MICROSTRUCTURE OF TITANIUM AND ITS ALLOYS

George F. Vander Voort
Director, Research & Technology, Buehler Ltd., Lake Bluff, Illinois, 60044, USA

ABSTRACT

A three-step preparation procedure was developed for titanium and its alloys. Attack polishing is utilized in the third step for optimal results, particularly for imaging alpha-Ti with polarized light. Two-phase α-β alloy specimens and all β alloys are easier to prepare than single-phase α specimens. Kroll's reagent appears to be adequate for most alloys. A modification of Weck's reagent was used for color metallography.

INTRODUCTION

Titanium and its alloys have become quite important commercially over the past fifty years due to their low density, good strength-to-weight ratio, excellent corrosion resistance and good mechanical properties. On the negative side, the alloys are expensive to produce.

Titanium, like iron, is allotropic and this produces many heat treatment similarities with steels. Moreover, the influences of alloying elements are assessed in like manner regarding their ability to stabilize the low temperature phase, alpha, or the high temperature phase, beta. Like steels, Ti and its alloys are generally characterized by their stable room temperature phases - alpha alloys, alpha-beta alloys and beta alloys, but with two additional categories: near alpha and near beta.

Titanium and its alloys are more difficult to prepare for metallographic examination than steels. As for all refractory metals, titanium and its alloys have much lower grinding and polishing rates than steels. Deformation twinning can be induced in alpha alloys by overly aggressive sectioning and grinding procedures. It is safest to mount relatively pure Ti specimens, especially those from service in a hydrogen-containing environment, in castable ("cold") resins rather than using hot compression mounting due to the potential for altering the hydride content and morphology. However, these resins must be used in such a way as to minimize the heat of polymerization. Elimination of smearing and scratches during polishing can be difficult.

Early mechanical preparation procedures [1-5] tended to be rather long, involving procedures nearly always incorporating an attack polishing solution in the last step or last two steps. Some of the more commonly used attack polishing solutions are summarized in [6]. The problems associated with obtaining well-prepared surfaces have prompted considerable

interest in electropolishing procedures [3-5, 7, 8]. The inherent danger of some of these electrolytes has prompted interest in chemical polishing procedures [9]. Electrolytic and chemical polishing solutions for Ti and Ti alloys are also summarized in [6].

Mechanical polishing methods for titanium and its alloys continued to rely upon these older procedures into the 1970's [10] and 1980's [11]. Perhaps the first publication of a modern approach for preparing titanium was that of Springer and Ahmed [12] in 1984. This was a three-step procedure, assuming that the planar grinding step can be performed with 320-grit SiC paper, which may not always be possible. If the specimens are sectioned using a wafering blade or an abrasive blade of the proper bond strength, which produce a smooth surface with minimal damage, then 320-grit SiC paper may be used. If a rougher surface with greater damage was produced, such as would result from use of a power hacksaw, then grinding must commence with a coarser grit paper in order to remove the damage in a reasonable time. Grinding and polishing rates of Ti are much lower than for many other metals and alloys.

SPECIMEN PREPARATION

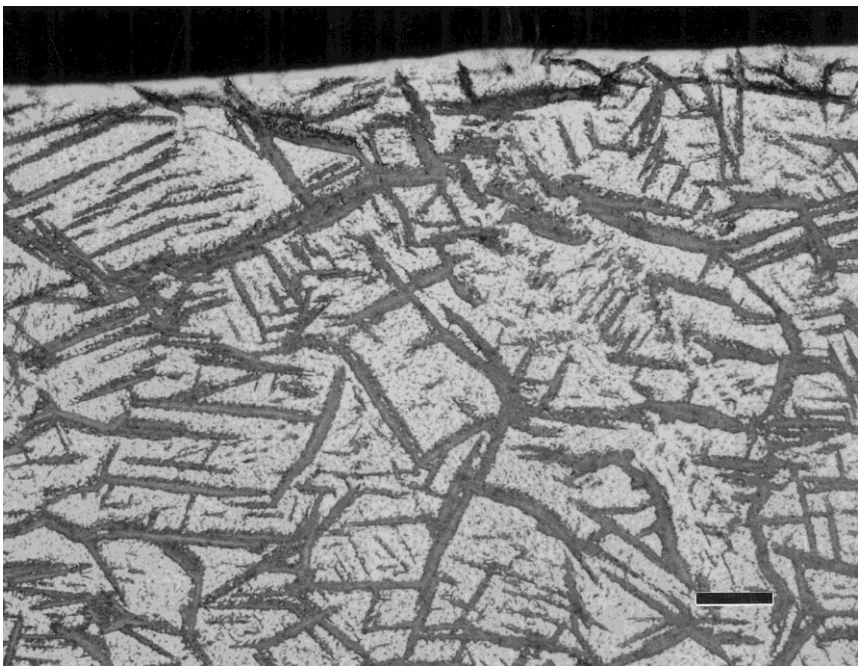
Although Ti and its alloys can be readily sectioned using band saws, power hack saws and similar machine shop tools, these devices produced a great deal of damage. Figure 1 demonstrates the substantial depth of damage that can be produced when sectioning commercial purity (CP) titanium. If the left edge was chosen for the plane-of-polish, then at least 200 µm must be ground away to get through the sectioning damage. This damage will be difficult to remove in rough grinding, as the grinding rate is very low. Consequently, to obtain perfect surfaces, section Ti and its alloys with only laboratory abrasive saws or precision saws using blades designed for metallography (avoid using blades made for production machining).

Figure 1. Polished surface of alpha-Ti, ASTM F67, Grade 2, in the annealed (1038 °C) condition showing (left edge) extreme surface damage due to band sawing (modified Weck's reagent, polarized light plus sensitive tint). The magnification bar is 100 μm in length).

