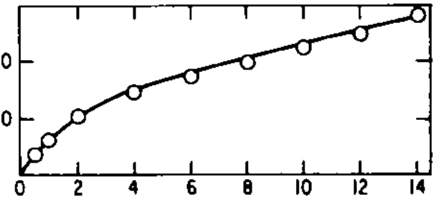
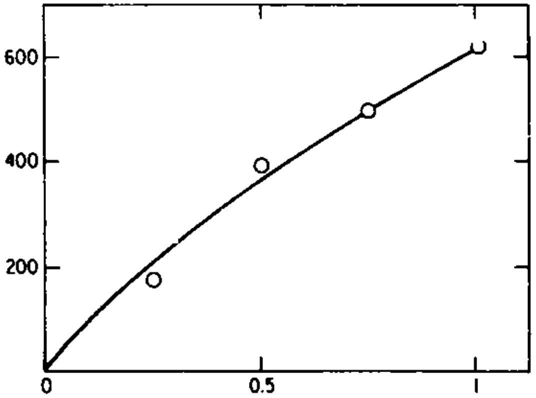
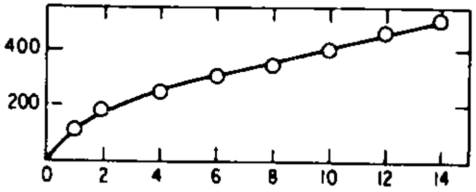
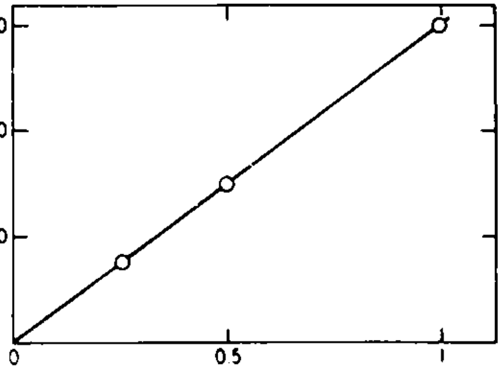
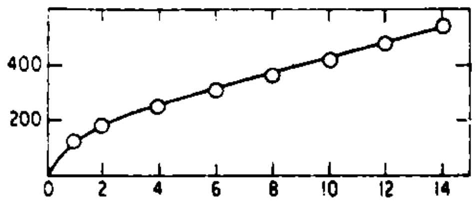
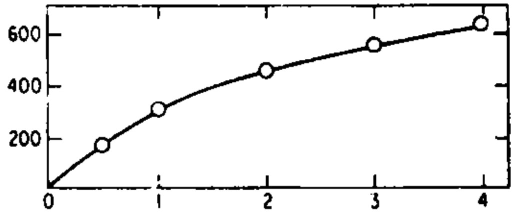
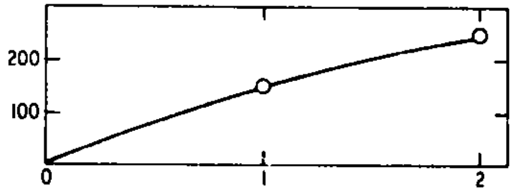
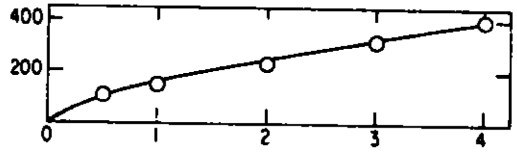
[a] As defined in Table I.
[b] As defined in Section II.B.1.

Table V. Sectioning of 3-mm-dia Foil Specimens by Beaker Method: Electrolytes, Conditions, and Results (Contd.)

Material	Electrolyte	Temp., °C	Orientation[a]	Stir Rate[b]	Volts	Current, mA	Depth of Material Removed (nm) vs Polishing Time (s)
Incoloy 901 (annealed)	20% H_2SO_4, 80% methanol	0	HD	Medium	10	100	
Incoloy 901 (annealed and bombarded with Ni^+ at 700-800°C)	10% $HClO_4$, 90% ethanol	-60	HD	Medium	235 (no load)	350	
Incoloy 901 (aged)	20% H_2SO_4, 80% methanol	0	HD	Medium	10	100	
Inconel 625 (annealed and bombarded with Ni^+ at 700-800°C	10% $HClO_4$, 90% ethanol	-60	HD	Medium	235 (no load)	350	

Inconel 625 (20% cold worked)	20% H_2SO_4, 80% methanol	0	HD	Medium	10	100	
Inconel 722X (annealed)	10% $HClO_4$, 90% ethanol[c]	-60	V	Medium	As reqd.	275	
Fe-15Cr-20Ni	20% $HClO_4$, 80% ethanol	-60	HD	Medium	70	200	
Nickel (annealed)	20% H_2SO_4, 80% methanol	20	HD	Medium	23	150	

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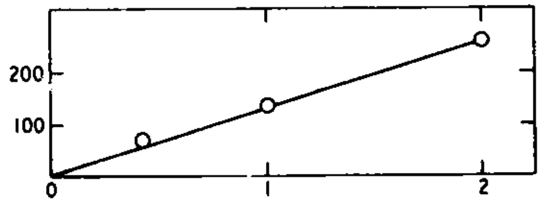
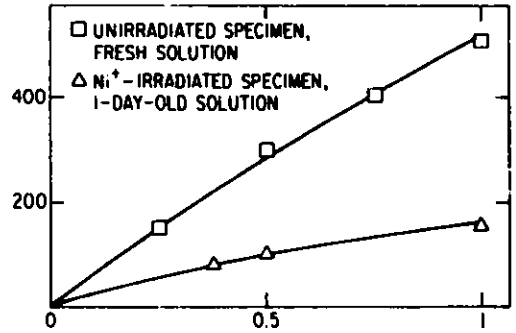
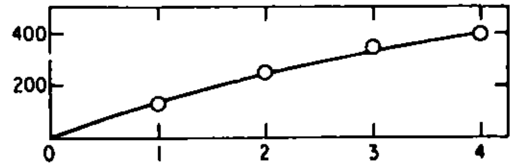
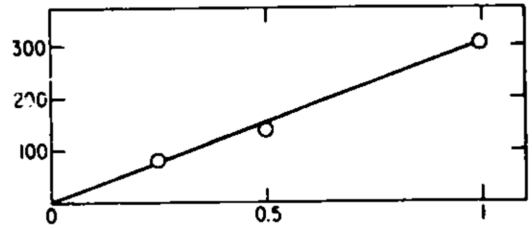
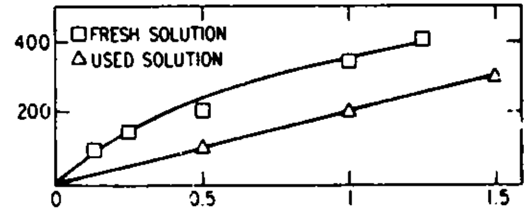
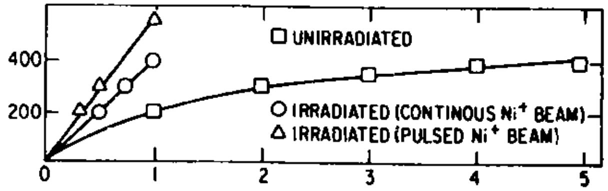
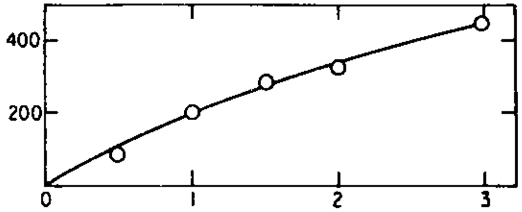
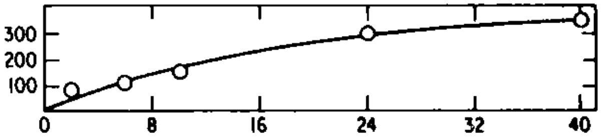
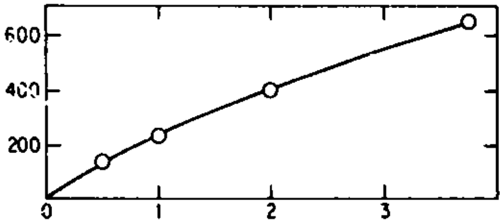
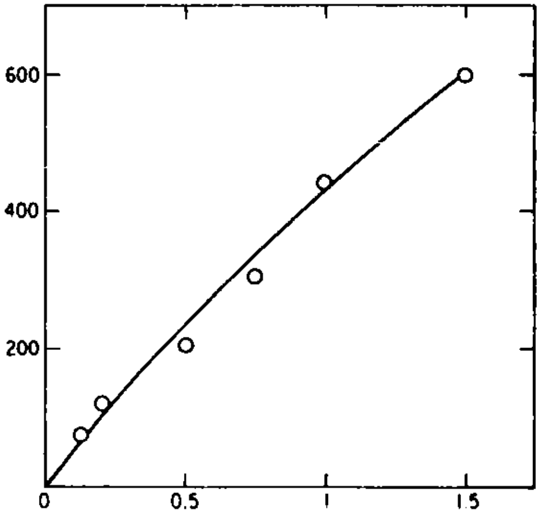
[a] As defined in Table I.
[b] As defined in Section II.B.1.
[c] High viscosity of electrolyte necessitated use of 500-ml beaker.

Table V. Sectioning of 3-mm-dia Foil Specimens by Beaker Method: Electrolytes, Conditions, and Results (Contd.)

