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Color Metallography

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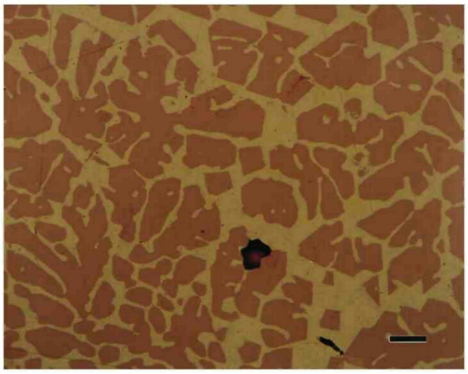
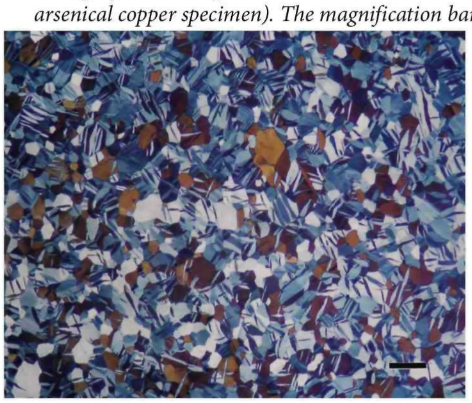
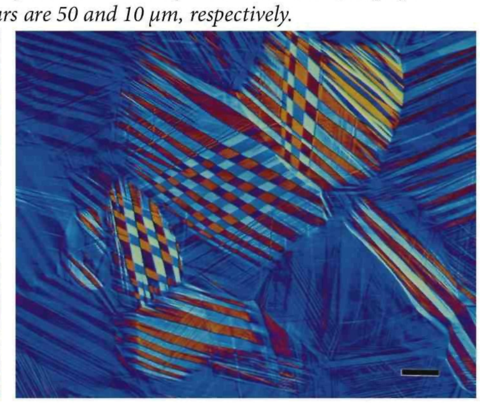
Color has historically seen limited use in metallography, mainly due to the cost of film and prints and the difficulty and cost of reproducing images in publications. However, with the growth of digital imaging, capturing color images is much simpler and cheaper. Also, printing images in color is inexpensive for in-house reports, and can be distributed cheaply on CDs, although reproduction in journals is still expensive. Color does have many advantages over black and white. First, the human eye is sensitive to only about forty shades of gray from white to black, but is sensitive to a vast number of colors. Tint etchants reveal features in the microstructure that often cannot be revealed using standard black and white etchants. Color etchants are sensitive to crystallographic orientation and can reveal if the grains have a random or a preferred crystallographic texture. They are also very sensitive to variations in composition and residual deformation. Further, they are usually selective to certain phases and this is valuable in quantitative microscopy.



Figures 1 (left) and 2 (right) showing natural reddish-purple color of the $AuAl_2$ intermetallic (left) in bright field and cuprous oxide's characteristic ruby red color in dark field illumination (tough-pitch arsenical copper specimen). The magnification bars are 50 and 10 μm, respectively.





Figures 3 (left) and 4 (right): Grain structure on high-purity Zr (left) that was hot worked and cold drawn (note mechanical twins) and viewed in polarized light and of Spangold (Au – 19Cu-5Al) that was polished and cycled through the shape-memory effect to produce martensite and Nomarski differential interference illumination was used to image the surface upheaval due to the shear reaction at the free surface. The magnification bars are 100 and 50 μm, respectively.

The use of color in metallography has a long history with color micrographs published over the past eighty-some years. Examples of natural color in metals are rare (Figure 1). Gold and copper exhibit yellow color under bright field illumination. Color can be produced using optical methods, as in dark field illumination (Figure 2), polarized light (Figure 3) and differential interference contrast illumination (Figure 4). The microstructure of metals with non-cubic crystal structures can be examined without etching using polarized light but color is not always observed. The specimen must be prepared completely free of residual damage for color to be observed, and even then, some non-cubic metals still exhibit little color. However, many metals and alloys can be etched with reagents that deposit an interference film on the surface that creates color in bright field illumination. If it is difficult to grow such a film to the point where the color response is excellent, the color can be enhanced by examination with polarized light, perhaps aided with a sensitive tint filter (also called a lambda plate or first-order red filter).

