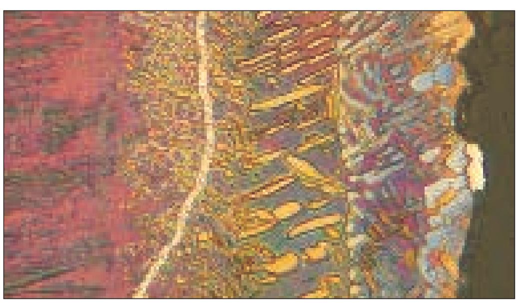
Refractory Metals

REFRACTORY METALS: Ti, Zr, Hf, Cr, Mo, Nb, Re, Ta, V and W

Titanium

Pure titanium is soft and ductile, but is very easily damaged by twinning in sectioning and grinding. Preparation of commercially pure titanium, which is a popular grade, is very difficult, while preparation of the alloys is somewhat easier. Some authors have stated that titanium alloys should not be mounted in phenolic resins as the alloys can absorb hydrogen from the resin. Further, it is possible that the heat from mounting could cause hydrides to go into solution. This is also possible with castable resins if the exothermic reaction of polymerization generates excessive heat. If the hydride phase content is a subject of interest, then the specimens must be mounted in a castable resin with a very low exotherm (long curing times favor lower heat generation, and vice versa). Titanium is very difficult to section and has low grinding and polishing rates. The following practice for titanium and its alloys demonstrates the use of an attack-polishing agent added to the final polishing abrasive to obtain the best results, especially for commercially pure titanium, a rather difficult metal to prepare free of deformation for color etching, heat tinting and/or polarized light examination of the grain structure. Attack polishing solutions added to the abrasive slurry or suspension must be treated with great care to avoid burns. Use good, safe laboratory practices and it is advisable to wear protective gloves. This three step practice could be modified to four steps by adding a 3 or 1µm diamond step, but this is usually unnecessary, see Table 16.



Alpha at the surface of heat treated (1038 °C, water quench) Ti – 3% Cr alloy after tint etching with Beraha's reagent (polarized light, 500X).

Table 16: 3-Step Method for Ti Alloys

Sectioning	Abrasive Cutter with a wheel recommended for use on ductile materials
Mounting	Compression, typically with EpoMet

Surface	Abrasive / Size	Load - lbs [N] / Specimen	Base Speed [rpm]	Relative Rotation	Time [min:sec]
CarbiMet 2	320 [P400] grit SiC water cooled	6 [27]	300		Until Plane
UltraPad	9µm MetaDi Supreme Diamond*	6 [27]	150		10:00
ChemoMet	0.02 - 0.06µm MasterMet Colloidal Silica**	5 [22]	150		10:00

= Platen *= Specimen Holder*

** Plus MetaDi Fluid Extender as desired*
*** Attack polish may be used, 1 part Ammonium Persulfate solutions (10g Ammonium Persulfate per 100mℓ distilled water) or 30% Hydrogen Peroxide to 5 parts Silica.*

Imaging & Analysis	Grain Size, Measurement & Analysis Applications
Hardness Testing	Vickers

A number of attack polishing agents have been used. The simplest is a mixture of 10mℓ hydrogen peroxide (30% concentration – avoid skin contact) and 50mℓ colloidal silica. Some metallographers add either a small amount of Kroll's reagent to this mixture, or a few mℓ of nitric and hydrofluoric acids (avoid contact). These latter additions may cause the suspension to gel. In general, these acid additions do little to improve the action of the hydrogen peroxide (the safer 3% concentration is not effective). Polarized light response of CP titanium can be improved by following this procedure with a brief vibratory polish using colloidal silica.

Basket-weave alpha-beta structure of as-cast Ti – 6% Al – 4% V revealed by heat tinting (polarized light, 100X).

Zirconium and Hafnium

Pure zirconium and pure hafnium are soft, ductile hexagonal close-packed metals that can deform by mechanical twinning if handled aggressively in sectioning and grinding. As with most refractory metals, grinding and polishing removal rates are low and eliminating all polishing scratches and deformation can be difficult. It may even be possible to form mechanical twins in compression mounting. Both can contain very hard phases that make relief control more difficult. To improve polarized light response, it is common practice to chemically polish specimens after mechanical polishing. Alternatively, attack polishing additions can be made to the final polishing abrasive slurry, or vibratory polishing may be employed. Table 17 is a four-step procedure that can be followed by either chemical polishing or vibratory polishing.