Material	Electrolyte	Temp., °C	Orientation[a]	Stir Rate[b]	Volts	Current, mA	Depth of Material Removed (nm) vs Polishing Time (s)
Ni-6.35Al[d] (annealed or aged)	20% $HClO_4$, 80% ethanol	-60	HC	Medium	80	200	
Ni-14Al (with γ precip.)	20% $HClO_4$, 80% ethanol	-50	HC	Medium	95	350	
Ni-0.3Be (annealed)	20% H_2SO_4, 80% methanol	0	HD	Medium	27.5	300	
Ni-4Si (annealed)	13% HCl, 87% methanol	-60	HD	Fast	110	400	
Ni-6.5Si (aged)	13% HCl, 87% methanol	-60	HD	Fast	90 (no load)	300	

Nickel, Ni-1Ti, Ni-0.5Ti-1Si (annealed)[c]	40% H_2SO_4, 60% methanol	22	HD	Medium	△, □:23 ○:27	△, □:250 ○:450	
Ni-8.75Ti[c]	20% $HClO_4$, 80% ethanol	-60	HU	Medium	90[d]	175	
PE-16 (annealed)	10% $HClO_4$, 90% ethanol	-60	HD	Medium	50	40	
PE-16 (annealed or aged)	20% H_2SO_4, 80% methanol	0	HD	Medium	40	400	
PE-16 (annealed and aged)	20% $HClO_4$, 80% ethanol	-10 to -15	HD	Medium	50	400	

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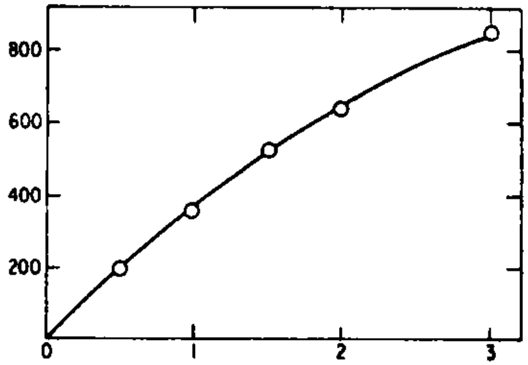
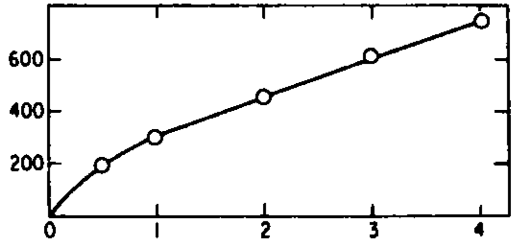
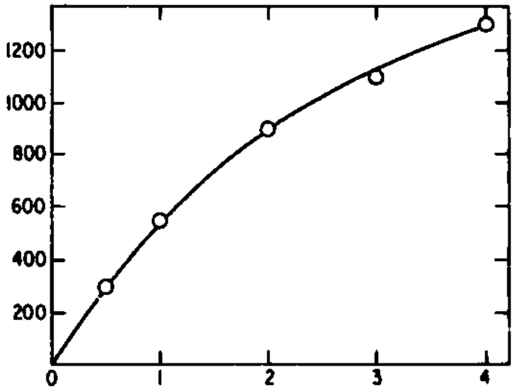
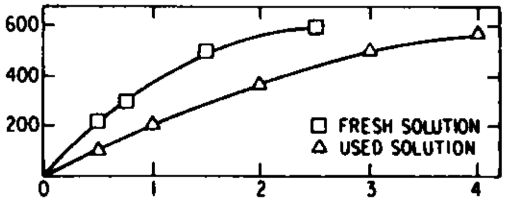
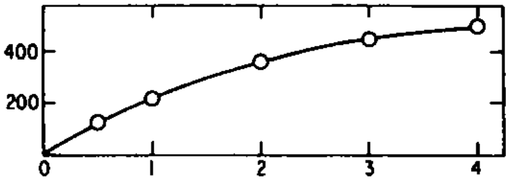
[a] As defined in Table I.
[b] As defined in Section II.B.1.
[c] High viscosity of electrolyte necessitated use of 500-ml beaker.
[d] Polishing intervals <1 s give best results. Use 86 V on irradiated material.

Table V. Sectioning of 3-mm-dia Foil Specimens by Beaker Method: Electrolytes, Conditions, and Results (Contd.)

Material	Electrolyte	Temp., °C	Orientation[a]	Stir Rate[b]	Volts	Current, mA	Depth of Material Removed (nm) vs Polishing Time (s)
18-8 SS-1Cu	10% $HClO_4$, 90% ethanol	20	HD	Medium	As reqd.	300	
18-8 SS-1Mn	20% H_2SO_4, 80% methanol	20	HD	Medium	As reqd.	600	
18-8 SS-1Pt	10% $HClO_4$, 90% ethanol	5	HD	Medium	As reqd.	500	

316 SS	20% H_2SO_4, 80% methanol	20	HD	Medium	20	400 320	
Vanadium, V-1Ti, V-15Cr (annealed)	20% H_2SO_4, 80% methanol	20	HD	Medium	20	400	

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[a] As defined in Table I.

[b] As defined in Section II.B.1.

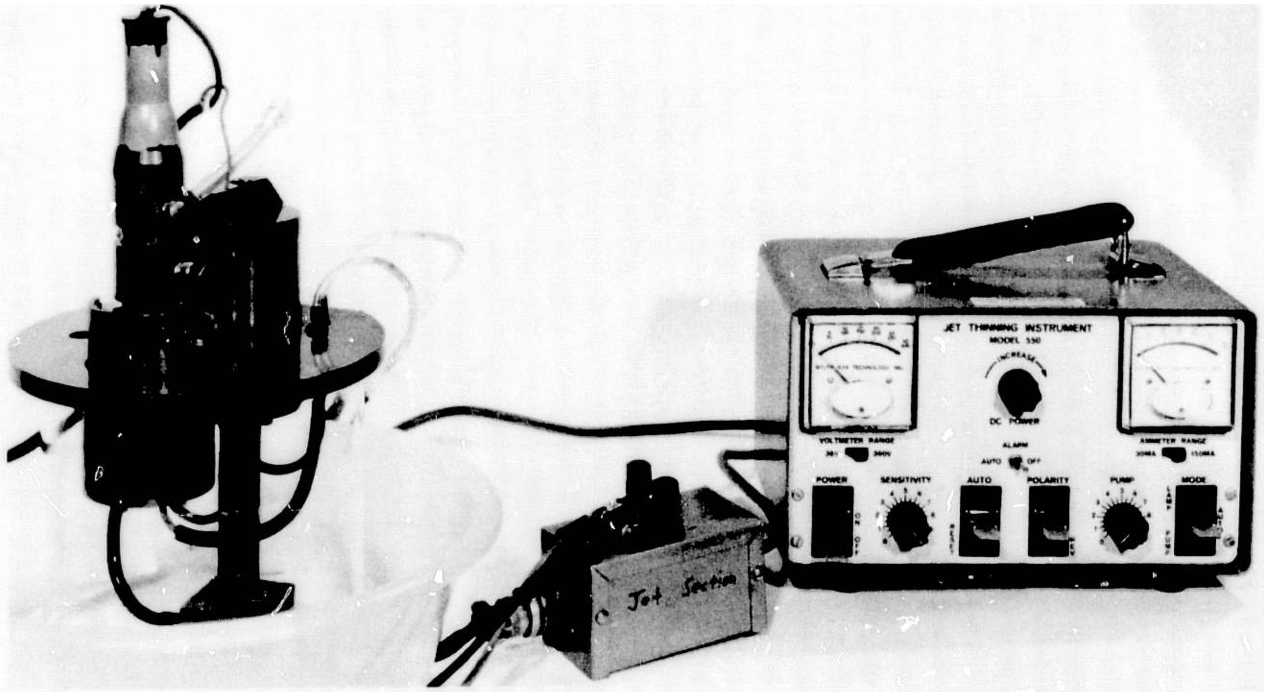


Fig. 13. Apparatus for Sectioning by Jet Method. ANL Neg. No. 306-80-233.

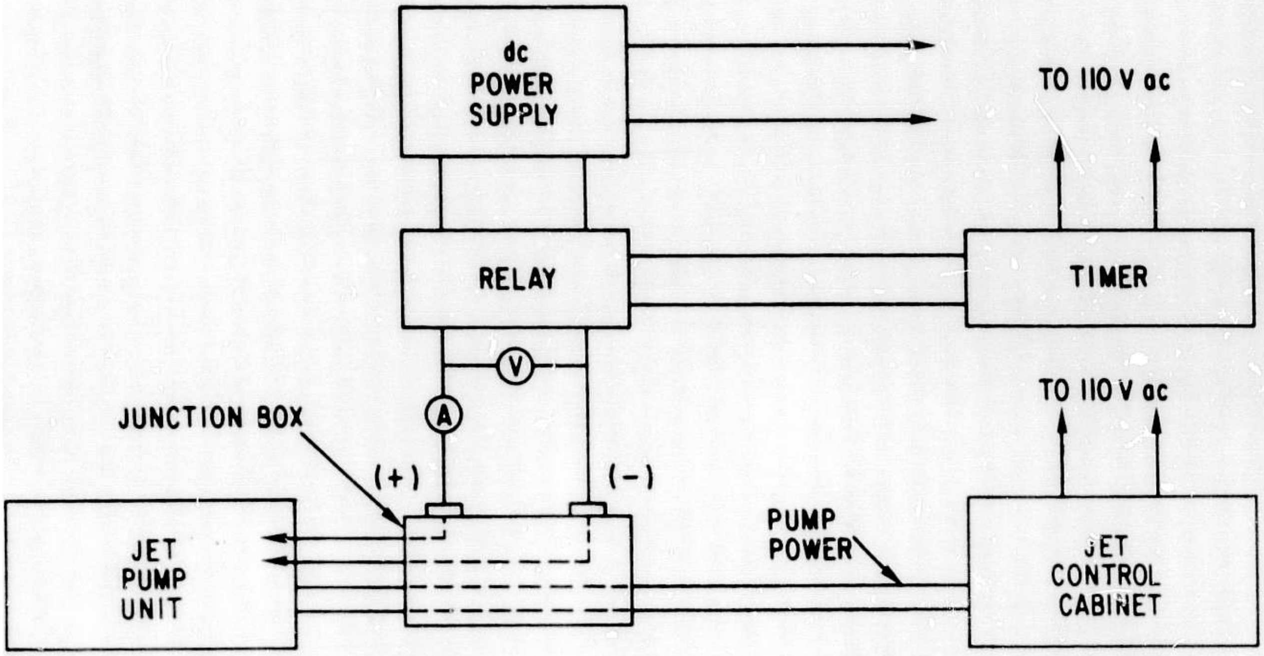


Fig. 14. Schematic of Jet Sectioning Apparatus.

3. Thinning by Jet Method

To convert the jet instrument from the sectioning to the thinning mode, a 1.5-mm nozzle with light-pipe centering ring is substituted for the larger nozzle described in Section II.B.2, and the junction box is removed from the circuit. A polyethylene diaphragm is used as a specimen retainer. When the narrow-bore nozzle is used, the electropolishing procedure produces a concavity, or dimple, in the specimen. Unless the instrument is shut off manually, removal of material continues until the specimen is perforated; light (usually infrared) can then pass through the perforation to a photocell, automatically shutting off both the electrolyte pump and the polishing current. At shutoff, excess current is "dumped" through a resistor to prevent arcing, which could ignite flammable polishing solutions.