Anodizing

There are a number of electrolytic etching reagents that can be used to produce color. Second-phase constituents can be colored and viewed with bright field. Anodizing aluminum specimens with Barker's reagent, or similar solutions, does not produce an interference film, as color is not observed in bright field. This procedure produces fine etch pitting on the surface. The grain structure can be seen in black and white in polarized light, and in color if a sensitive tint plate is added. Figure 5 show an example of anodizing to reveal the grain structure of super-pure aluminum.

Color Etching

Many metals etched with standard reagents to reveal the grain boundaries often yield only a high percentage of the boundaries, rather than all of the boundaries. Color etchants, however, reveal the grain structure completely. In the case of metals with annealing twins, it can be very difficult to rate the grain size when a standard etchant reveals a portion of the grain and twin boundaries. In fact, it can be quite difficult to make a precise measurement of the grain size, even manually, with such a specimen, as distinguishing between grain and twin boundaries (the latter must be ignored in the measurement), is not simple. However, with a color etched microstructure it is relatively easy to separate grain from twin boundaries, at least manually. Further, the films grow as a function of crystal orientation. Therefore, one can detect any preferred crystallographic orientation by the narrowness of the color range present. If a wide range of colors is present in a random pattern, the crystal orientation is

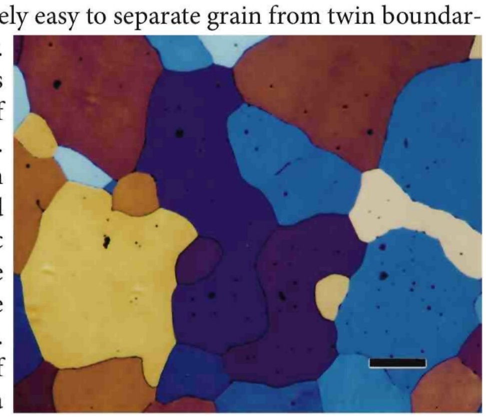


Figure 5. Super-pure aluminum anodized with Barker's reagent (30 V dc, 2 minutes). The magnification bar is 200 μm long.