Several attack polishing agents have been used for Zr and Hf. One is a mixture of 1-2 parts hydrogen peroxide (30% concentration – avoid all skin contact) to 8 or 9 parts colloidal silica. Another is 5mL of a chromium trioxide solution (20g CrO_3 to 100mℓ water) added to 95mℓ colloidal silica or MasterpPrep alumina slurry. Additions of oxalic, hydrofluoric or nitric acids have also been used. All of these attack polishing addi-

Table 17: 4-Step Method for Zirconium and Hafnium

Sectioning	Precision Saw with a 15LC blade recommended for use on hard brittle materials				
Mounting	Compression, typically with EpoMet				

Surface	Abrasive / Size	Load - lbs [N] / Specimen	Base Speed [rpm]	Relative Rotation	Time [min:sec]
CarbiMet 2	320 [P400] grit SiC water cooled*	5 [22]	300		Until Plane
UltraPad	9µm MetaDi Supreme Diamond**	5 [22]	150		5:00
TriDent	3µm MetaDi Supreme Diamond**	5 [22]	150		3:00
ChemoMet	0.02 - 0.06µm MasterMet Colloidal Silica	5 [22]	150		7:00

= Platen *= Specimen Holder*

**Rub candle was lightly across rotating disc prior to grinding* ***Plus MetaDi Fluid Extender as desired*

Imaging & Analysis	Grain Size, Measurement & Analysis Applications
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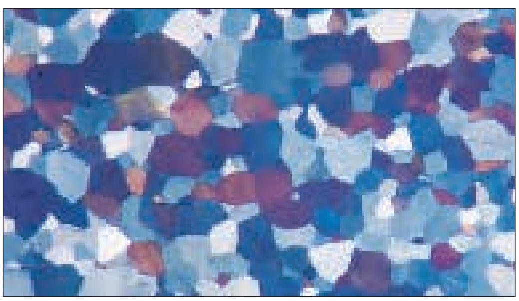
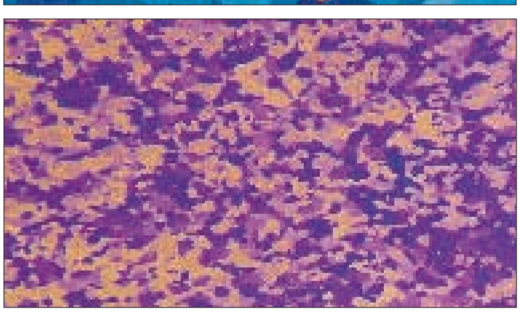
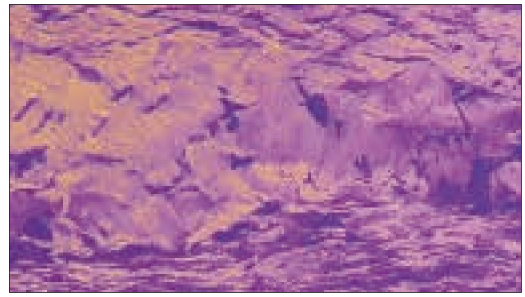
Refractory Metals

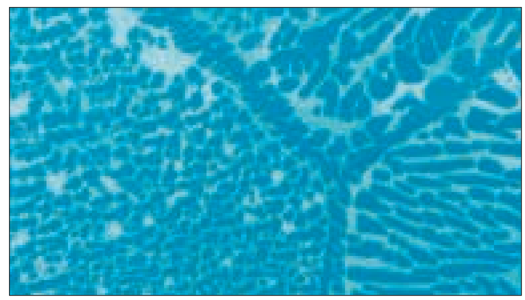
tions must be handled with care as they are strong oxidizers. Skin contact must be avoided. Chemical polishing solutions are reviewed in [2]. Cain's has been popular. Use under a hood and avoid skin contact. Ann Kelly developed an excellent chemical polish for refractory metals, such as Zr, Hf, and Ta. It consists of 25mℓ lactic acid, 15mℓ nitric acid and 5mℓ hydrofluoric acid. Swab vigorously for up to 2 minutes. To prepare ultra-pure Zr and Hf, the above method is unsatisfactory and a procedure, such as in Table 15 (add a 5 or 3µm alumina step) is needed, as diamond is ineffective. Use the chromium trioxide attack polish with the alumina and conclude with Kelly's chemical polish.





(top) Equiaxed grain structure of wrought zirconium (unetched, crossed polarized light, 100X). (middle) Equiaxed grain structure of wrought hafnium (unetched, crossed polarized light plus sensitive tint, 100X). (bottom) Fine grain recrystallized microstructure of wrought Zr - 1.14% Cr strip in the as-polished condition at 200X using polarized light plus sensitive tint.





(top) Cold worked microstructure of wrought zirconium alloy XL (Zr - 3% Sn - 0.8% Nb - 0.8% Mo) in the as-polished condition at 200X with polarized light plus sensitive tint. (bottom) Microstructure (α-Zr + $AlZr_3$) of wrought Zr - 8.6% Al in the as-polished condition at 200X with polarized light.