With the aid of a stereo microscope, the electropolished side of the specimen to be thinned is coated with Microshield lacquer; the rim is left uncoated to allow good contact with the pedestal mount. A #1 or smaller artist's brush is used. For best results, the lacquer should be dispensed from a 1-oz bottle, which is refilled at least every two weeks with a fresh aliquot from the one-gallon shipping container. This obviates the need to thin the lacquer, which might cause it to loosen at -60°C. After it is dipped in the lacquer, the brush is pressed against the side of the bottle a few times to wet all the bristles and squeeze out excess lacquer. This should be done gently to avoid depositing air bubbles on the specimen; bubbles can trap acid, which causes etching upon perforation. Any lacquer inadvertently brushed onto the rim should be allowed to dry slightly and then, while still pliable, carefully pushed toward the center with a pointed tweezer until the entire rim is clear. The specimen is then mounted in the jet instrument with the uncoated side toward the nozzle.

The dimple shape can be controlled by changing the distance from the jet nozzle to the specimen. The desired flat dimple bottom is shown schematically in Fig. 15a. Too great a nozzle-to-specimen distance will result in a more V-shaped dimple (Fig. 15b), while too little distance will result in a small hump in the center of the dimple (Fig. 15c). Increasing the electrolyte flow rate will cause a deeper dimple center when other parameters are kept constant. Specimen thickness also affects dimple shape; the dimple produced in a specimen $\gtrsim$ 0.4 mm thick will generally be V-shaped, with little thin area around the perforation.

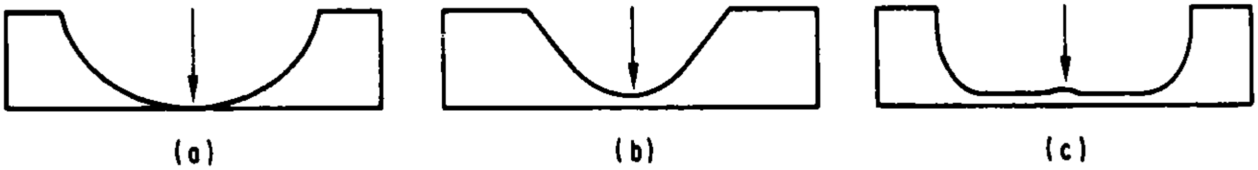
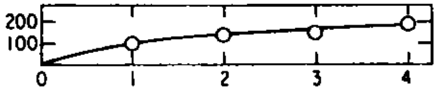
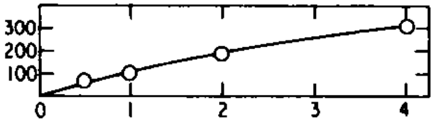
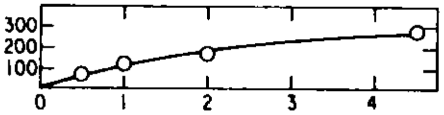
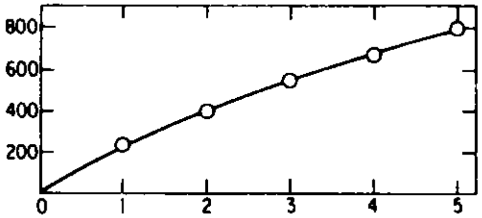
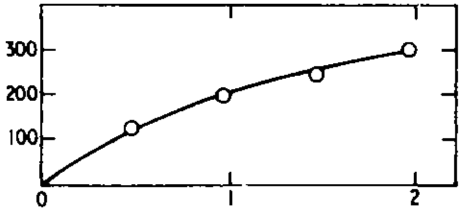
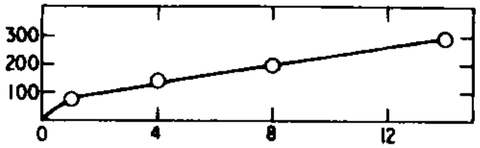


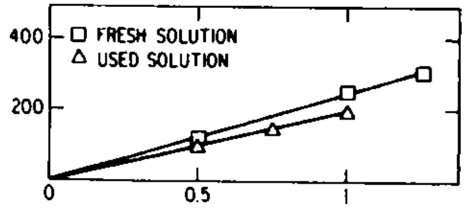
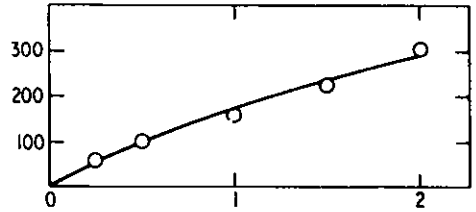
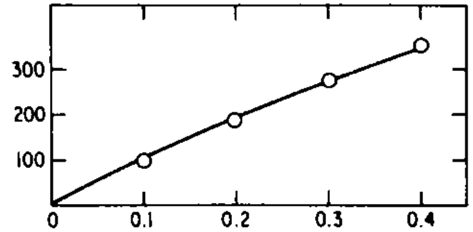
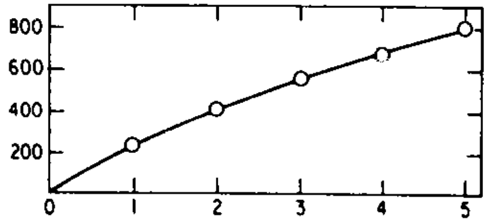
Fig. 15. Dimple Shapes Produced When Nozzle is (a) At Correct Distance, (b) Too Far, and (c) Not Far Enough from Specimen. Arrow indicates flow of electrolyte.

Pure metals usually require less voltage and current for a good polish than alloys of the same metals. As the percentage of alloying elements increases, a higher voltage and current and a faster electrolyte flow are required to sweep away the increased quantity of gas bubbles from the specimen surface.

Conditions used to thin various specimens by jet electropolishing are given in Table VII.

Table VI. Sectioning of 3-mm-dia Foil Specimens by Jet Method: Electrolytes, Conditions, and Results

Material	Electrolyte	Temp., °C	Jet Height, mm	Flow Rate^a	Volts	Current, mA	Depth of Materials Removed (nm) vs Polishing Time (s)
CE 3177	20% $HClO_4$, 80% ethanol	-60	3.17	Fast	80	75	
Cu-40Ni	30% HNO_3, 70% methanol	-60	4.76	Fast	40	100	
Ni-10Cu	20% $HClO_4$, 80% ethanol	-60	4.76	Fast	80	75	
Ni-40Nb (amorphous)	13% HCl, 87% methanol	-60	3.17	Medium	200	120	
Ni-23.8Si	13% HCl, 87% methanol	-45	4.76	Medium	50	60	
304 SS (cold worked)	20% $HClO_4$, 80% ethanol	-60	4.76	Fast	80	50	

316 SS (annealed)	20% H_2SO_4, 80% methanol	20	3.17	Fast	20	120	
Ti-14.4 Al (annealed)	13% HCl, 87% methanol	-60	3.17	Medium	60	70	
Ti-6Al-4V, Ti-811 (annealed)	20% $HClO_4$, 80% methanol	-60	3.17	Fast	100	200	
Ti-15333	13% HCl, 87% methanol	-60	3.17	Medium	200	120	

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[a] As defined in Table III.

Current to the specimen sometimes decreases during thinning, especially at -60°C, with resultant etching (see Fig. 1). The cause may be a loose pedestal mount (hex base) or diaphragm. If adjusting these parts does not solve the problem, the rim of the specimen is probably corroded. The specimen should be unmounted, rinsed in alcohol, and dried with a cool air flow to avoid scorching the lacquer. With the aid of a stereo microscope and sharp tweezers, small scratches are made on the rim of the specimen to expose fresh metal for contact on the pedestal mount. The specimen is then remounted. If a very cold electrolyte is being used, the holder should be chilled by running the pump briefly, and then retightened; finally, the pump and electrical power are readjusted to the desired levels.

The Model 550 B jet instrument may also be used to thin a specimen from both sides. The first side is thinned until the dimple extends about halfway through the specimen. The specimen is cleaned with acetone followed by ethyl alcohol, dried with a warm air blower, and placed on a glass slide with the dimpled side up. (A piece of double-faced masking tape may be used to fasten the specimen to the slide, but care must be taken not to press the specimen so firmly against the tape that it retains adhesive, which would interfere with subsequent electropolishing.) The slide with specimen is placed on a stereo microscope stage and a thin dot of Microshield lacquer is applied to the dimpled surface only. After drying, the specimen is mounted with the unlacquered side toward the nozzle and thinned to perforation.

After perforation, the singly or doubly thinned specimen is rinsed well with alcohol and then soaked in a gently stirred dish of acetone for at least 5 minutes to remove the lacquer. A second 5-minute soak in fresh acetone is desirable. The specimen is then immersed in three successive ethanol baths. The tweezer should be removed from the specimen in each dish to allow capillary action to clean the tweezer tips. The specimen is then grasped crosswise between the tweezer tips, lifted out of the last alcohol bath, and held with the tweezers below it while excess alcohol is drawn off with a small Kimwipe or similar tissue. Finally, the specimen is dried with a stream of warm air. Both sides of the finished specimen are examined at 200X in a metallurgical microscope. If any stains are seen, the specimen is recleaned. Otherwise, the stains would be permanantly scorched onto it by the electron beam of the TEM.

Specimens should be stored in labeled containers that will protect them from mechanical damage and contamination. Small polyethylene vials, or gelatin capsules inside glass vials, work well.

3. Chemical Thinning

Certain materials, such as silicon and MgO, may be thinned with the Model 550 B jet instrument by chemical action alone. Since some of the solutions used for chemical thinning contain strong acids such as HF, instrument components that are easily corroded should not be used. The quartz light pipes are usually replaced by sapphire rods. The stainless steel nozzle, pedestal mount post, and specimen pedestal are replaced by parts made of plastic, and a polyethylene tank is used to hold the polishing solution. (All of the above parts are available from South Bay Technology, Inc.) The 3-mm-diameter disc specimen is secured to a 4-mm-diameter Mylar disc (South Bay Technology, Inc.) with lacquer or beeswax. The Mylar disc is then placed in a recess in the top of the PVC specimen mount. A perforated polyethylene diaphragm, sized for 2.3-mm specimens, is placed over the disc with the hole centered over the specimen, and held in place by sliding a standard O-ring-type retainer down over it.