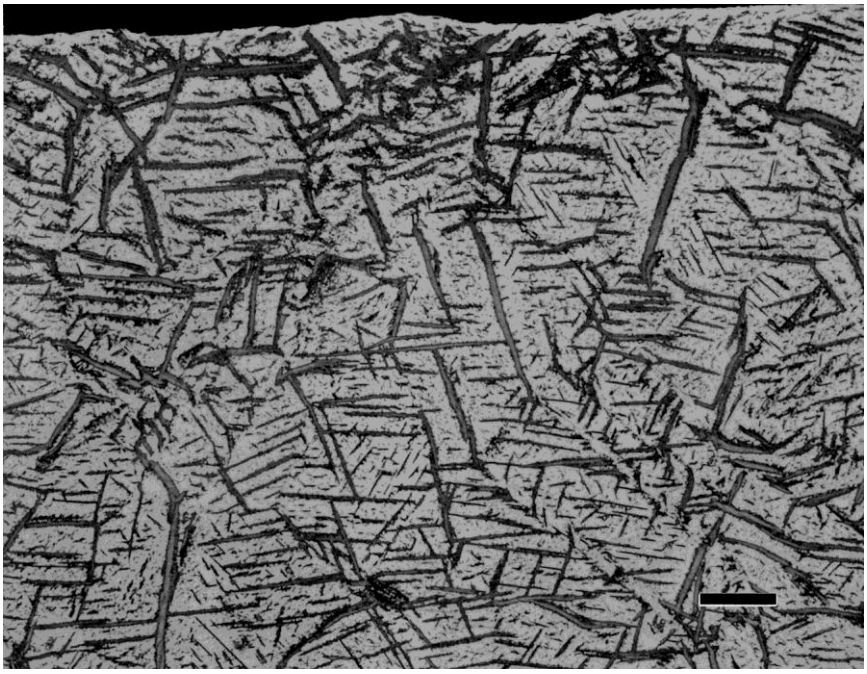
Strictly speaking, any mounting compound can be used for Ti and its alloys. However, if specimens of Ti used in applications where hydrogen can be picked up are to be mounted, it is best to use a low-viscosity epoxy resin and a conductive mounting approach to minimize the exotherm during polymerization. If the heat involved in polymerization is substantial, titanium hydrides could be dissolved. Specimens never placed in service are unlikely to contain hydrides, and more freedom of choice in mounting is possible. To minimize the heat of polymerization, wrap aluminum foil, as used in cooking, around a block of steel or copper (a heat sink). Then, glue a phenolic ring form (a cylinder) to the foil to create a mold. Place the specimen inside the ring form and add the epoxy. If a low-viscosity epoxy such as EpoThin® resin is used, which cures slowly, the exotherm during curing will be <10 ºC above room temperature. If a plastic or silicone rubber mold is used with the same epoxy, the exotherm will be higher. The faster the epoxy cures, the higher the exotherm. Acrylic resins cure in less than 10 minutes and the exotherm is very high – high enough to burn your fingers if you touch the mold while it is curing. That is not "cold" mounting! Mounting of your specimens facilitates specimen identification, simplifies automation and yields far better edge retention than unmounted specimens. But, choose a resin that does not produce shrinkage gaps.

To illustrate the effect of mounting temperature, Figure 2 shows the microstructure of a CP Ti tube, 19-mm in diameter with a 1-mm wall thickness that was used in a hydrogen-bearing atmosphere. The tube became plugged and broke in service. The writer cut several rings from the tube and mounted them with different compounds: EpoMet® thermosetting resin using a hot mounting press, EpoKwick® fast-curing (~45 minutes) epoxy, EpoThin® low-viscosity, slow curing (~8 hours) epoxy, and several others, including a cast acrylic resin. The specimen mounted in EpoThin resin contained the most TiH; all others, regardless of the type of resin, contained somewhat less TiH. Interestingly, the interface between the alpha-Ti matrix and the TiH was not as sharp in the specimen mounted with the slow-curing epoxy using a conductive molding approach as the interfaces for all other mounted specimens. The hot-mounted specimen (using a mounting press at 150 ºC) appears to have at least as much TiH, if not more, than the specimen mounted using a fast curing epoxy in a plastic mold.

a) ID of tube mounted in EpoThin resin using the conductive mounting approach.



b) ID of tube mounted in fast-curing EpoKwick resin with a polymeric mold.



c) ID of a tube mounted in a press at 150 ºC using EpoMet thermosetting resin.

Figure 2. Appearance of titanium hydride at the inner diameter of a CP Ti tube that broke in service showing the greatest amount of TiH in (a) where a low-viscosity, slow curing epoxy was used with a conductive mounting approach to keep the heat of polymerization below 30 ºC. Magnification bars are 20 µm long in each image. The specimens were not etched.

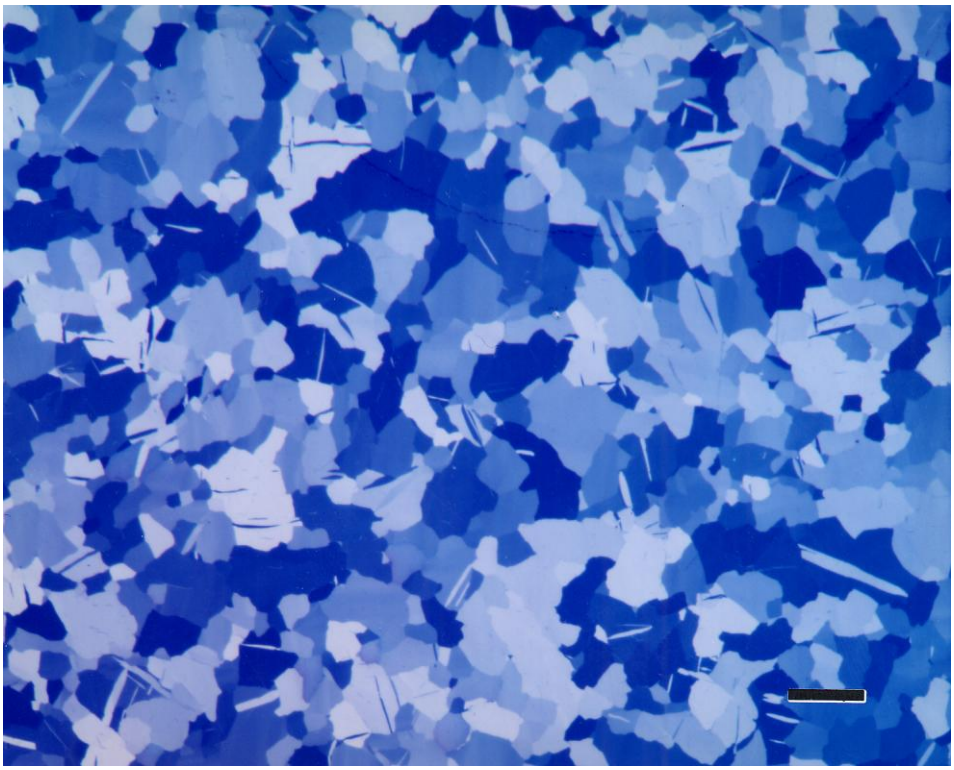
A series of experiments was conducted to develop an improved method to prepare titanium and its alloys. Numerous surfaces were tried with the aim of producing a damage free surface in CP Ti so that good polarized light images can be obtained after the last step. The method developed works best when cutting damage is minimized. Sectioning is a violent process and the vast majority of problems encountered in specimen preparation can be attributed to failure to remove the damage from sectioning. So, the first rule for successful preparation is: introduce the least possible amount of damage in sectioning (which will also produce a good surface finish). Next, mount the specimen for ease of identification and for facilitation of edge retention. Then, commence grinding with the finest possible SiC grit size, 240-grit is usually adequate and 320-grit SiC may be used if you are careful in placing the specimens in the specimen holder so that the surfaces are flat and parallel to the SiC paper surface. The next rule is: commence grinding with the finest possible abrasive that will remove the sectioning damage in a reasonable time. Coarse abrasives introduce more damage than fine abrasives. Automated grinding and polishing is highly recommended, not only because it yields superior results compared to hand polishing, but also because the final step employs an attack-polishing agent.