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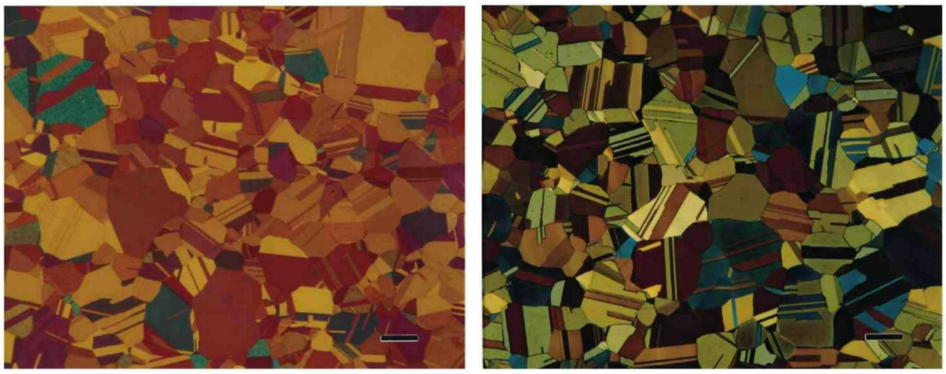
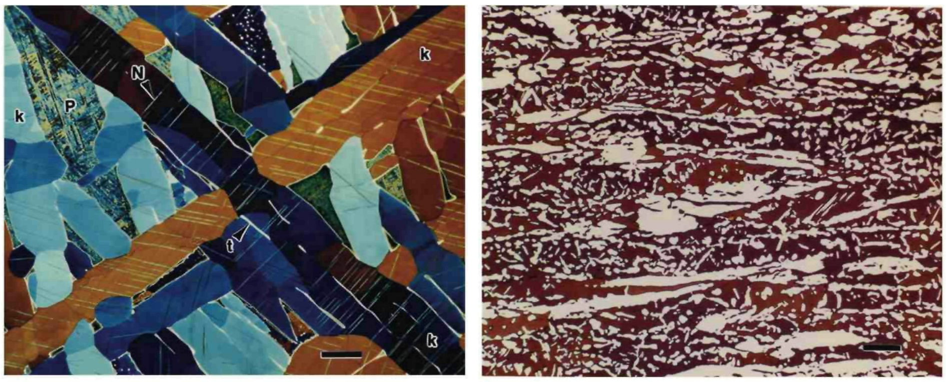
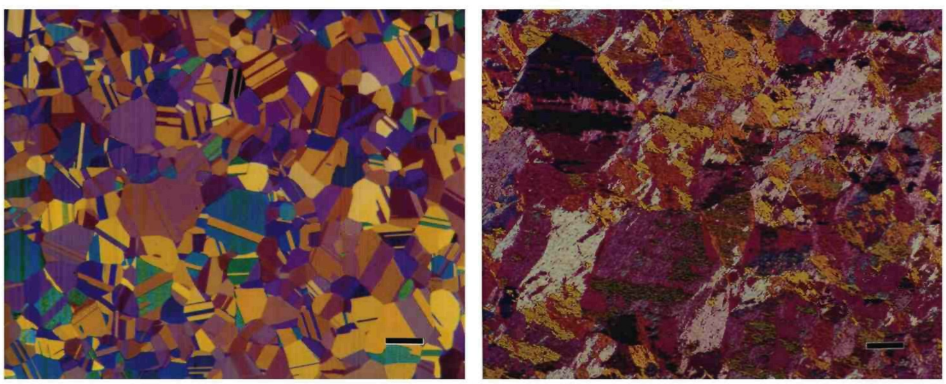


Figures 6 and 7: FCC twinned grain structure of cartridge brass, Cu – 30% Zn, after cold reduction by 50% and full annealing, tint etched with Klemm's I (left) and Klemm's III (right) reagents and viewed with polarized light plus sensitive tint. Magnification bars are 200-μm long.



Figures 8 and 9: Fine octahedrite grain structure of the Gibeon meteorite (left) revealed with Beraha's reagent (100 mL water, 10 g $Na_2S_2O_3$ and 3 g $K_2S_2O_5$) and ferrite in 7 Mo PLUS duplex stainless steel plate revealed using Beraha's reagent (85 mL water, 15 mL HCl, 1 g $K_2S_2O_5$). The magnification bars are 500 and 50 μm long, respectively.



Figures 10 and 11: FCC twinned grain structure of heading quality Custom Flo 302 stainless steel revealed using Beraha's B1 reagent and lath martensite grain structure of over-austenitized (1093 °C) AerMet 100 ultra-high strength steel revealed using 10% sodium metabisulfite. Both viewed with polarized light plus sensitive tint. The magnification bars are 100 μm long.

random. If a narrow range of colors is present in the grains, then a preferred orientation is present. Tint etch compositions are given at the end of the article.

Specimen preparation must be better when using color methods compared with black and white methods because the epitaxially grown films are sensitive to residual preparation-induced damage that was not removed. This level of preparation is required in image analysis work and can be easily obtained by a knowledgeable metallographer with the proper equipment. Electrolytic polishing is not required to get damage-free surfaces.