(a) Silicon. Because silicon is transparent to infrared light, a green LED light source is substituted for the infrared LED in the jet head assembly. Since the green LED operates on the same current as the standard infrared LED, the control-cabinet circuit does not need to be modified. The silicon specimen is slightly transparent to the green light, so automatic shutoff can be obtained before perforation by adjusting the brightness of the LED with the sensitivity knob on the front of the control box; this minimizes formation of bend contours in the specimen. Shutoff will occur when the specimen is still 1 to 1.5 μm thick if the green LED is operated at full brightness (a sensitivity setting of 10). With a lower sensitivity setting, shutoff will occur closer to perforation. The specimen can be thinned further by holding it in the electrolyte stream with tweezers for about one second at a time. The specimen is immediately washed with water and then alcohol, dried, and inspected at 200X magnification with backlighting. This will reveal a thin area that transmits visible light, which appears as a reddish glow. When the specimen is ~ 300 nm thick, the transmitted light becomes yellowish. At this point, the backlight is switched off and the specimen is illuminated through the objective lens. When the specimen thickness is reduced to ~ 100 nm, circular interference fringes are observed (reduction of the light intensity enhances their visibility). Further details of the procedure for chemical thinning of silicon are summarized in Table VIII.

(b) MgO. MgO is transparent to both red and green light. In order to obtain automatic shutoff with the standard infrared light source, the edge and one flat surface of the 3-mm disc specimen are coated with a layer of vapor-deposited aluminum. (Specimens that have been bombarded with heavy ions are coated on the irradiated surface.) The aluminized surface and edge are then sprayed uniformly with clear Krylon lacquer and allowed to dry overnight. Finally, a layer of Microshield lacquer is painted on the coated surfaces. The three layers are shown in Fig. 16.

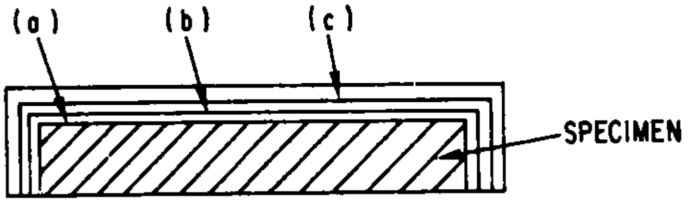

Fig. 16. Schematic Cross Section of MgO Specimen with Aluminum Coating (a), Protected by Clear Krylon Lacquer (b) and Acid-resistant Microshield Lacquer (c).

The uncoated surface may be carefully scratched with a sharp tweezer to break any lacquer film that is present. The specimen is then mounted on a 4-mm Mylar disc, coated side down, by applying Microshield lacquer around the edges and partway over the uncoated top surface as shown in Fig. 17. Only the unlacquered area will be exposed to the jet. A diaphragm normally used for thinning 2.3-mm specimens is used in the first stage of polishing.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimens

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
A286	10% $HClO_4$, 90% ethanol	0	4.7	3.5	150	110	
A286 (annealed)	20% H_2SO_4, 80% methanol	0	3.9	5.5	45	65	
A286 (annealed and aged)	20% H_2SO_4, 80% methanol	20	3.9	5.5	30	70	No flow marks; good retention of precipitates.
Aluminum (pure)	20% $HClO_4$, 80% ethanol	-60	3.9	6	90	10-12	
Al-0.25Ge (annealed 600°C, 3h + 150°C, 24 h; water quenched)	20% $HClO_4$, 80% ethanol	-60	3.9	2-4	40-50	10	Rinse quickly with ethanol after shutoff. If pitting occurs, lower voltage and current.
Al-9.5Mg (annealed 488°C, 1 h)	20% $HClO_4$, 80% ethanol	-60	4.7	2-4	As reqd.	100	Narrow voltage and current ranges. Electrolyte flow over specimen should resemble an "inverted mushroom".
Al-1Ag	20% $HClO_4$, 80% ethanol	-60	4.7	10	80	15-20	Use solution on pure Al first to pick up ions. After shutoff, rinse specimen with ethanol + methanol + ethanol.
Beryllium	25 ml HNO_3, 5 ml H_2SO_4, 5 ml HCl, 165 ml ethylene glycol, 335 ml ethyl alcohol	0	4.7	3.5	85	70	Current is critical parameter. Most precipitates were retained.
Cadmium	100 ml $HClO_4$, 50 ml glycerol, 150 ml methanol, 200 ml ethyl alcohol	0	4.7	5	20	50	Maintain current slightly below setting at which brown film forms.
Copper	90% H_3PO_4, 10% H_2O	20	6.3	8-10	2	70	

Cu-25Au	5% $HClO_4$, 95% ethanol	-60	4.7	7	170	25	Different grains tend to polish at different rates.
Cu-40Ni (annealed)	30% HNO_3 70% methanol	-60	4.7	5	40	35	
D979 (annealed)	20% H_2SO_4, 80% methanol	0	3.9	5.5	50	65	
Germanium	30 ml HF, 90 ml H_2SO_4, 100 ml butyl cellosolve, 500 ml methanol	-50	4.7	5	50	20	IR LED will trip off polisher before perforation. Lower sensitivity to obtain desired hole size.
Au-50Zn	500 ml HCl, 350 ml ethanol, 150 ml glycerine	-40	3.9	10	70	75	Use IR LED as light source, at maximum brightness.
Hafnium (as rolled)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	-45	4.7	5	70	25	Second phase visible but polish is good.
Incoloy 901 (annealed)	20% $HClO_4$, 80% ethanol	0	4.7	5.5	80	95	
Inconel 625 (annealed or cold worked) (1)	20% H_2SO_4, 80% methanol	0	3.9	6	55	85	Some loss of precipitates.
(2)	20% $HClO_4$, 80% ethanol	-60	3.9	6	55	10	Good precipitate retention.
Inconel 722X	10% $HClO_4$, 90% ethanol	0	4.7	3.5	170	110	
Iron	100 g Na_2CrO_4 (anhydrous), 500 ml acetic acid	20	3.9	7	35	15	
Iron (pure)	13% HCl, 87% methanol	-60	3.9	7	75	25	
Fe-Cr-Ni-Mo (RAC 218)	20% $HClO_4$, 80% ethanol	-50	4.7	5	80	35	

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[a] Nozzle and specimen diameters 1.5 and 3 mm, respectively, except where noted.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimens (Contd.)

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
Fe-Cr-Ni-Mo-Sc (RAC 222)							
Unirradiated:	20% $HClO_4$, 80% ethanol	-50	4.7	6	110	70	
Ion-irradiated:	30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	4.7	2-4	50	50	Good precipitate retention.
Fe-Cr-Ni-Mo-Si (RAC 220), Fe-Cr-Ni-Si (RAC 221)	20% $HClO_4$, 80% ethanol	-50	4.7	6	80	35	
Fe-Cr-Ni-Si-Sc (RAC 223)	20% $HClO_4$, 80% ethanol	-50	4.7	5	130	80	
Fe-Ni-Cr (RAC 224)	20% $HClO_4$, 80% ethanol	-50	4.7	6	100	75	Some loss of precipitates near perforation.
Fe-20Ni-15Cr (annealed)	20% $HClO_4$, 80% ethanol	-60	3.2	7	60	20	Precipitates attacked if voltage exceeds 60 V.
Fe-Ni-Cr-P-B	20% $HClO_4$, 80% methanol	-40	4.7	5-6	40	50	
Fe-Ni-Cr-Si (RAC 226 and 227)							
Unirradiated:	20% $HClO_4$, 80% ethanol	-50	4.7	6	100	75	
Ion-irradiated:	30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	4.7	2-4	50	50	Excellent precipitate retention.
Lead	20% $HClO_4$, 80% ethanol	-40	3.5	6	100	85	
Metglass, Fe-20B (amorphous)	30 ml HCl, 100 ml butyl cellosolve, 670 ml methanol	-60	4.7	5	100	25	

Molybdenum (as rolled)	20% H_2SO_4, 80% methanol	0	4.7	5	22	75	
Nickel (pure)	20% $HClO_4$, 80% ethanol	-60	3.9	7	75	14	Voltage > 80 or current > 20 may cause different grains to be polished at different rates.
Nickel (pure, annealed)	30% HNO_3, 70% methanol	-60	4.7	2-4	40	45	
Ni-6.35Al (annealed or aged)	20% $HClO_4$, 80% ethanol	-60	4.7	2-4	50	15-20	Electrolyte flow over specimen should resemble an "inverted mushroom". After shutoff, rinse specimen immediately to avoid etching of Al.
Ni-50Al (single crystal)	30 ml $HClO_4$ 175 ml butyl cellosolve 295 ml methanol	0	4.7	5	63	45	
Ni-10Al-10Si (annealed)	30 ml $HClO_4$ 175 ml butyl cellosolve 295 ml methanol	0	3.5	3.5	40	30	
Ni-0.1Be, Ni-0.3Be, Ni-0.7Be	20% $HClO_4$, 80% ethanol	-50	4.7	6.5	75	20	
Ni-10Co	10% $HClO_4$, 90% ethanol	0	3.9	2-4	20	35	After shutoff, rinse specimen immediately.
Ni-40Nb (amorphous)	13% HCl, 87% methanol	-60	3.9	7	80	25	
Ni-1Pt (annealed)	30% HNO_3, 70% methanol	-60	4.7	5-7	45	55	No grain boundaries visible.
Ni-1Si, Ni-2Si	20% $HClO_4$, 80% ethanol	-60	3.2	7	80	25	After shutoff, rinse specimen immediately.
Ni-4Si (annealed)							
(1)	13% HCl, 87% methanol	-60	3.2	6	65	30	
(2)	20% $HClO_4$, 80% ethanol	-60	3.2	7	80	25	After shutoff, rinse specimen immediately.

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[a] Nozzle and specimen diameters 1.5 and 3 mm, respectively, except where noted.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimen (Contd.)