Step 2 utilizes psa (pressure-sensitive adhesive) backed UltraPol® silk cloth and 9-µm diamond abrasive. I charge the cloth with diamond in paste form by setting the platen speed at about 100 rpm, placing the syringe tip at the center of the cloth and slowly pulling the tip towards the cloth periphery. This deposits a concentric track of diamond on the cloth. Turn off the polisher and rub the paste into the cloth surface. Then, add some MetaDi® Fluid (a petroleum-based lubricant) and commence polishing at 150 rpm, 6 lbs (27 N) load using "contra" rotation. In this approach, the head rotates clockwise while the platen rotates

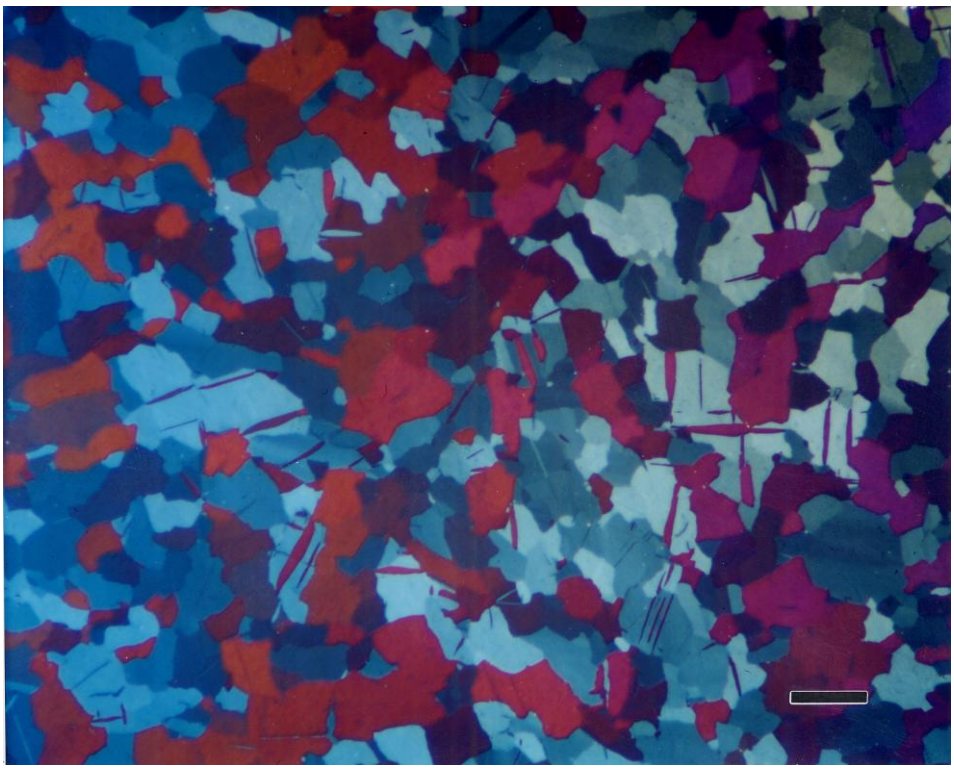
counterclockwise. Every 30 seconds, I squirt onto the cloth a small amount of 9-µm MetaDi Supreme® diamond suspension to keep the cutting rate high. Continue polishing for 10 minutes. After 10 minutes, clean the specimens and the holder and change the surface.

For step 3, I use a psa-backed, napped MicroCloth® pad (synthetic suede) with the same load, rpm, time and rotation direction using MasterMet® colloidal silica as the abrasive. Mix 5 parts colloidal silica with 1 part hydrogen peroxide (30% concentration – avoid skin contact) as the attack-polish agent. Contra rotation works best when the head speed is under 100 rpm. The machines used for these experiments have a 60-rpm head speed. This helps to keep the abrasives on the cloth surface. If the head and platen both rotate in the same direction (called "complementary" rotation), centrifugal force throws the abrasive and the lubricant off the surface almost as fast as you add it. A rule for polishing is: keep the polishing surfaces uniformly covered with abrasive and lubricant to minimize smearing, pull-out and deformation. After step 3, clean the specimen and holder. I stop adding any abrasive at least 20 seconds before the 10 minute polishing cycle ends. With 10 seconds remaining, direct the water jet onto the polishing cloth to clean both the cloth and the specimens. Colloidal silica is more difficult to remove from specimens than other abrasives. Table 1 summarizes the three-step preparation method and the sidebar lists details on the rules for pain-free, successful specimen preparation.