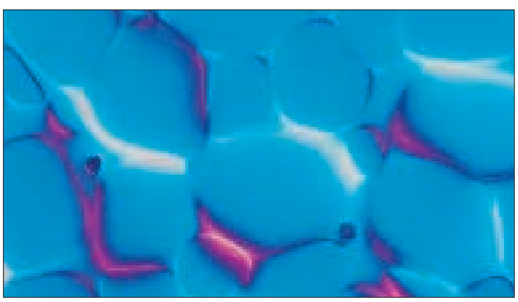
Helpful Hints For Refractory Metals

Due to their very low rate of grinding and polishing, the more aggressive contra rotation gives suitable surfaces in less time.

Refractory metal preparation is aided by using attack-polishing additives. Polarized light response may be improved by following preparation by swabbing with a chemical polishing solution.

OTHER REFRACTORY METALS: Cr, Mo, Nb, Re, Ta, V and W

These refractory metals have body-centered cubic crystal structures (except for rhenium which is hexagonal close packed) and are soft and ductile when pure, but some are brittle in commercial form. They can be cold worked easily, although they do not work harden appreciably, so it may be difficult to get completely deformation-free microstructures.



Microstructure of powder-made W – 5.6% Ni – 2.4% Fe revealing tungsten grains surrounded by a nickel-iron matrix (unetched, Nomarski DIC, 200X).

Pure chromium is soft and brittle; but, when encountered commercially, for example, as a plated layer, it is hard and brittle. Chromium alloys are relatively easy to prepare, although difficult to etch. Molybdenum may be tough or brittle depending upon composition. It is susceptible to deformation damage in sectioning and grinding. Pure niobium (columbium) is soft and ductile and difficult to prepare while its alloys are harder and simpler to prepare. Grinding and polishing rates have been reported to vary with crystallographic orientation. Rhenium is very sensitive to cold work and will form mechanical twins. Tantalum is softer than niobium and more difficult to prepare as it easily forms damaged layers in sectioning and grinding. Tantalum may contain hard phases that promote relief control problems. Vanadium is a soft, ductile metal but may be embrittled by hydrogen; otherwise it can be prepared much like a stainless steel. Tungsten is not too difficult to prepare, although grinding and polishing rates are low. Hard carbides and oxides may be present in these metals that introduce relief control problems.

Mechanical polishing often incorporates an attack-polishing agent in the final step or is followed by vibratory polishing or chemical polishing. Manual preparation of these metals and their alloys tends to be very tedious due to their low grinding and polishing rates. Automated approaches are highly recommended, especially if attack polishing is performed. Following is a generic four step practice suitable for these metals and their alloys, see Table 18.

Many attack-polishing additives [2] have been suggested for these metals and their alloys. A good general purpose attack polish consists of a mixture of 5mℓ chromium trioxide solution (20g CrO_3 in 100mℓ water) to 95mℓ MasterMet colloidal silica. Avoid skin contact as this is a strong oxidizing solution. A number of chemical polishing solutions have been suggested [2]. For Nb, V and Ta, use a solution consisting of 30mℓ water, 30mℓ nitric acid,

Table 18: 4-Step Method for Refractory Metals*

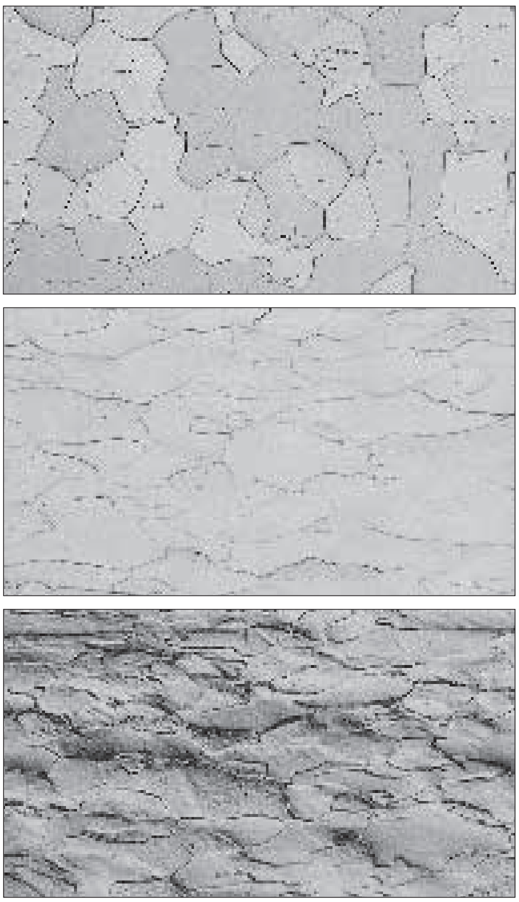
Surface	Abrasive / Size	Load - lbs [N] / Specimen	Base Speed [rpm]	Relative Rotation	Time [min:sec]
CarbiMet 2	320 [P400] grit SiC water cooled	6 [27]	300		Until Plane
UltraPad	9µm MetaDi Supreme Diamond*	6 [27]	150		10:00
TriDent	3µm MetaDi Supreme Diamond*	6 [27]	150		8:00
ChemoMet	0.02 - 0.06µm MasterMet Colloidal Silica plus attack polish agent**	6 [27]	150		5:00