The most common tint etchants are those that deposit a sulfide-based interference film on the specimen. These are the best-known tint etches and usually the easiest to use. Klemm and Beraha have developed the most widely used sulfide-based tint etchants using sodium thiosulfate, $Na_2S_2O_3$, and potassium metabisulfite, $K_2S_2O_5$. Klemm's I, II, III (Figures 6 and 7) and one of Beraha's reagents utilize both ingredients (Figure 8), while Beraha recommends a range of HCl concentrations used with potassium metabisulfite (Figure 9) for etching a variety of iron-based alloys. These etchants can be used to color ferrite and martensite in cast iron, carbon and low-alloy steels. The HCl-based reagents vary widely in concentration and can be used to color the grain structures of stainless steels (Figure 10), Ni-based and Co-based alloys. Sodium metabisulfite has been used in a number of concentrations, from about 1 to 20 g per 100 mL water, and is a safe, reliable, useful color etch for irons and steels (Figure 11).

Beraha also developed etchants based upon sulfamic acid, a weak organic acid, which has not been used much, although they are quite useful, reliable and easy to employ. The sulfamic acid-based reagents are applicable to cast iron, low-carbon and alloy steels, tool steels, and martensitic stainless steels (Figure 12). Beraha also developed two rather specialized tint etches that deposit cadmium sulfide (Figure 13) or lead sulfide (Figure 14) films on the surfaces of steels and copper-based alloys. These two etchants are quite useful, although tedious to make. His CdS reagent is useful for carbon and alloy steels, tool steels, and ferritic, martensitic and precipitation hardenable stainless steels, while the PbS reagent does an excellent job on copper-based alloys and can be used to color sulfides in steels white (the specimen is pre-etched with nital and the etch colors the darkened matrix, so that the white sulfides are visible).

Beraha also developed two tint etchants that utilize molybdate ions in nitric acid. They color cementite in steels (Figure 15). He also developed tint etchants that deposit elemental selenium on the surface of steels (Figure 16), nickel-based alloys and copper-based alloys (Figure 17).

There are a number of other tint etchants that have been developed by a variety of metallographers. Lichtenegger and Blöch, for example, developed an unusual reagent that will color austenite (Figure 18) in duplex stainless steels, rather than ferrite (as nearly all others do).

Weck developed a number of tint etchants, while utilizing many of them in her research. Several were developed to color aluminum (Figure 19) or titanium alloys (Figure 20). In each case, it is easier to develop good color with the cast alloys than with the wrought alloys. Two etchants have been found useful for coloring theta phase, $AlCu_2$, in Al-Cu alloys; Lienard developed one of the

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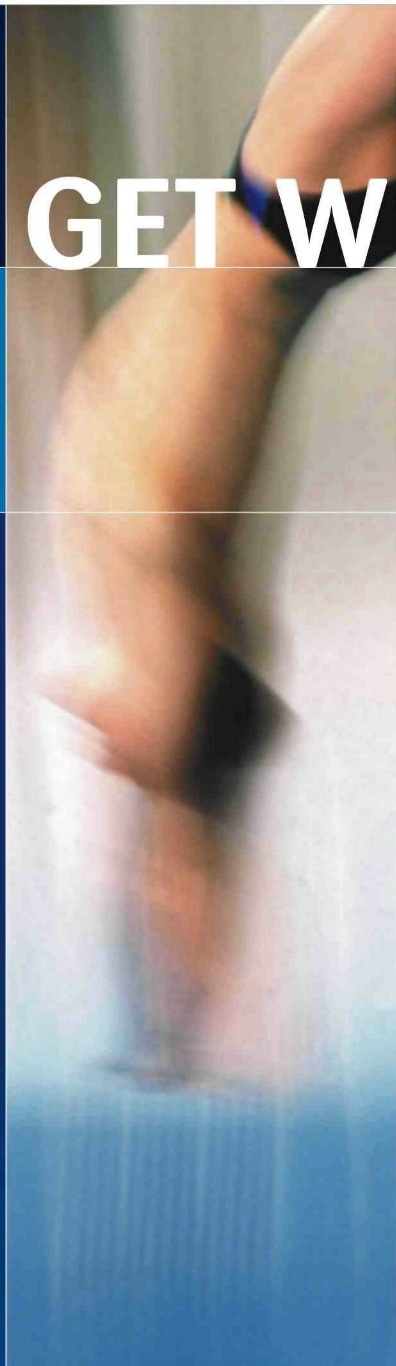