After step 3, CP Ti can be examined as polished with crossed polarized light to observe the grain structure. Figure 3a shows an example of ASTM F67 Grade 2 CP Ti examined after the 3-step preparation procedure. This is an as-rolled specimen and it contains some mechanical twins. If the specimen is placed on the VibroMet® 2 vibratory polisher, using only colloidal silica (no attack polishing agent), better coloration can be obtained although no further detail is detected, as shown in Figure 3b.



a)



b)

Figure 3. Microstructure of as-hot rolled ASTM F67 Grade 2 CP Ti revealed (a) after the three-step method and (b) after 20 minutes of vibratory polishing after the three-step method. The specimens are in cross-polarized light and are not etched. The magnification bars are 100 µm long.

Examination of CP Ti is actually more effective with polarized light in the as-polished condition, when using a properly prepared specimen, than with bright field illumination after etching. Figure 4 shows the microstructure of CP Ti in bright field after etching with Kroll's reagent. The grain structure is reasonably well delineated, but details are not as good as using polarized light on an as-polished specimen. Color etching with a modification of Weck's reagent also produces better grain structure development than Kroll's reagent, Figure 5. Weck's reagent for Ti contains: 100 mL water, 50 mL ethanol and 2 g $NH_4F{\cdot}HF$. This composition will produce white "butterfly-shaped" artifacts in the color image, which can be eliminated using only 25 mL ethanol. Etch by immersion until the surface is colored, usually about 15-25 seconds. Coloration is enhanced with examination using polarized light and a sensitive tint filter. It is often helpful to move slightly off the crossed position.

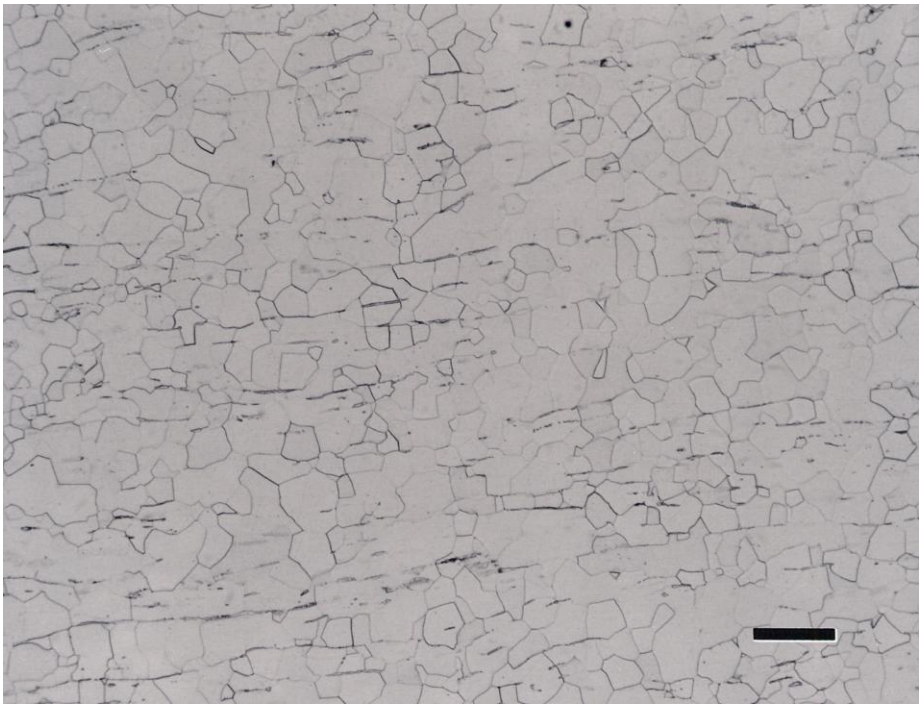


Figure 4. CP Ti (ASTM F67, Grade 4, longitudinal plane, annealed) prepared using the three-step method followed by etching with Kroll's reagent and viewing with bright field illumination. The magnification bar is 50-µm long.

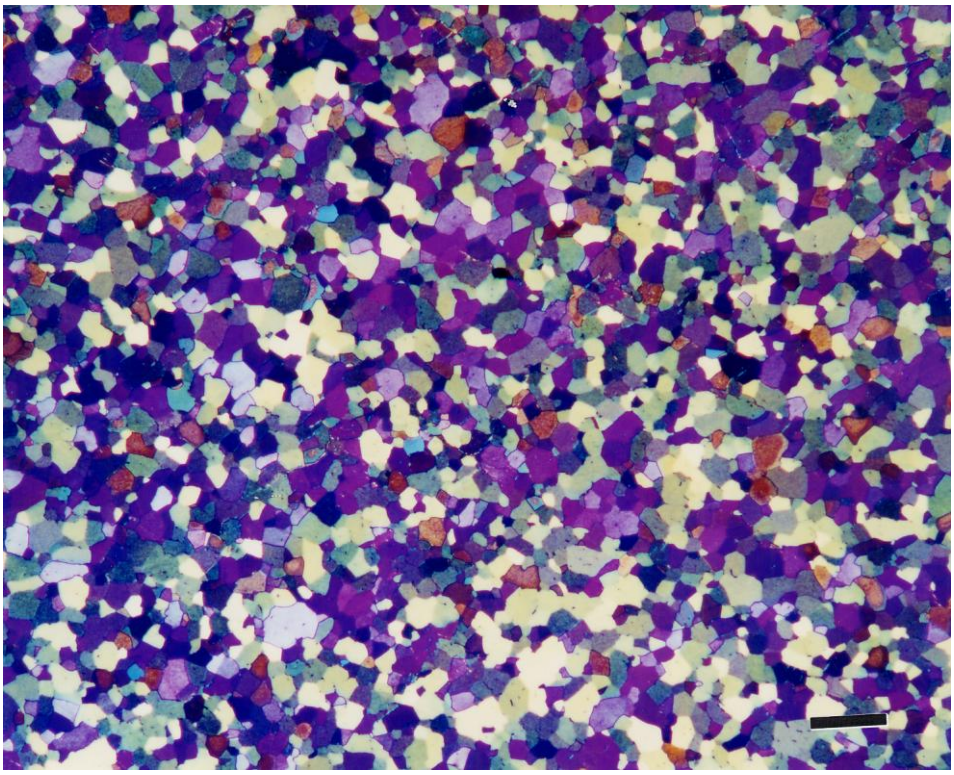


Figure 5. CP Ti (ASTM F67, Grade 4, transverse plane, annealed) prepared using the three-step method and tint etched with modified Weck's reagent. The specimen was examined with cross-polarized light and sensitive tint to enhance coloration. The magnification bar is 100 µm long.