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
N-6Si	13% HCl, 87% methanol	-60	4.7	6	70	30	
Ni-6Si (annealed)	295 ml methanol, 175 ml butyl cellosolve, 30 ml $HClO_4$	0	4.7	5	30	30	Areas of high Si content in ion-irradiated samples not attacked.
Ni-6.5Si (aged)	13% HCl, 87% methanol	-50	4.7	5	70	23	
Nb + O_2, Nb + Ti	11.16 g $Mg(ClO_4)_2$, 1 ℓ methanol	20	4.7	3.5	150-160	15	Removes ~ 430 nm/s. Diaphragm for 2.3-mm specimens used for both 2.3- and 3-mm specimens, with 1.0-mm nozzle.
PE-16 (annealed or aged)	20% H_2SO_4, 80% methanol	0	3.2	2-4	30	75	Low jet height and slow electrolyte flow chosen to obtain flat-bottomed dimple.
Silver (pure), Silver alloys (dilute)	46 ml H_2SO_4, 115 ml acetic acid at 0°C, 77 g thiourea (added slowly), 350 ml methanol	20	3.9	7	5-9	28	Rinse periodically with methanol during thinning. After shutoff, rinse with same before unmounting; then rinse successively with carbon disulfide and methanol.
304 SS							
	(1) 20% $HClO_4$, 80% ethanol	-60	4.7	9.5	90	12	Removes ~ 60 nm/s.
	(2) 20% H_2SO_4, 80% methanol	20	4.7	6	25	75	May attack precipitates in grain boundaries.
	(3) 30 ml $HClO_4$, 175 ml butyl cellosolve, 295 ml methanol	0	3.9	5	30	30	Good precipitate retention.
316 SS (annealed and aged)	30 ml $HClO_4$, 175 ml butyl cellosolve, 295 ml methanol	0	3.2	3	40	35	Good precipitate retention. Use IR LED as light source.

Steel	100 g Na_2CrO_4 (anhydrous), 500 ml acetic acid	20	3.9	7	35	15	
Tantalum	30 ml HF, 90 ml H_2SO_4, 100 ml butyl cellosolve, 500 ml methanol	-50	4.7	5	40	20	Polishes over wide voltage range but at 60-80 volts grains polish at different heights.
Titanium (pure)	30 ml $HClO_4$, 175 ml butyl cellosolve, 295 ml methanol	0	3.2	4	30	25	Narrow voltage range.
Ti-8.65Al (annealed)	13% HCl, 87% methanol	-60	3.9	5	90	35	Etching occurs at lower voltage settings.
Ti-6Al-4V, Ti-811, Ti-15333	13% HCl, 87% methanol	-60	3.9	7	70	25	
Ti-0.8Mo, Ti-4Nb, Ti-4Ta, Ti-3V, Ti-20Zr (annealed)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	0	4.7	4	40	50	Some alloys are two-phase.
Ti-13Sn (annealed)	130 ml HCl, 100 ml butyl cellosolve, 670 ml methanol	-60	4.7	5	150	60	A few seconds are required before a good polishing film develops.
W-25Re	30 ml HF, 90 ml H_2SO_4, 100 ml butyl cellosolve, 500 ml methanol	-50	4.7	5	40	20	If solution attacks specimen at diaphragm hole rim, increase jet height. Use 2.3-mm specimen diaphragm to ensure hole position near center of disc.
Vanadium (pure or commercial grade)	20% H_2SO_4, 80% methanol	20	4.7	4	25	85	
V-5Al	20% H_2SO_4, 80% methanol	-60	3.9	10	100	75	Visible precipitates retained in matrix.
V-1Ti	20% H_2SO_4, 80% methanol	20	4.7	5	27	95	Alloys of vanadium tend to require more voltage, current, and pump speed than pure material.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimens (Contd.)

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
Zr-1.2Sn-0.18Fe-0.07Cr	130 ml HCl, 100 ml butyl cellosolve, 670 ml methanol	−60	4.7	5	150	75	Good retention of small precipitates.
Zr-11.6Ti (annealed)	60 ml $HClO_4$, 350 ml butyl cellosolve, 590 ml methanol	−55	4.7	4	70	15	
Addendum: polishing procedures documented between mid-1981 and mid-1985							
Aluminum Al-1.95Zn (annealed)	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	−45	3.9	4	80	65	Excellent polish in TEM check.
Copper	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	−20	3.9	2.5	40	75	Excellent polish in TEM check. Lower temperatures result in an uneven foil surface.
Cu-7Be	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	−60	3.9	4	30	20	Excellent polish in TEM check. Low temperature helps to polish grain boundaries at the same rate as the matrix.
Cu-7Si Cu-9Si	150 ml HNO_3, 350 ml methanol, 40 ml ethylene glycol	−40	3.9	4	50	75	Excellent polish in TEM check. No Cu residue or oxide on foil surface. (Oxide from other solutions can be removed with a 5-10 sec. dip in 10% HF in distilled water followed by alcohol rinses.)
Gold	500 ml HCl, 300 ml ethanol (200 proof), 100 ml glycerine	−40	3.9	10	60	75	Excellent polish in TEM check. Set sensitivity knob on control cabinet at 10 (maximum).

Incoloy 750-x (aged), Cast SS	75 ml HNO_3, 50 ml acetic acid, 425 ml methanol, 100 ml ethylene glycol	-22	3.9	4	40	50	Excellent precipitate retention. Different phases at almost the same rate. Adding four drops of wetting agent (Kodak Photo-flo) improves precipitate retention. Current is critical.
Indium	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	-50	3.9	4.5	75	35	In TEM check, foil was smooth but of non-uniform thickness.
Iron	130 ml HCl, 670 ml methanol, 100 ml butyl cellosolve	-60	4.7	5	100	60	Excellent polish in TEM check.
Fe-0.23Cr-0.056Y	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	3.9	3.8	100	60	Excellent polish in TEM check.
Ni <112> (single crystal)	33% HNO_3, 66% methanol	-60	3.9	5	45	80	Excellent polish in TEM check. Store solution at 0°C or below to minimize explosion hazard.
Ni (as rolled)	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve	-45	3.9	5	70	75	Excellent polish in TEM check. Current is critical.
Ni (as rolled), Ni-21Al	5.3 g LiCl, 11.16 g $Mg(ClO_4)_2$, 500 ml methanol, 100 ml butyl cellosolve	-60 to -40	3.9	4.5	150-200	25-30	TEM check revealed a clean foil surface and good retention of precipitates in Ni-21Al grain boundaries. (This solution reduces hydrogen pick-up during electropolishing.) Higher temp., voltage, and current are best for Ni-21Al.
Nickel oxide	30 ml HF, 90 ml H_2SO_4, 500 ml methanol, 100 ml butyl cellosolve	-50	4.7	7	80	25	Good polish in TEM check.

[a] Nozzle and specimen diameters 1.5 and 3 mm, respectively, except where noted.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimens (Contd.)

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
Ni plated on Ni-12.7Si	7.62 g $Mg(ClO_4)_2$, 500 ml methanol, 200 ml butyl cellosolve	-60	3.9	3	240	17	On optical inspection, Ni plating was shiny and had a dendritic structure; the interface was smooth because both metals were polished at the same rate.
Ni-6Ge, Ni-10Ge	20% $HClO_4$ 80% ethanol	-50	4.7	4.5	80	25	Excellent polish in TEM check.
Ni-12.7Si	130 ml HCl, 670 ml methanol, 190 ml butyl cellosolve	-60	4.7	3	100	20	Grains were polished at different rates, but surface was good in TEM check.
Ni-0.1Y	100 ml $HClO_4$, 400 ml ethanol, 50 ml butyl cellosolve	-55	3.9	5	70	25	Excellent polish in TEM check. Addition of butyl cellosolve reduces second-phase attack.
Ni-4Al-4Ge, Ni-8Al-4Ge, Ni-8Al-8Ge	60 ml $HClO_4$, 590 ml methanol, 350 ml butyl cellosolve	0	3.9	4.5	70	75	Excellent polish in TEM check. In Ni-8Al-8Ge alloy, some grains are polished faster than others.
Ni-8Al-8Ge	150 ml HNO_3, 350 ml methanol, 40 ml butyl cellosolve, 1 drop Photo-flo (wetting agent)	-50	3.9	4	125	100	Excellent polish in TEM check. Grains are polished at different rates. Changing voltage, current density, or temperature may minimize this effect.
Ni-12.7Al, Ni-6Al-6Ge, Ni-6Al-6Si, Ni-8Al-8Si, Ni-10Al-10Si, Ni-12Al-12Si, Ni-6Si-6Ge	30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	3.9	3.5	40	30	Excellent polish in TEM check. Thin area intact after perforation. (It sometimes broke when a solution of 20% $HClO_4$, 80% ethanol was used at -60°C.)

Niobium	(1) 30 ml HF, 90 ml H_2SO_4 500 ml methanol 100 ml butyl cellosolve	-60	4.7	6	50	25	Good polish obtained over wide voltage range.
	(2) 100 ml NH_4F-saturated methanol; 900 ml methanol	20	3.9	5	200	100	Excellent polish in TEM check. No significant oxide found in diffraction check of specimen in TEM.
Scandium	300 ml HNO_3, 700 ml methanol, 100 ml butyl cellosolve	-60	3.9	6	70	40	Good polish except for small areas of oxide which do not polish. Addition of 30 ml of HF might solve this problem. Cool methanol to -40°C before adding HNO_3.
Silicon <110> (doped)	30 ml HF, 90 ml H_2SO_4, 500 ml methanol, 100 ml butyl cellosolve	-60	4.7	6	50	25	Excellent polish in TEM check. Use green LED light source for shutoff before perforation. Finish with short polishing cycles and inspection with an optical microscope.
304 SS with sensitized grain boundaries							
	(1) 30 ml $HClO_4$, 295 ml methanol, 175 ml butyl cellosolve	0	3.9	3	70	70	Excellent polish in TEM check. Tends to result in perforation at grain boundaries.
	(2) 75 ml HNO_3, 10 ml acetic acid, 425 ml methanol, 100 ml ethylene glycol	-22	3.9	3	60	75	Excellent polish in TEM check. Does not attack heavy grain-boundary precipitate. Usually makes a hole in the matrix. When one side of specimen was polished halfway through with solution (2), then with solution (1) from the opposite side until perforation occurred at the grain boundary, a good thin cross section of the grain boundary resulted.

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[a] Nozzle and specimen diameters 1.5 and 3 mm, respectively, except where noted.

Table VII. Electrolytes and Conditions[a] Used for Jet Thinning of Foil Specimens (Contd.)

