Color “Tint” Etching

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Guidelines

• Best results occur when etching right after polishing, time can create a passive surface
  • Specimen preparation must remove all damage
• Etch the specimen with a general-purpose etch, then re-polish and tint etch for best results
• Tint etching must be done by immersion, as swabbing will inhibit film formation
• The film grows epitaxially with the underlying grain structure with little “etch” depth
Tint Etching Reveals

- Grains are colored according to their crystallographic orientation (film thickness is a function of crystal orientation)
- Very sensitive to chemical inhomogenieties
- Very sensitive to residual deformation
- Etchants are phase specific, i.e., selective
Color by Anodizing

- Color Due to Surface Roughening by Electrolytic Etching
  - Most Successful for Aluminum and Alloys
  - Solutions Also for Nb, Ta, Ti, U and Zr
- Reveals Grain Orientations but not Segregation
Equiaxed alpha grains in the interior of a super-pure aluminum specimen anodized with Barker’s reagent, 30 V dc, 2 min. Viewed with crossed polarized light plus sensitive tint. The dark spots are intermetallic phases. The magnification bar is 200 µm long.
Wrought 2024-F aluminum (Al – 4.4% Cu – 1.5% Mg – 0.6% Mn) bar (28.5 mm diam.) showing the grain structure and intermetallics. Magnification bar is 200 µm long. Anodized with Barker’s reagent (30 V dc, 2 min.). Transverse plane.
As-cast (concast) 1100 Al (>99% Al) anodized with Barker’s reagent (30 V dc, 2 min.) revealing a dendritic solidification structure and intermetallics in the interdendritic areas. But anodizing does not reveal chemical segregation (“coring”) within the dendrites. Viewed with crossed polarized light plus sensitive tint. The magnification bar is 50 µm long.
Wrought 6061-F Al that was extruded. The micrograph shows part of the sheared end of the bar. It was anodized with Barker’s reagent (30 V dc, 2 min.) revealing highly elongated, thin grains. Shearing is a mechanical sectioning method that produces gross deformation. It was viewed with crossed polarized light plus sensitive tint. The magnification bar is 100 µm long.
Color Produced by “Standard” Etchants

- Alkaline Sodium Picrate (Ischewsky, 1903)
- Murakami’s Reagent (Murakami, 1918)
- Groesbeck’s Reagent (Groesbeck, 1924)
  - Malette’s Reagent (Malette, 1935)
- Electrolytic NaOH or KOH (Gilman, 1952)
- Solutions to Color Intermetallics in Al Alloys
Proeutectic cementite in heat treated Ni-Hard cast iron (Fe – 3.4% C – 0.9% Mn – 0.9% Si - 1.7% Cr – 4.5% Ni – 0.4% Mo). Etching with Vilella’s reagent (left) reveals the cementite (white, unetched) and tempered martensite. Graphite is present but hard to see. Etching with boiling alkaline sodium picrate (right) colors the cementite and the gray graphite is easily seen against the unetched martensite. Magnification bars are 50 µm in length.
Microstructure of alloyed white cast iron (Fe - 3.1% C – 0.8% Mn – 1% Si – 18.6% Cr – 2% Mo) containing substantial primary carbides. Etching with Groesbeck’s reagent (80 °C – 30 seconds) colored the carbides, including some very fine carbide. The black spots are small shrinkage cavities. The magnification bar is 50 µm long.
Microstructure of wrought 7-Mo duplex stainless steel (Fe - <0.1% C – 27.5% Cr – 4.5% Ni – 1.5% Mo) solution annealed and then aged 48 h at 816 °C to form sigma. Electrolytic etching with aqueous 20% NaOH (3 V dc, 10 s) revealed the ferrite as tan, the sigma orange, while the austenite was not colored. The arrows point to austenite that formed during the conversion of ferrite to sigma. Magnification bar is 10 µm in length.
Microstructure of as-cast ASTM A 890-5A duplex stainless steel (Fe – <0.03% C - <1.5% Mn - <1% Si – 25% Cr – 7% Ni – 4.5% Mo – 0.2% N) in the solution annealed condition. Etched with aqueous 20% NaOH, at 3 V dc for 10 seconds (left) and with modified Murakami’s reagent (20g NaOH, 20 g K$_3$Fe(CN)$_6$, 100 mL water (80 °C – 60 seconds). Both color ferrite while austenite is unaffected. The magnification bars are 100 µm long.
Standard “Black & White” Reagents That Produce Color in Polarized Light