Other cloths can be used for the final polishing step, e.g., MasterTex® and ChemoMet® cloths. The three-step method works very well on the alpha-beta alloys and the beta alloys. MasterPrep® alumina suspension works nearly as well as colloidal silica.

A few variants of the attack polishing solution have been tried. Leonhardt [14] uses a mixture of: 150mL colloidal silica, 150mL water, 30mL H_2O_2 (30%), 1-5mL HF and 1-5mL HNO_3. Results with this attack polishing additive to the abrasive were equivalent to the one used. Buchheit [6] added 5mL of a 20% aqueous CrO_3 solution to 30mL of an alumina slurry. To try this, but using colloidal silica instead, 10mL of the 20% CrO_3 solution was added to 75mL of colloidal silica. This also produced excellent results. In using these attack polishing solutions, care must be taken in handling, mixing and using these additives as they contain very strong oxidizers and acids. Avoid physical contact with the ingredients and the prepared attack polishing abrasives.

MICROSTRUCTURES

Quality control laboratories frequently check lots of titanium for the presence of an alpha case at the surface due to oxygen pick-up during heat treatment. Oxygen is an alpha stabilizer and the case is detrimental to machining, mechanical properties and service life. Good edge retention is important for this work and mounting is necessary. Edge retention is highly dependant upon elimination of shrinkage gaps between the specimen and the mount. EpoMet resin gives superb results but requires a mounting press. Of the cast resins, epoxy works best. The three-step method, despite step 3 being 10 minutes on a napped cloth, gives perfect results using either EpoMet resin or an epoxy, such as EpoThin, EpoHeat™, EpoxiCure® or EpoKwick resins. The specimens are perfectly flat coming into step 3. As long as the pressure is kept at 6 lbs, and not lower, flatness is not impaired. Figure 6 illustrates alpha case in an experimental Ti alloy prepared using the three-step method.

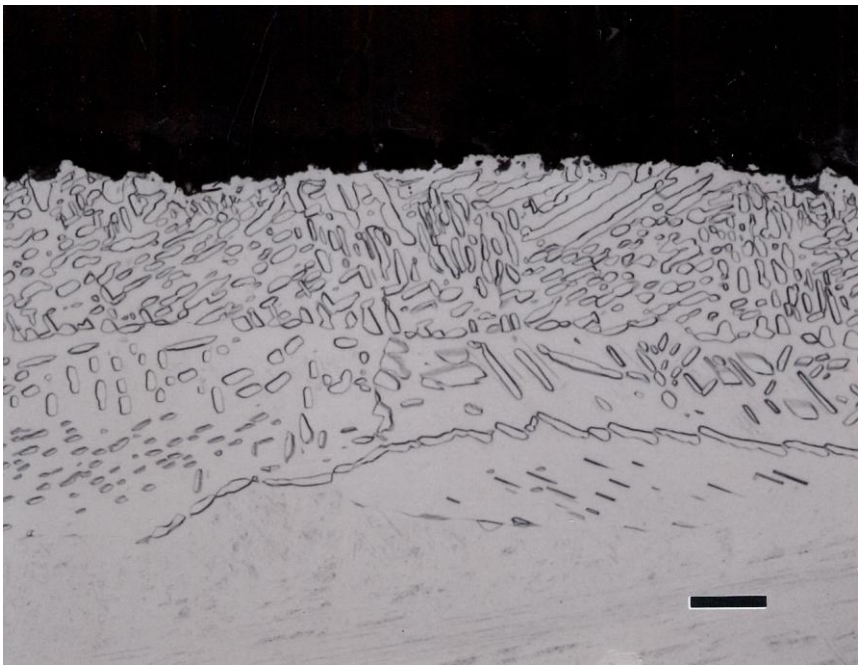
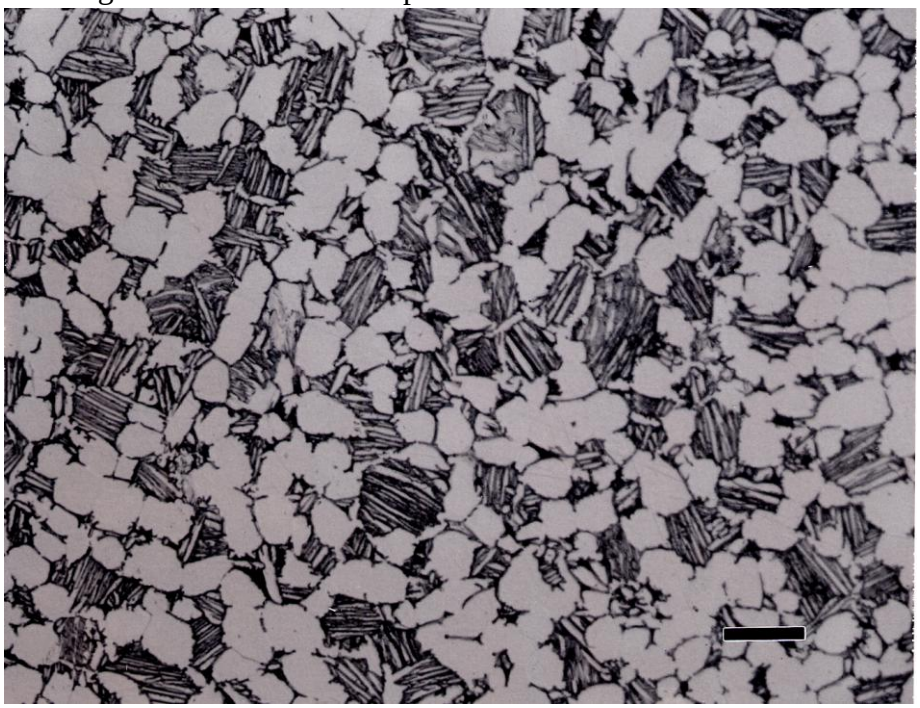
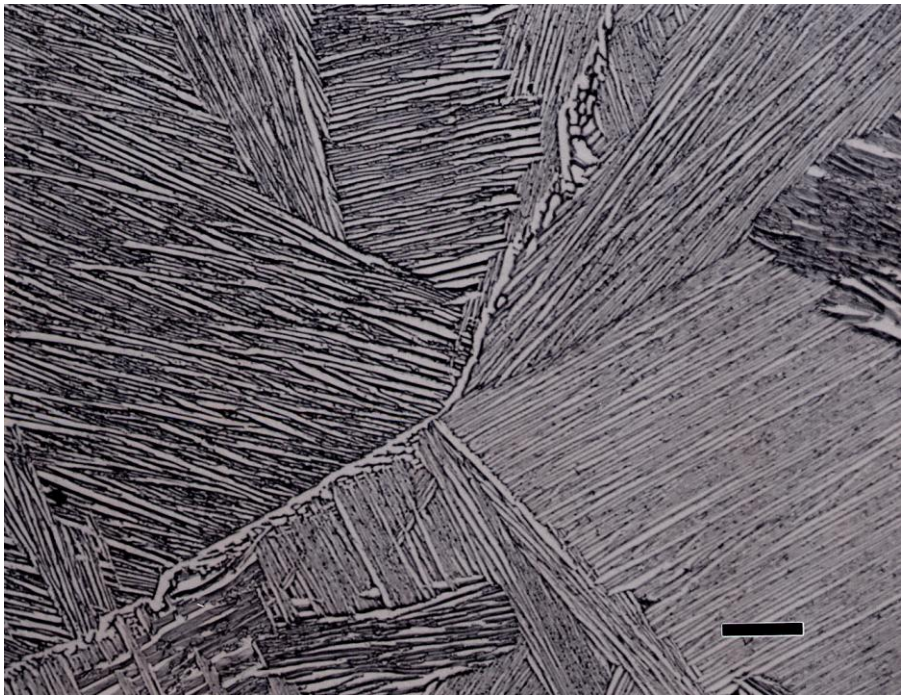