Material	Electrolyte	Temp., °C	Jet Height, mm	Pump Setting	Volts	Current, mA	Comments
304 SS	(1) 10% $HClO_4$, 90% acetic acid	20	4.7	2.5	50	30	Good retention of grain boundary precipitates if present on < 50% of boundaries.
	(2) 5.3 g LiCl, 11.16 g $Mg(ClO_4)_2$, 500 ml methanol, 100 ml butyl cellosolve	-60	3.9	4.5	210	30	Excellent polish in TEM check; foil appears clean with much thin area. This solution minimizes hydrogen pick-up during thinning.
Tin	75 ml $HClO_4$, 375 ml ethanol, 50 ml butyl cellosolve	-60	3.9	4	90	25	Good polish in TEM check. Precipitates retained well.
V-15Cr-5Ti	100 ml H_2SO_4, 400 ml methanol, 90 ml butyl cellosolve	0	3.9	5	40	75	Excellent polish in TEM check. Butyl cellosolve reduces precipitate attack.
V-20Ti	50 ml H_2SO_4, 450 ml methanol	-40	3.9	4	30	40	Good polish in TEM check. Slow to medium pump speed and proper current are critical.
Yttrium	1% $HClO_4$, 99% methanol	-50	3.9	4	90	20	Good polish in TEM check.
Zr-15Nb	5.0 g $Mg(ClO_4)_2$, 500 ml methanol, 200 ml butyl cellosolve	-60	3.9	3	270	15	Excellent polish in TEM check. Hydrides are retained and polished. No oxide noted on surface in TEM check. Use "2.3-mm" specimen diaphragm and slow pump speed to form a puddle of electrolyte on the specimen. This eliminates the uneven dimple surface obtained with a "3-mm" diaphragm.

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[a] Nozzle and specimen diameters 1.5 and 3 mm, respectively, except where noted.

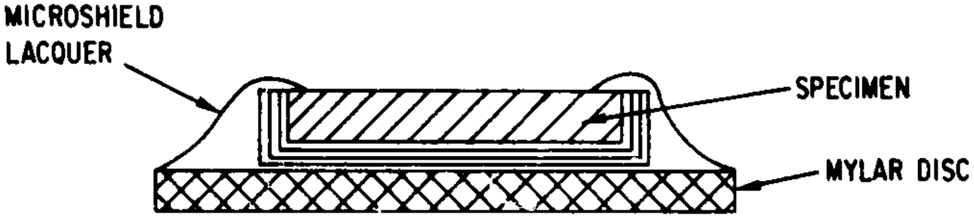

Fig. 17. Schematic of MgO Specimen Mounted on Mylar Disc.

The polisher reservoir is filled with about 500 ml of phosphoric acid of standard reagent concentration, and heated to 70-75°C with a thermostatically controlled hot plate. Temperature control is critical because too much heat will soften the PVC components, while too little will inhibit attack on the specimen by the acid. The sensitivity control is set to give maximum LED brightness (10), and the pump is run at maximum speed. Standard quartz light rods are used. After about an hour of polishing, a dimple should be formed in the top of the specimen. A diaphragm sized for 3-mm specimens may then be substituted to allow a larger dimple to form, giving a larger thin area in the finished specimen.

When the acid penetrates to the aluminum coating, it will quickly perforate it and shut off the pump. The specimen must be rinsed immediately with distilled water from a wash bottle to prevent etching, and then in acetone for several hours to dissolve the layers of lacquer. Since the dimple tends to have a flat bottom, the edges of the perforation are very thin and brittle and the specimen must be handled gently.

After the specimen has been cleaned and dried, a layer of Microshield is painted on the dimpled side and allowed to dry. The specimen is then dipped in a solution of 25% nitric acid in water to dissolve the aluminum coating. When the film falls off, the specimen is immediately washed in distilled water to prevent pitting, rinsed gently in several changes of ethanol, and dried. Further details of the procedure for chemical thinning of MgO are summarized in Table VIII.

IV. SPECIAL TECHNIQUES

A. Jet Polishing for Metallography

In many instances, the Model 550 B jet thinning instrument can be used directly to electropolish the surface of a specimen, using a 3-mm nozzle. Then, by reducing the current and voltage while observing the specimen through the splash guard viewer, one can usually etch the specimen with the same solution until the surface has a "frosty" appearance. For more control, the etching time could be determined with a timer and relay as described in Section III.D.2. Alternatively, a specimen could be electropolished with the 3-mm nozzle and then etched by conventional swab or electrolytic techniques. This technique is adequate for obtaining qualitative information on features such as grain size without time-consuming mounting and mechanical polishing. Although the polished specimen is not truly flat, the small area viewed in a single optical microscope field at about 200X is usually in good focus.

Table VIII. Polishing Solutions and Conditions Used for Chemical Thinning of 3-mm-dia Ceramic Specimens

Material	Solution	Temp., °C	Jet Height, mm[a]	Pump Setting	Comments
Silicon	20% HF, 80% HNO_3 (freshly prepared)	20	4.7	4-5	Use green LED light source as described in text.
MgO	H_3PO_4 (stock reagent)	70	7.9	4-5	Use standard infrared source. Coat specimen with aluminum as described in text. Install stainless steel support plate on pump base to retain discharge pipe.

[a] PVC nozzle, 1.5 mm dia.

B. Reperforation of a Thinned Foil

Occasionally, the area around a perforation will not provide useful information owing to etching at the perforation, wrong grain orientation, heavy ion damage not centered on the disc, etc. If a second perforation can be made near the original one, where the foil surfaces are still nearly parallel, the necessity of producing a duplicate specimen is avoided. A reperforation procedure has been developed for this purpose; it has been applied mainly to ion-damaged foils that had been sectioned and back-thinned as described in Section III.A.

The manipulations to be described are performed with the aid of a stereo microscope. First the central area of the flat side of the specimen is coated with stock Microshield lacquer. The rim is kept free of lacquer because it will later be used to make electrical contact with the specimen pedestal mount. Usually, surface tension prevents the lacquer from seeping through the original perforation. When the lacquer is dry, the specimen is placed on a glass slide and a 1/32-in. (0.8-mm) square of ordinary aluminum foil is positioned over the original perforation, using fine-point tweezers. The patch should be away from the area to be perforated next, as shown in Fig. 18; otherwise, automatic shutoff with the optical detector system will not occur. The patch is secured by brushing a little lacquer, diluted about 1:1 with acetone, onto the edge. The specimen is then inspected at about 200X magnification, with backlighting, to check for light leakage around the patch. The patch is repositioned if necessary, and dilute lacquer is painted over the remaining edges and surface of the patch to protect it from attack by the electrolyte. Finally, the patch is rechecked at 200X with backlighting to be sure it has not shifted. If necessary, the lacquer is softened by applying acetone with a brush, and the patch is repositioned with tweezers.

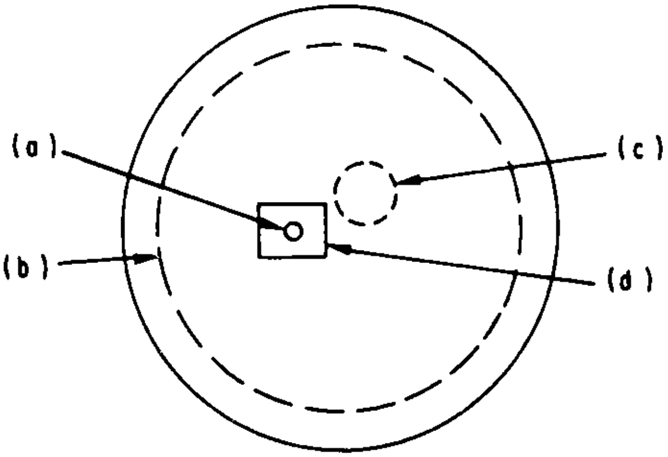

Fig. 18. Positioning of Aluminum Patch on Specimen to be Reperforated. (a) Original perforation; (b) edge of lacquered area; (c) area to be perforated next; (d) patch.

When the specimen is dry, additional diluted lacquer is carefully applied to the dimpled side in four straight strokes, leaving an ~ 1/32-in. (0.8-mm)-square area uncoated, as shown in Fig. 19. A trimmed #000 artist's brush is used. The brush should be wetted with acetone beforehand, and the excess absorbed with tissue; this helps the bristles to pick up lacquer without trapping air bubbles, which may be transferred to the specimen. For maximum control, the brush should be cleaned and refilled after each stroke. When the coating immediately around the selected area is finished, the remainder of the dimple and rim on the same side of the disc is coated.

When the lacquer is dry, the specimen is mounted with the uncoated square facing the jet nozzle. The area to be rethinned is typically a few μm thick, and perforation is achieved within a few seconds of polishing. The lacquer is then dissolved in acetone. Mild agitation will usually remove the foil patch.

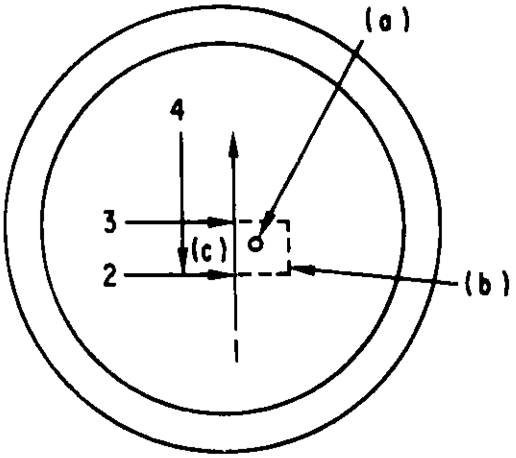

Fig. 19. Four-stroke Application of Lacquer to Side of Specimen That Will Face Jet Nozzle During Rethinning. (a) Original perforation; (b) patch on reverse side; (c) area to be left uncoated for reperforation.

The need for a thin lacquer layer and adequate uncoated specimen area is illustrated in Fig. 20. Owing to electrolyte surface tension and the flow restriction caused by the lacquer film, little material removal occurs very close to the film edges. If the uncoated area is too small, polishing will not occur.

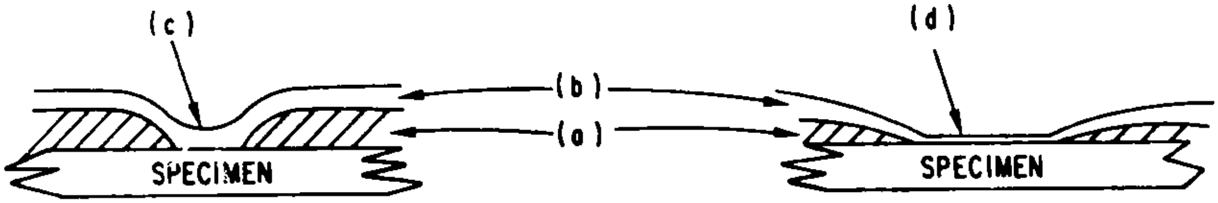

Fig. 20. Schematic Cross Sections of Specimens Undergoing Reperforation with Relatively Small (Left) and Large Uncoated Areas. (a) Lacquer coating; (b) polishing film; (c) and (d) areas of interaction between polishing film and specimen.