- Pearlite Etched with Nital
- Monel Etched with Woodard’s Solution
- Mg Etched with Acetic Picral
- Pb Etched with Acetic-$\text{H}_2\text{O}_2$-Ethanol-Water
- Cu and Alloys Etched with Alcoholic Ferric Chloride Solutions
- Cu Alloys Etched with Potassium Dichromate
Wrought aluminum brass, Cu – 22% Zn – 2% Al, annealed at 750°C (1382 °F) producing equiaxed alpha grains containing annealing twins. Potassium dichromate etch. Images in bright field (left) and crossed polarized light plus sensitive tint (right). The magnification bars are 50 µm long.
Microstructure of cold worked pure magnesium (99.98% Mg) after etching with the acetic-picral reagent and viewing with polarized light plus sensitive tint. Note the presence of numerous mechanical twins (yellow arrows). The magnification bar is 200 μm long.
The microstructure of Zn – 0.1% Ti – 0.1% Cu in the as-cast (left) and hot rolled (right) conditions after etching with the Palmerton reagent and viewing with polarized light plus sensitive tint. Compare the image on the right to the as-polished specimen viewed with polarized light shown next. The as-cast structure shows alpha grains containing mechanical twins and an interdendritic eutectic. Hot working produced a banded structure (longitudinal plane shown) of elongated HCP alpha grains (some mechanical twins can be seen) and intermetallic phases. The magnification bars are both 50 µm long.
Microstructure of Zn – 0.1% Ti – 0.1% Cu hot rolled to 6-mm thickness, in the as-polished condition, using polarized light, revealing elongated HCP grains containing mechanical twins. Some fine precipitates are present in the grain boundaries but are not clearly revealed (see below, for comparison, the structure after etching with the Palmerton reagent and viewing with polarized light plus sensitive tint). The magnification bar is 50 µm long.
Wrought, solution annealed and aged beryllium copper, Cu – 1.8% Be – 0.3% Co in the heat treated condition: 790 °C (1454 °F), hold 1 h, oil quench, age at 315 °C (600 °F) for 2 h. Hardness 380 HV. Swab etched with equal parts ammonium hydroxide and hydrogen peroxide (3% conc.). Polarized light brings out the diffuse “criss-cross” markings due to the sub-microscopic γ’ precipitates that create elliptical polarization response. There is some over-aging at the grain boundaries where γ can be found. Viewed with crossed polarized light plus sensitive tint. The magnification bar is 50 µm long.
Color by “Tint” Etching

- Color From Interference Effects Due to Film Formation
- Polarized Light and Sensitive Tint Often Improve Color Response
  - Solutions Developed for Many Metals and Alloys
  - Film Thickness (and Color) Depends on Crystal Orientation, Composition, Segregation, and Residual Deformation
# Klemm’s Color Etchants

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Composition</th>
<th>Uses</th>
</tr>
</thead>
</table>
| I       | 50 mL Stock Solution  
1 g K₂S₂O₅ | Cast Iron, Steels, β in 
Brass, Cu Alloys, Zn and 
Alloys |
| II      | 50 mL Stock Solution  
5 g K₂S₂O₅ | Alpha Brass, Sn, Mn 
Steels |
| III     | 5 mL Stock Solution  
45 mL Water  
20 g K₂S₂O₅ | Bronze, Monel |