Figure 6. Alpha phase stabilized at the surface of a heat-treated Ti – 3% Cr experimental alloy prepared using the three-step method and etched with Kroll's reagent. The magnification bar is 20 µm long.

Alpha-beta alloys respond perfectly to the three-step method, as they are easier to prepare than the alpha alloys. Figure 7 shows the microstructure of an alpha-beta alloy, Ti6242, after alpha-beta forging and alpha-beta annealing compared to the same alloy after beta forging and beta annealing. The beta transus temperature for this alloy is 995 ºC ± 15 ºC. Forging and annealing below the beta transus results in a fine grained alpha-beta microstructure (primary alpha and transformed beta) while forging and annealing above the beta transus results in a coarse grained basket weave alpha-beta microstructure.



a)



b)

Figure 7. Microstructure of Ti – 6% Al – 2% Sn – 4% Zr – 2% Mo – 0.1% Si after (a) alpha-beta forging at 954 ºC and alpha-beta annealing at 969 ºC and (b) after beta forging at 1038 ºC and beta annealing at 1024 ºC. The specimens were prepared using the three-step method and etched with Kroll's reagent. The magnification bars are 20 μm long.

Modified Weck's reagent can also be used with alpha-beta alloys with good results. As an illustration, Figure 8 shows the microstructure of as-cast and heat treated Ti - 4% Zr while Figure 9 shows the microstructure of a laser weld in Ti- 6% Al – 4% V. Both were etched in modified Weck's reagent and are viewed in polarized light plus sensitive tint.

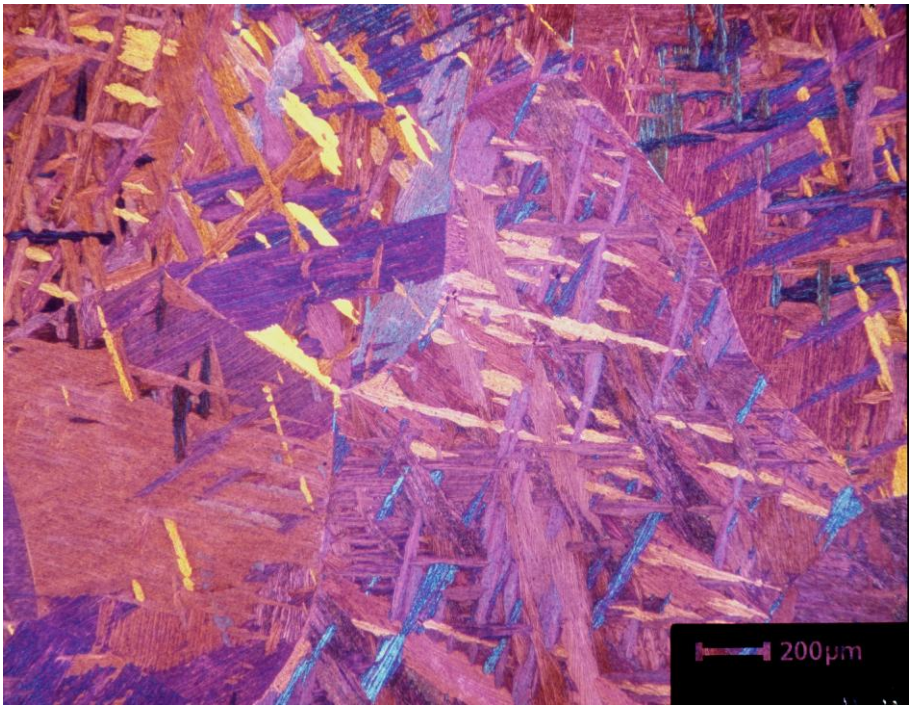


Figure 8. Basket weave alpha-beta microstructure of as-cast Ti – 4% Zr annealed at 800 °C after etching with modified Weck's reagent and viewed with polarized light plus sensitive tint.