Another consideration exists in choosing the size of the uncoated area. If the area is small, more of the specimen is left intact; this affords additional chances for successful reperforation if the first attempt fails, as it frequently does. Successive attempts are usually made in a sequence along an arc around the original hole, as shown in Fig. 21.

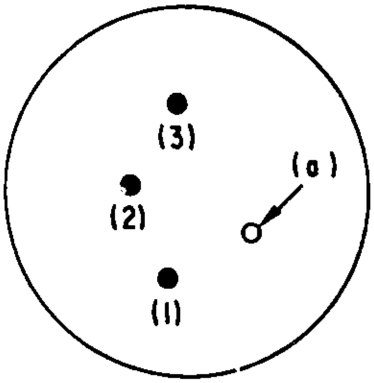

Fig. 21. Typical Locations (1,2,3) of Successive Reperforation Attempts on a Specimen Originally Perforated at (a).

C. Undersized Specimens

The technique described below allows examination of specimens with very small surface areas, such as cross sections of thin foils or wires. It is essentially an adaptation of the technique for rethinning a perforated foil.

The specimen is cleaned and then electroplated with a metal of similar composition until the thickness of the specimen plus the plating is at least 3 mm. The electroplating must be of high quality, with good adhesion to the specimen. The procedure is usually started with a brief reversal of polarity to clean the specimen, followed by a few minutes of plating at a fairly low current (to give good bonding) and about 24 hours of faster plating to build up a uniform, fine-grained deposit of sufficient thickness.

1. Foil Specimens

By either spark cutting or mounting in cold mount and mechanically grinding, the plated specimen is then reduced to a wafer 10 mils (0.25 mm) thick and 3 mm in diameter. Each side is mechanically polished with 9- and then 3-μm alumina slurry on Microcloth with a vibratory polisher. The alumina is suspended in ethylene glycol to prevent electrolytic cell action between the specimen and metal polisher parts. The pH should be adjusted to 7. When this step is completed, the foil specimen will have the configuration shown in Fig. 22.

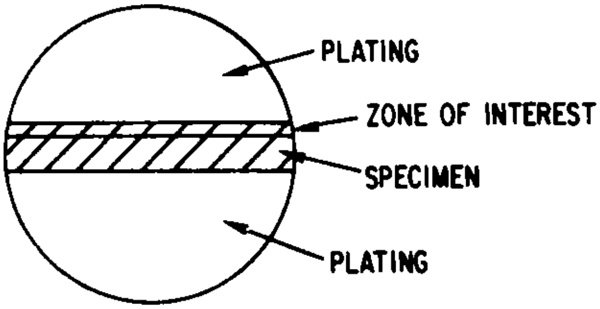

Fig. 22. Schematic of 3-mm-dia Wafer Cut from Electroplated Foil Specimen, with Zone of Interest Centered in Disc.

Since the zone of interest is very narrow and the final thinning must be positioned accurately, the best approach is to perform a preliminary thinning of a much larger area, patch the perforation, and rethin within a more controlled area defined by lacquer.

The disc is coated on one side (except for the rim) with Microshield lacquer, mounted coated side down on the jet polisher, and polished about halfway through at the center with a 1.5-mm nozzle. After cleaning, the dimple is coated with lacquer. The specimen is then remounted and jet thinned from the opposite side until perforation and automatic shutoff occur. A hole will usually appear first in the fine-grained plating material next to the specimen. The specimen, now a few μm thick, is cleaned in acetone to remove lacquer and small amounts of trapped acid.

A thin coating of lacquer is then painted on the surface of the shallower dimple, except at the rim. A small patch of aluminum foil is laid over the perforation and fastened by coating with thinned lacquer. The disc is then inverted and the second surface is coated with lacquer except for a small (~ 0.05-mm) square spanning the zone of interest but not overlapping the patch on the opposite side. The result is shown schematically in Fig. 23.

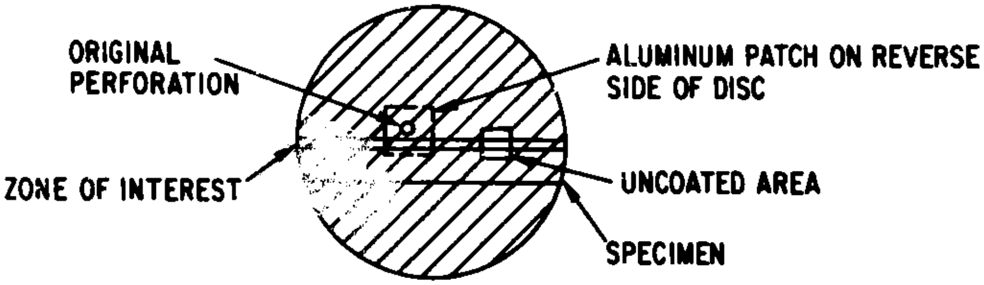

Fig. 23. Electroplated Specimen Ready for Reperforation.

The disc is mounted with the uncoated area facing the nozzle, and jet thinned with a slow pump speed until perforation and automatic shutoff occur. The lacquer is then removed with acetone and the location of the second perforation is checked. Several reperforation attempts may be made along a given zone of interest, if needed.

Choice of electrolyte and other parameters will determine in which material the reperforation will occur. For example, on Ni-1Be specimens plated with pure nickel, reperforation usually occurred in the plating. Good results were obtained with an electrolyte consisting of 295 ml methanol, 175 ml butyl cellosolve, and 30 ml perchloric acid at $0^{o}C$; 30 V; 30 mA; and a medium pump speed. A solution of 140 ml phosphoric acid, 43 ml water, 10 ml sulfuric acid, and 2 mg chromium trioxide at $5^{o}C$ was reported to work well on a 3-mm-dia ion-damaged nickel specimen plated with nickel [G. Fenske, ANL, personal communication (1977)]. The beaker method was used with 3-4 V, 300 mA, and a medium stirring speed. Changes in the electrolyte and the placement of the uncoated area may also increase the size of the thinned region containing the reperforation.

2. Wire Specimens

Several types of studies utilize TEM examination of transverse wire sections. These include investigations of structural changes induced by twisting and by irradiation with certain types of charged particles. The method described below was applied to a 316 SS wire only 5 mils (0.13 mm) in diameter. With practice, a choice can be made between centered and off-center perforation.

An ~ 1-in. (25-mm) length of 316 SS wire was cleaned, then electroplated with nickel. A flash plating was first deposited at a very slow rate, followed by a long, faster plating to build up the wire diameter with fine-grained nickel. (This step was developed by C. Steves.) When the wire reached just over 1/8 in. (3.2 mm) in diameter, the plating was stopped. After cleaning, the resultant slug was cut into 0.020-in. (0.5-mm)-thick wafers with a slow-speed diamond wheel running in water.

The wafers were individually embedded in 1-1/4-in. (32-mm)-dia cold mounts, with one surface flush with the end. About 0.005 in. (0.13 mm) was ground off the mounted specimen, finishing with 600-grit paper. The surface was then mechanically polished through 0.05-μm alumina on a vibratory polisher. The cold mount was then dissolved with acetone and the wafer was cleaned. Wafers that were too large in diameter were attached to a wood stick with wax and ground down, then cleaned again.

Each wafer was then remounted in cold mount, ground on 600-grit paper to a thickness of 10 mils (0.25 mm), and again vibratory-polished on both sides in 0.05-μm alumina slurry on microcloth. The ideal thickness at this stage was 8-9 mils (0.20-0.23 mm). The cold mount was again dissolved and the wafer cleaned. It was then coated on one side (except for the rim) with Microshield lacquer, mounted on the 550 B jet instrument with the lacquered side down, and thinned with a 1.5-mm nozzle until the dimple extended about halfway through the specimen. The electrolyte was 295 ml methanol, 175 ml butyl cellosolve, and 30 ml perchloric acid at $0^{o}C$. Best results were obtained at 30 V, 30 mA, and a slow pump speed. The specimen was unmounted and cleaned in acetone to remove the lacquer. Next, the dimple was coated with lacquer and the specimen was remounted with the dimple side down, held in place by the usual plastic diaphragm. Thinning was continued until perforation resulted in automatic shutoff. Because the electrolyte attacked the nickel plating somewhat faster than the stainless steel wire, perforation occurred just outside the wire, as shown schematically in Fig. 24.

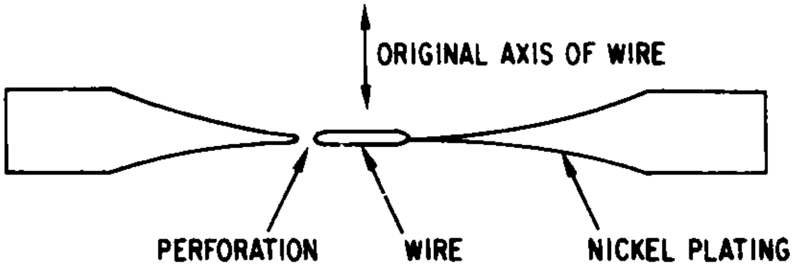

Fig. 24. Schematic Cross Section of Plated Wire Specimen Thinned from Both Sides.

Next, the specimen was cleaned, patched, and relacquered except for the rim and a small square encompassing the area of interest on the wire, as described in Section IV.C.1 above. Care was taken to make the uncoated area fairly large [a 2-mil (0.05-mm) square was sufficient for the present specimen] and the lacquer coating thin, as discussed earlier.

The prepared specimen was then remounted on the jet polisher with the uncoated square facing the nozzle, and polished until perforation and automatic shutoff occurred. The lacquer was dissolved in acetone and the specimen cleaned and dried as described earlier. The area suitable for TEM viewing is limited with this method, but adequate for many applications.

D. Longitudinal Wire Sections

It is sometimes desirable to make a TEM foil from a longitudinal section of wire to study microstructural features such as precipitate size and location and grain size. The following procedure works well for wire specimens > 15 mils (0.38 mm) in diameter; thinner specimens should first be electroplated as described above.

First, the wire is embedded in a block of removable material, such as cold mount. The block and wire specimen are ground and polished through about 6-μm diamond paste. A total of 5 mils (0.13 mm) should be removed from the side of a 15-mil (0.38-mm) wire, as shown in Fig. 25.