= Platen = Specimen Holder *Plus MetaDi Fluid Extender as desired **See text for agent

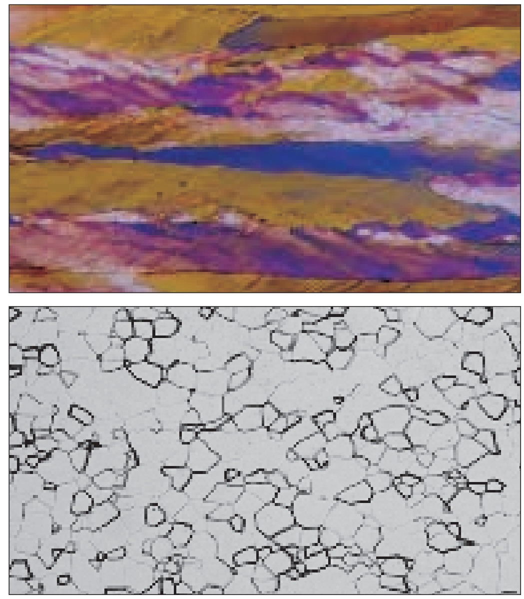
The variables in this group of materials is too large to make further recommendations

Other Refractory Metals

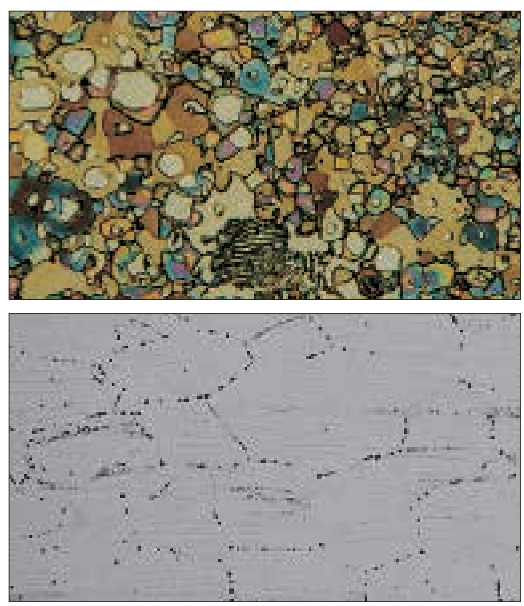
30mℓ hydrochloric acid and 15mℓ hydrofluoric acid. Swab or immerse at room temperature. An alternative chemical polish for Nb, V and Ta consists of 120mℓ water, 6g ferric chloride, 30mℓ hydrochloric acid and 16mℓ hydrofluoric acid. Eary and Johnson recommend immersing the specimen in this solution 1 minute for V, 2 minutes for Nb and 3 minutes for Ta. Vibratory polishing is also very helpful for these metals and their alloys.



(top) Alpha grains in Mo – 47.5% Re. The small spots are sigma phase (Murakami's reagent, 200X).
Deformed alpha grains in W – 25% Re containing sigma phase (black spots) revealed using (middle) bright field and (bottom) Nomarski DIC which reveals the cold work much better (Murakami's reagent, 500X).



(top) Non-recrystallized grain structure of wrought pure molybdenum, longitudinal plane (500X, polarized light, etch of water, hydrogen peroxide (30% conc) and sulfuric acid in 7:2:1 ratio).
(bottom) Equiaxed alpha grain structure in wrought pure vanadium (200X, etch: glycerol-nitric acid-hydrofluoric acid, 1:1:1 ratio).



(top) Wrought tungsten - 10 atomic % Ti containing a small amount of alpha-Ti, beta-Ti-W eutectic and grains of beta-Ti,W of varying composition and crystal orientation (500X, Kroll's reagent/Murakami's reagent at room temperature). (bottom) Fine grain boundary precipitates (not identified) in wrought, cold worked Fan Steel 85-03 alloy (Nb - 28% Ta - 10.5% W - 0.9% Zr), longitudinal plane (500X, etchant: lactic acid-nitric acid-hydrofluoric acid, 30:10:5 ratio).