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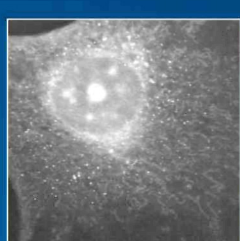
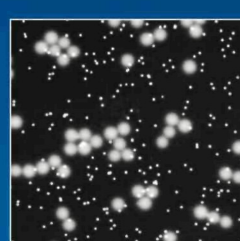


NIH-3T3 cell



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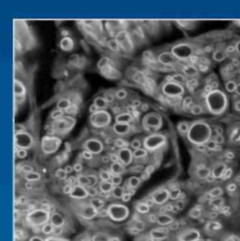

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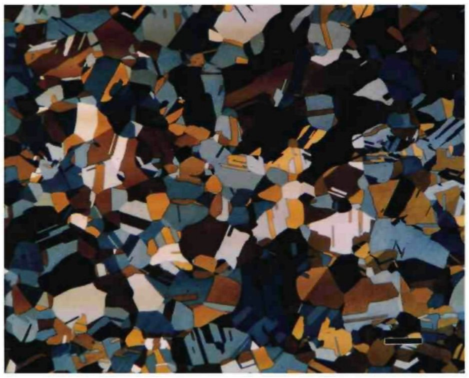
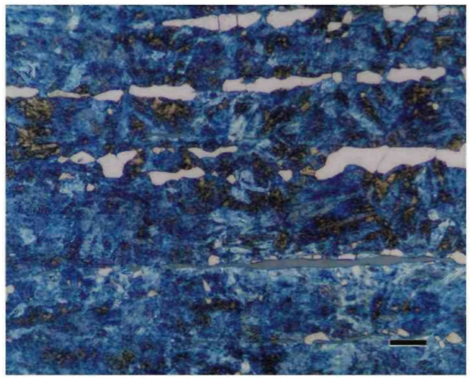
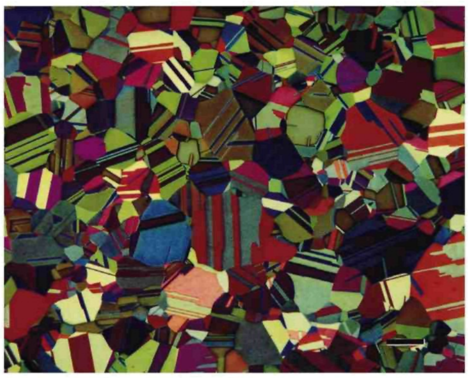
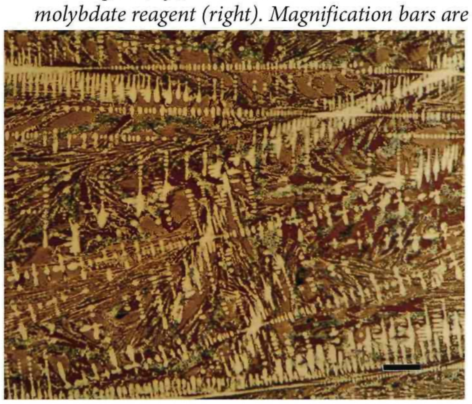
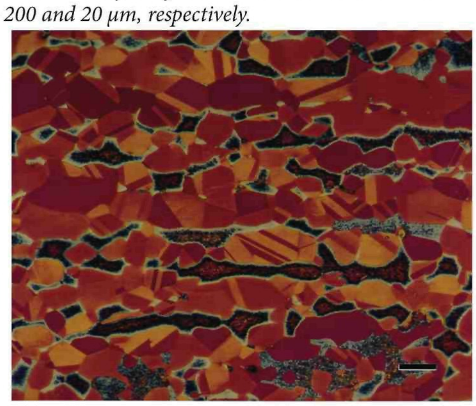