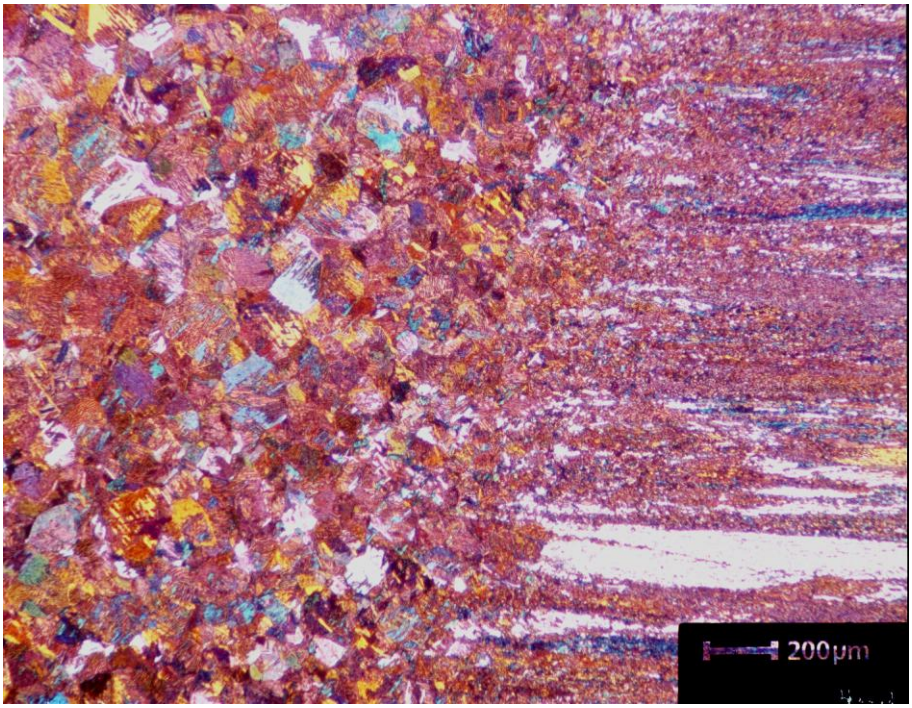
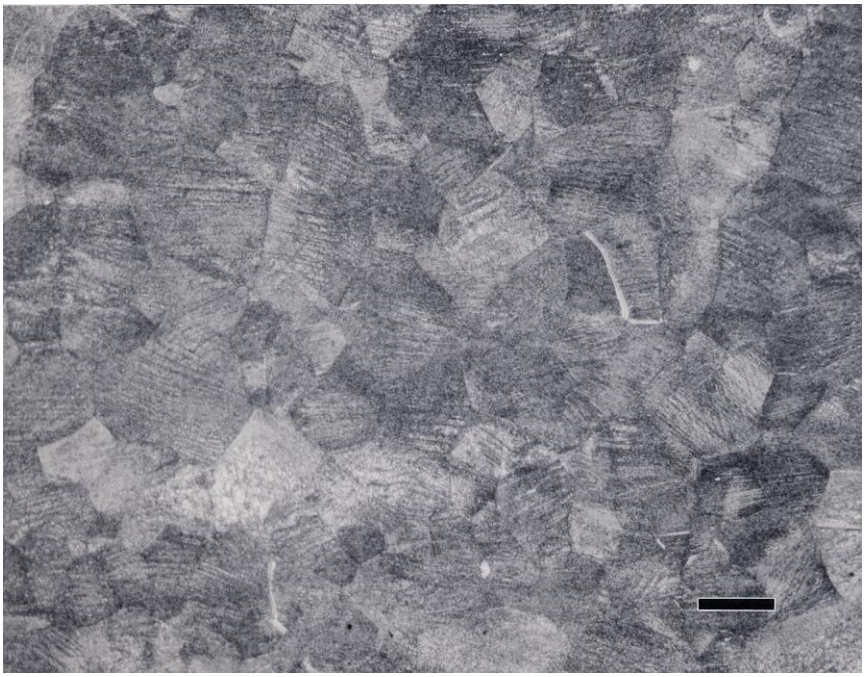
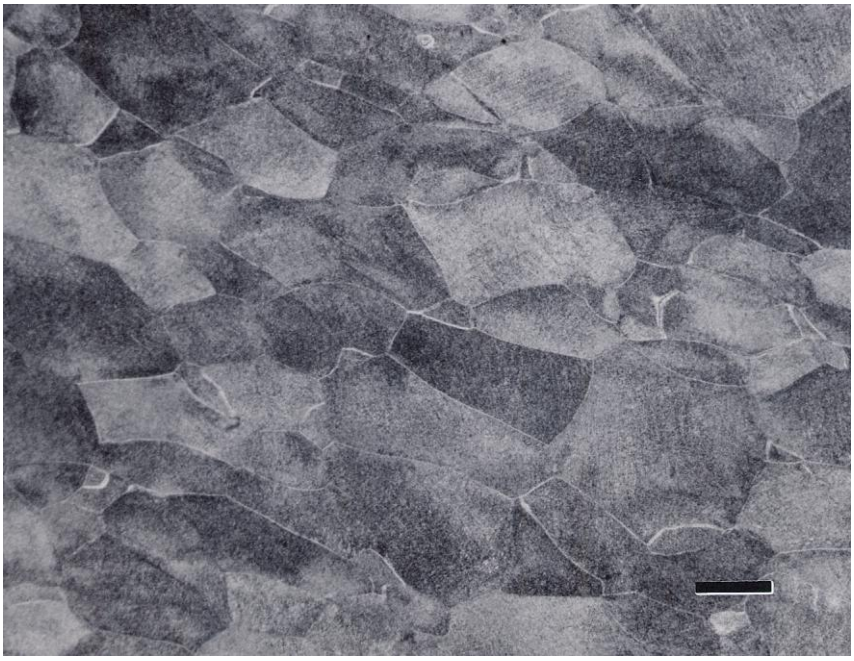


Figure 9. Microstructure of a laser weld in Ti – 6% Al – 4% V etched with modified Weck's reagent and viewed with polarized light plus sensitive tint.

Beta alloys can also be prepared easily with the three-step method. Figure 10 illustrates the microstructure of two beta alloys, Ti-5333 and Beta C.



a)



b)

Figure 10. Microstructure of beta alloys prepared using the three-step method: a) Ti – 5% V – 3% Al – 3% Cr – 3% Sn (beta transus is ~760 °C); and, b) Ti – 3% Al – 8% V – 6% Cr – 4% Mo – 4% Zr, called Beta C (beta transus is 730 °C). Both etched with Krolls. Magnification bars are 20 μm long.