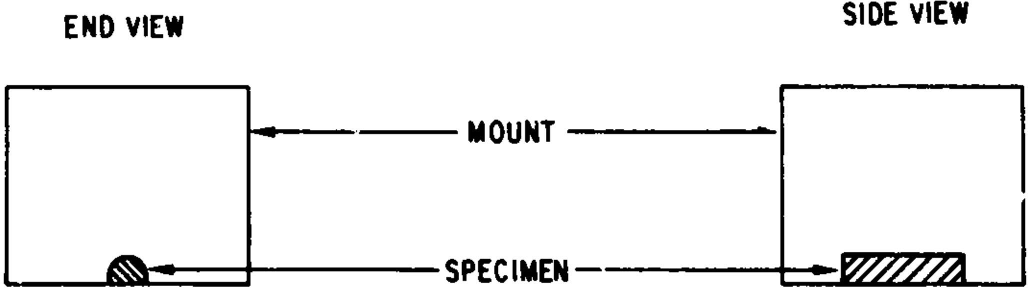

Fig. 25. Preliminary Grinding Step in Preparation of Longitudinal Wire Section.

The mount is dissolved in acetone and the specimen is cleaned. It is then positioned in the mounting mold with the flat side up, secured with a small metal clip, and carefully covered with fresh cold mount. The grinding, polishing, and cleaning steps are repeated, producing a wire section (now essentially a sheet of metal) that resembles Fig. 26 when viewed from one end.

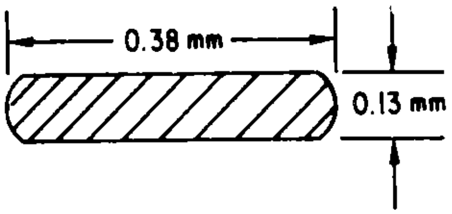

Fig. 26. End View of Longitudinal Wire Section After Second Grinding/Polishing Step.

With the aid of a stereo microscope, a sharp scalpel is used to cut a piece of the sectioned wire with length equal to the outside diameter of the platinum tip portion of the pedestal mount. Next, a 3-mm disc is punched from ordinary aluminum foil, and a small scalpel is used to cut a rectangular opening in the disc just large enough to hold the wire piece. The wire is inserted, and lacquer is painted on each end at the wire/aluminum interface. When the lacquer has dried, securing the ends, the gaps parallel to the long dimension of the wire are coated. After drying, the disc is inspected microscopically for light leaks around the edges of the wire, and these are sealed with ink from a black felt-tip pen. The remainder of the upper surface of the disc, including all but the central area of the specimen, is then painted with lacquer as shown in Fig. 27.

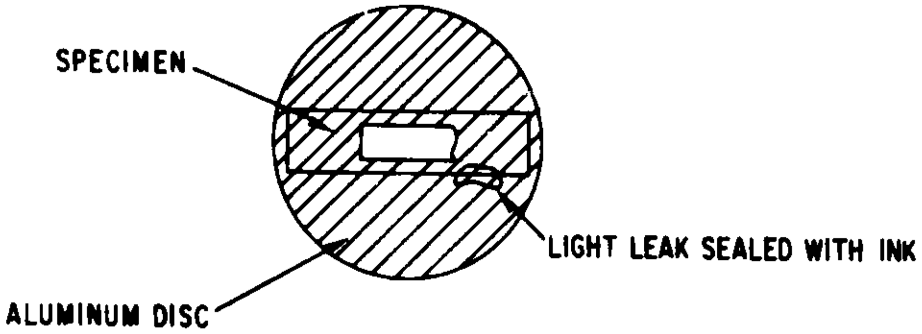

Fig. 27. Schematic of Upper Surface of Longitudinal Wire Specimen Held in Aluminum Disc. Shaded area has been painted with lacquer.

The opposite side of the disc is then lacquered as shown in Fig. 28; the ends of the specimen are left uncoated to allow electrical contact with the top of the pedestal mount. [Most aluminum foil is only about 2 mils (0.05 mm) thick; therefore, a 5-mil (0.13-mm)-thick specimen will protrude from it somewhat.] Silver conductive paint is not used on the uncoated specimen ends because it might be difficult to clean from the finished specimen.

The lacquered disc is then mounted with the uncoated rectangle facing the jet nozzle; the instrument is operated until the specimen is about half the starting thickness, i.e., 2 or 3 mils (0.05-0.08 mm), and is shut off manually. The lacquer is dissolved in acetone and the specimen is remounted and relacquered, with the central area of the formerly protected side left

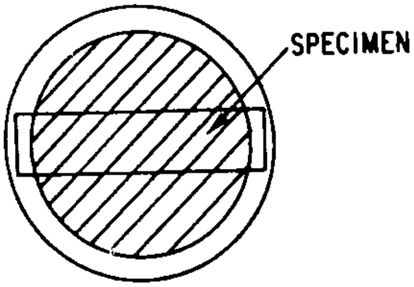

Fig. 28. Opposite Surface of Disc Shown in Fig. 27. Lacquer coating (shaded area) protects rear surface of specimen from electrolyte.

uncoated. The disc is again mounted on the jet polisher with the uncoated area facing the jet, and electropolished until perforation and automatic shutoff occur. The configuration of the perforated specimen after acetone cleaning is shown in Fig. 29. The specimen is long enough to be placed directly in a TEM for examination.

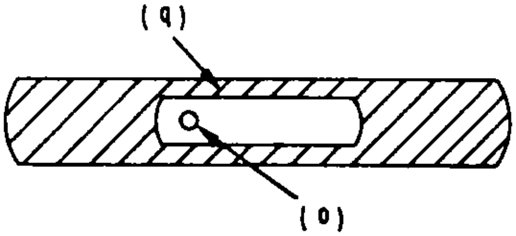

Fig. 29. Longitudinal Wire Specimen After Perforation. Shading indicates area protected by lacquer during electropolishing. Perforation (a) is in thin central area of specimen; thick areas (b) on either side provide support.

V. CONCLUSIONS

The techniques that have been described should help workers unfamiliar with TEM specimen preparation to find a starting point for development of optimal polishing methods. The choice between beaker and jet methods will be based on equipment availability and desired results as well as specimen size. For those who already have jet polishing equipment, ways of expanding its application have been presented.

Inexperienced workers are strongly urged to read the discussion of hazards in the Appendix and to become familiar with a good reference book on the subject (e.g., Ref. 1).

ACKNOWLEDGMENTS

I wish to express my appreciation to Dr. Hartmut Wiedersich, under whose supervision the present work was done, for the opportunity to undertake this publication. D. Ryding, P. Baldo, A. McCormick, S. Gerber, C. Steves, S. Rothman, and G. Fenske (all of ANL) developed several of the techniques described in this report. The efforts of E. Stefanski in organizing and editing this report are greatly appreciated. S. Ruffatto and D. Livengood patiently typed preliminary and final drafts of the manuscript.

REFERENCE

1. N. Irving Sax, Dangerous Properties of Industrial Materials, 5th Ed., Van Nostrand Reinhold Co., New York (1979).

APPENDIX

HAZARDS OF SPECIMEN PREPARATION

Some of the solutions used for specimen preparation are intrinsically hazardous. However, they are used because they are relatively safe when the proper precautions are taken and they produce excellent results. Before using any of the hazardous solutions discussed below, one should read detailed references in a suitable safety handbook. Only a brief discussion of safe handling procedures will be given here.

A. Hydrofluoric Acid (HF)

This acid must not come into contact with skin because it will cause severe burns. Suitable gloves must therefore be worn when handling HF solutions. Also, fumes from the acid are very irritating to the mucous membranes, especially when inhaled, and may cause ulcers of the upper respiratory tract. For this reason, operations involving HF must always be done in a fume hood with adequate exhaust flow. The solution should be cooled while mixing to prevent splattering.

B. Perchloric Acid ($HClO_4$)

Perchloric acid is irritating to the skin and mucous membranes. It is a powerful oxidizer and must not come in contact with materials containing carbon. These include rubber, grease, sulfur, bismuth, powdered magnesium and aluminum, charcoal, benzene, sulfuric acid, paper, and wood. If the acid dries on paper or wood, it may later spontaneously ignite or become shock sensitive.

Alcohol solutions of $HClO_4$ are unstable above room temperature. The acid should be cooled to 0°C or lower before mixing with alcohol, while for maximum safety, the alcohol should be chilled to -50°C or lower with a dry ice and alcohol bath. The acid is then added to the alcohol very slowly while the mixture is stirred. Generally, mixtures containing 5% to 20% acid can be used safely below 0°C. However, care should be taken to prevent sparks and to avoid high current densities that may heat the solution excessively at the surface of an electrode, creating the risk of explosion. Even gentle heating causes vapors to be given off which can collect in hoods and ducts, creating a fire and explosion hazard. Special ventilation systems are therefore required for operations involving heating of $HClO_4$. The acid is usually obtained in aqueous solution at a reagent strength of 70%. Higher concentrations should be avoided. Alcohol mixtures should not contain more than 30% stock acid because of the possibility of spontaneous combustion or explosion at higher concentrations. If a prepared solution is exposed to the air for long periods, the alcohol will evaporate and cause the $HClO_4$ concentration to increase, possibly to hazardous levels. Also, an $HClO_4$/alcohol mixture can form esters which may become explosive. For this reason, used solution should be discarded at least monthly by diluting it with cool water and then slowly neutralizing it. Solutions to be used repeatedly for a few days should be stored in an explosion-proof refrigerator or freezer to slow any undesirable reactions. The reagent acid should be stored in a double container in a secure location to protect it from accidental breakage with consequent severe cleanup problems.

C. Nitric Acid (HNO_3)

Nitric acid vapors are very irritating to the skin, eyes, and mucous membranes and can affect the teeth. The acid is a powerful oxidizing agent and reacts violently with acetic acid and many other chemicals.

Before nitric acid is mixed with methanol, the methanol should be chilled to -50°C in a dry ice and methanol bath. Then the acid is added slowly while the mixture is stirred well to prevent heat buildup. If the methanol is not chilled, it boils when the acid is added and much of it is lost as vapor. The splattering mixture is also a hazard to the skin and eyes.

After use, the mixture should be stored in a polyethylene bottle with a small vent hole in the cap. This allows the escape of gases which are given off by the reaction of the solution with metal ions picked up during electropolishing. Failure to vent the bottle will result in bursting and a very difficult cleanup problem. Even with venting, the bottle should be placed in an open jug, and the jug kept in an explosion-proof refrigerator or freezer to slow any hazardous reactions. Frequent disposal of the solution by diluting it with cool water and neutralizing it is recommended.