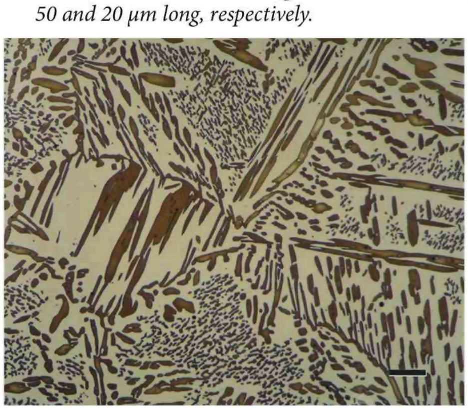
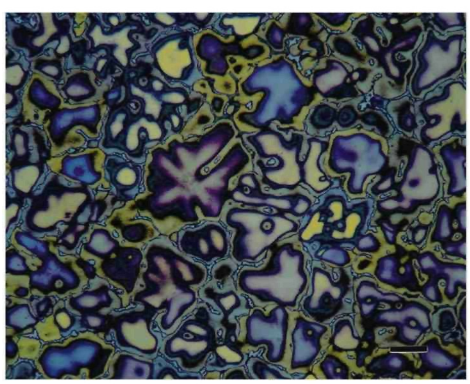
Figures 12 and 13: Twinned FCC grain structure in Fe-39% Ni revealed by Beraha's sulfamic acid reagent (left) and tempered martensite grain structure of Carpenter Project 70 type 416 martensitic stainless steel revealed with Beraha's CdS reagent (right). The white grains are delta ferrite and the gray inclusions are sulfides. Viewed with polarized light plus sensitive tint. The magnification bars are 100 and 200 μm long, respectively.




Figures 14 and 15: Cartridge brass micrograph shown in Figures 6 and 7 tint etched with Beraha's PbS reagent (left) and cementite in a hot rolled Fe-1% C binary alloy colored with Beraha's sodium molybdate reagent (right). Magnification bars are 200 and 20 μm, respectively.

Figures 16 and 17: Cementite in the chill cast surface of gray iron etched with Beraha's selenic acid reagent for cast iron (left) and twinned FCC alpha phase and beta phase (mottled and outlined) in Cu-40% Zn revealed using Beraha's selenic acid reagent for copper alloys. Magnification bars are 50 and 20 μm long, respectively.

Figures 18 and 19: Austenite colored in ASTM A890 Grade 5A cast duplex stainless steel with the LB1 reagent (left) and the cast grain structure of 206 aluminum revealed using Weck's reagent for Al alloys (right). The magnification bars are 100 and 50 μm long, respectively.

easiest to use. Several color etchants have been developed for molybdenum (Figure 21) and for tungsten. Details on these etchants can be found in [1].

Conclusions

The examples shown have demonstrated the great value of color and tint etching for examining microstructures of metals. Solutions exist to develop color with most commercial alloy systems. The examples clearly demonstrate the value of these reagents in revealing the grain structure fully, even for the most difficult to etch specimens. Further, they are selective in nature that can be quite useful for quantitative metallographic studies. Tint etchants reveal segregation very clearly and either EDS or WDS can be performed on a tint-etched surface without any problems from the interference surface layer. ■

Reference

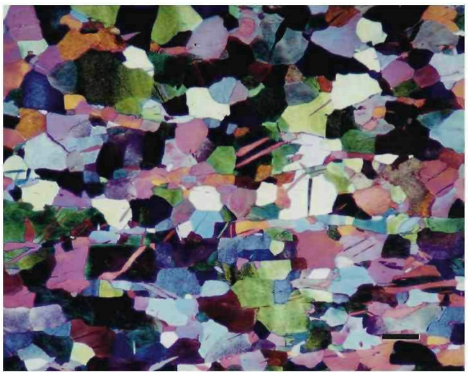
[1]. G. F. Vander Voort, Metallography: Principles and Practice, McGraw-Hill Book Co., NY, 1984 and ASM International, Materials Park, Ohio, 1999.