CONCLUSIONS

A three-step procedure was developed and found to be quite successful for preparing titanium and titanium alloys. Use of an attack polish additive in step 3 is required to obtain good results with CP titanium and alpha Ti alloys. Most two-phase Ti alloys can be satisfactorily prepared without using an attack-polishing additive, although results were better when it was used. Polarized light is very effective for examining the microstructure of alpha-Ti. Color etching can be used to reveal the microstructure of alpha and alpha-beta alloys. Kroll's reagent works well for alpha-beta and beta alloys.

REFERENCES

1. Finlay, W. L., Resketo, J. and Vordahl, M. B., "Optical Metallography of Titanium", Industrial and Engineering Chemistry, **42**, p.218-222 (February 1950).
2. Craver, C. B., "Differentiation of Grain Size and Phases in Titanium", Metal Progress, **59**, p. 371-373 (March 1951).
3. Osadchuk, R., Koster, W. P. and Kahles, J. F., "Recommended Techniques for Polishing Titanium for Metallographic Examination", Metal Progress, **64**, p.129-131, 236, 240 (October 1953).
4. McQuillan, A. D. and McQuillan, M. K., Titanium, Academic Press, N.Y., p.447-458 (1959).

5. Echer, C. J., Cooney, J. E. and Kish, A. J., "Metallography of 5Al-2.5Sn Titanium Alloy", Metals Engineering Quarterly, **7**, p.58-63 (February 1967).
6. Vander Voort, G. F., Metallography: Principles and Practice, McGraw-Hill, N.Y., p.548 (1984); ASM International, Materials Park, Ohio (1999).
7. Jacquet, P. A., "Electrolytic Polishing and Oxidation of Titanium", Metal Treatment and Drop Forging, **18**, p. 176, 182 (April 1951).
8. Coons, W. C. and Isoty, L. R., "Electrolytic Polishing System for Space Age Materials", Metal Progress, **109**, p.36-40 (May 1976).
9. Simmer, B. and Schmalfuss, D., "Comments on The Preparation of Metallographic Specimens of Titanium with Particular Reference to Chemical Polishing", Praktische Metallographie, **15**, p.78-85 (February 1978).
10. "Metallographic Techniques for Titanium and Titanium Alloys", Metals Handbook, 8th ed., Metallography, Structures and Phase Diagrams, ASM, Metals Park, OH, **8**, p.140-141 (1973).
11. Boyer, R. R., "Titanium and Titanium Alloys", Metals Handbook, 9th ed., Metallography and Microstructures, ASM, Metals Park, OH, p.458-475 (1985).
12. Springer, C. and Ahmed, W. U., "Metallographic Preparation of Titanium", Praktische Metallographie, **21**, p.200-203 (1984).
13. G. F. Vander Voort, "Metallographic Preparation of Titanium and its Alloys," Buehler Tech-Notes, Vol. 3, Number 3, 1999.
14. Leonhardt, T., Rhemium Alloys, private communication.

Table 1. Three-Step Procedure to Prepare Titanium and Its Alloys

Surface	Abrasive and Size	Load, Lbs. (N) per Specimen	Platen Speed (rpm)/Direction	Time (minutes)
CarbiMet® Abrasive Discs	320- (P400) grit SiC, water cooled	6 (27)	240-300 Contra[3]	Until Planar
UltraPol™ silk cloth	9-µm MetaDi Supreme® diamond suspension[1]	6 (27)	120-150 Contra	10
MicroCloth® or Veltex cloths	~0.05-µm MasterMet® colloidal silica[2]	6 (27)	120-150 Contra	10

Notes:

[1] Charge the cloth first with 9-µm MetaDi diamond paste (natural or synthetic monocrystalline or polycrystalline), and add MetaDi Fluid before commencing polishing. During the 10-minute cycle, add some 9-µm MetaDi Supreme suspension every 30 seconds to keep the cutting rate high throughout the cycle.

[2] Mix one part hydrogen peroxide (30% concentration) to five parts MasterMet colloidal silica as an attack-polish agent. Avoid skin contact as 30% H_2O_2 will cause burns.

[3] Contra rotation is best utilized when the specimen holder rotates at <100 rpm. With a 60-rpm specimen holder, the liquid abrasives stay much longer on the surface than when complementary rotation is used. In complementary rotation, both the platen and the specimen holder are rotating counterclockwise. Thus, centrifugal force throws the liquid abrasives and lubricants off the platen and down the drain almost as fast as they are added to the polishing surface. With certain specimens, and this is highly material specific and relatively uncommon, contra rotation in step 3 may produce a relief pattern around precipitates that are much harder or much softer than the matrix. If this is observed, and it is not usually seen with Ti, repeat the final step in complementary rotation for about 2 minutes and the relief pattern will be eliminated.

Sidebar

Rules to Make Perfect Metallographic Specimen Preparation Painless and Easy

1. Sectioning is a very violent process. Minimize the damage introduced in sectioning by using abrasive blades developed for metallography, rather than for production cutting. Use an abrasive cut-off machine, an IsoMet® low-speed saw or an IsoMet precision saw.

2. To obtain good edge retention, use a mounting compound that does not produce shrinkage gaps. For hot compression mounting, use EpoMet® thermosetting resin. Use a mounting press that cools the specimen back towards room temperature under pressure. Epoxy cast resins also do not produce shrinkage gaps as they physically adhere to the specimen. Other cast resins will produce some degree of shrinkage gap between the specimen and the mount.

3. After obtaining a relatively smooth surface with minimal sectioning damage, commence grinding using the finest possible abrasive size. Avoid excessively coarse abrasives as they introduce substantial damage to the structure.

4. Use flat woven cloths, such as silk, nylon, polyester, and chemotextiles for diamond polishing. These keep the specimen flat. Rigid grinding disks yield exceptional flatness. For final polishing, various napped cloths, as well as polyurethane, can be used without introducing relief as long as the correct pressure is used.

5. Keep all polishing surfaces as uniformly coated with lubricants and abrasives as possible to avoid or minimize smear, pull-out of second-phase particles, and deformation of the matrix.