Appendix

Etch Compositions

- Klemm's I: 50 mL stock solution, 1 g $K_2S_2O_5$ (stock solution is water saturated with $Na_2S_2O_3$
- Klemm's III: 5 mL stock solution, 45 mL water, 20 g $K_2S_2O_5$ (stock solution as for Klemm's I)
- Beraha's 10/3 reagent: 10g $Na_2S_2O_3$, 3g $K_2S_2O_5$ and 100 mL water
- Beraha's BI: 100 mL stock solution (1000 mL water, 200 mL HCl, 24 g NH_4FHF) plus 0.1 – 0.2 g $K_2S_2O_5$ for martensitic stainless steel and 0.3 – 0.6 g $K_2S_2O_5$ for austenitic and ferritic stainless steels.
- Beraha's sulfamic acid reagent No. III: 100 mL water, 3 g $K_2S_2O_5$, 2 g NH_2SO_3H (two other similar compositions were published) for carbon and alloy steels.
- Beraha's sulfamic acid reagent No. IV: 100 mL water, 3 g $K_2S_2O_5$, 1 g NH_2SO_3H, 0.5 – 1 g NH_4FHF for high-Cr tool steels and martensitic stainless steels.
- Beraha's CdS and PbS reagents: CdS stock solution: 1000 mL water, 240 g $Na_2S_2O_3 \cdot 5H_2O$, 20-25 g cadmium chloride (or cadmium acetate), 30 g citric acid; PbS stock solution: 1000 mL water, 240 g $Na_2S_2O_3 \cdot 5H_2O$, 30 g citric acid, 24 g lead acetate.

Mix each in order given. Age solutions in a dark bottle, in darkness, for 24 hours before use. To use the CdS reagent, filter excess precipitates from about 100 mL of solution. CdS regent will color microstructure of a wide



Figures 20 and 21: Grain structure of as-rolled CP Ti (ASTM F67, Grade 2) containing mechanical twins (left) etched with modifided Weck's reagent and cold rolled pure molybdenum (right) colored with the reagent developed by Oak Ridge National Laboratory. Magnification bars are 100 and 20 µm long, respectively.

range of irons and steels in 20 to 90 s. To use the PbS reagent, do not filter excess precipitates when you pour about 100 mL of the stock solution for use. The PbS reagent will color the microstructure of most copper-based alloys. It will also etch steel microstructures.

- Beraha's sodium molybdate reagent: Stock Solution: 1000 mL water, 10 g $Na_2MoO_4 \cdot 2H_2O$. Pour off about 100 mL of the stock solution and add HNO_3 to bring the pH to 2.5 – 3.0. For steels, add small amounts of NH_4FHF to control coloration (none for cast iron). Colors cementite.
- Beraha's selenic acid reagent for cast iron: 100 mL ethanol, 2 mL HCl, 1 mL selenic acid.
- Beraha's selenic acid reagent for Cu alloys: 300 mL ethanol, 2 mL HCl, 0.5-1 mL selenic acid
- Lichtenegger and Blöch LB1 reagent: of 20 g of ammonium bifluoride, NH_4FHF, and 0.5 g potassium metabisulfite, $K_2S_2O_5$, dissolved in 100 mL water (use hot water). Etch at 25-30 °C.
- Weck's reagent for Al: 100 mL water, 4 g $KMnO_4$ and 1 g NaOH
- Modified Weck's reagent for Ti: 100 mL water, 25 mL ethanol and 2 g ammonium bifluoride. The original formula specified 50 mL of ethanol, but that produces etch artifacts.
- ORNL tint etch for Mo: 70 mL water, 10 mL sulfuric acid and 20 mL hydrogen peroxide (30% conc.). The specimen is immersed for 2-3 minutes. Swab etching produces a flat etched microstructure (no color).

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