Stock Solution: Water Saturated with Na₂S₂O₃
Heinz Klemm

Born in Freiberg, Germany, 22 December 1915

Died on 5 January 1991, age 75

\( \text{Na}_2\text{S}_2\text{O}_3 \) Based Color
Regents Developed in 1950
Microstructure of Muntz metal, Cu – 40% Zn, heated into the alpha + beta phase field at 716 °C, held 1 hour and water quenched, producing an alpha/beta grain structure. The specimen was etched with Klemm’s I to color the beta phase (left, in bright field). Imaging of this field with Nomarski DIC (right) reveals annealing twins in the non-colored alpha phase. The magnification bar is 100 µm long.
Microstructure of Muntz metal, Cu – 40% Zn, heated into the beta field, 843 °C, held 1 hour and air cooled. Beta transformed on cooling to alpha+beta. Etching with Klemm’s I revealed three prior-beta grains containing alpha and beta where the beta is colored uniformly within each prior-beta grain (beta is ordered), but a different color results for beta in each grain due to differences in crystal orientation. The specimen is viewed in bright field. The magnification bar is 100 µm long.
Annealed and cold drawn Naval Brass (Cu – 39.7% Zn – 0.8% Sn) viewed on a transverse plane after etching with Klemm’s I reagent, which colors the beta phase. Imaging with bright field (left) reveals some detail of the annealing twins in the alpha grains while polarized light plus sensitive tint (right) reveals them better. Same field shown. Original at 200X.
Microstructure of cartridge brass, Cu – 30\% Zn, that was cold reduced 50\% in thickness and annealed at 704 °C for 30 minutes producing a fully annealed alpha FCC grain structure with annealing twins. Etching with Klemm’s II reagent for 2 minutes produced line etching within certain twins and grains. The lines are parallel to specific crystal planes. The specimen was viewed in bright field. The magnification bar is 50 µm long.
Microstructure of a welded carbon steel specimen etched with Klemm’s I reagent to reveal the ferritic grain structure and imaged with polarized light plus a sensitive tint filter. The magnification bar is 200 µm long. The arrows point to the ends of the line of fusion.
Ferrite grains in lamination sheet steel revealed using Klemm’s I tint etch. This is a duplex condition where there are much larger grains near the surface. Magnification bar is 100 µm in length. Viewed with polarized light plus sensitive tint.
Microstructure of a scrapped portion of a musket barrel made in the 19th century at the Henry gun factory near Nazareth, Pennsylvania etched with Klemm’s I and viewed with polarized light plus sensitive tint. The surface layer is scale (iron oxide) from forging the wrought iron. Beneath the scale is a layer of columnar ferrite grains. Below this zone, the grains are smaller and equiaxed. At the bottom of the filed, the ferrite grains are larger and show evidence of segregation (the area probably saw less heat and forge work). The fine black spots are slag particles. The magnification bar is 200 µm long.
Microstructure of a W – 27% Cu powder metallurgy composite material after hot isostatic pressing. The specimen was etched with Klemm’s III for 20 seconds and imaged with bright field. The magnification bar is 20 µm long.
Beraha’s “10/3” Version of Klemm’s I

100 mL Water
10 g Na$_2$S$_2$O$_3$
3 g K$_2$S$_2$O$_5$

Immerse at room temperature.
Microstructure of a copper-infiltrated, porous powder metallurgy high-carbon steel (after heat treatment which produced coarse martensite and retained austenite. The copper, which did not completely fill the pores (arrows), exhibits its natural yellow color and twins can be seen (green arrows). The martensite was revealed with Beraha’s 10/3 reagent, similar to Klemm’s I, and viewed with polarized light plus sensitive tint. The magnification bar is 20 µm in length.
Lower bainite (blue and gray), undissolved cementite (white) and as-quenched martensite (brown) in 5160 alloy steel (Fe – 0.6% C - 0.85% Mn – 0.25% Si – 0.8% Cr) that was austenitized at 830 °C (1525 °F) for 30 min., isothermally held at 343 °C (650 °F) for 20 minutes to partially transform the austenite, and then water quenched (untransformed austenite forms martensite). Etched with aqueous 10% Na$_2$S$_2$O$_3$ and 3% K$_2$S$_2$O$_5$. 
Microstructure of Gibeon, a fine octahedrite meteorite that fell in Southwest Africa (Fe – 7.93% Ni – 0.41% Co – 0.04% P) tint etched with Beraha’s “10/3” reagent and viewed with polarized light plus sensitive tint. The elongated BCC kamacite (k) grains (ferrite) follow the octahedral planes and the color varies with their orientation. Note the Neumann (N) bands (mechanical twins) in the kamacite due to extraterrestrial collisions. The white films (t) are FCC taenite (austenite) and the cross-hatched patches are plessite (p), a mix of kamacite and taenite. Two types of plessite can be seen. The magnification bar is 500 µm in length.
10% Sodium Metabisulfite

100 mL Water
10 g Na$_2$S$_2$O$_5$

Immerse at room temperature

Colors improved using polarized light plus sensitive tint

Good for constituents in steels
Upper bainite and as-quenched martensite 5160 alloy steel (Fe – 0.6% C - 0.85% Mn – 0.25% Si – 0.8% Cr) that was austenitized at 830 °C (1525 °F) for 30 min., isothermally held at 538 °C (1000 °F) for 30 sec to partially transform the austenite, and then water quenched (untransformed austenite forms martensite). Etched with 2% nital (left) and aqueous 10% Na₂S₂O₅ (right) which colored the martensite light brown and the upper bainite blue.
Low-carbon, “lath” martensite in an over-austenitized specimen of AerMet 100 (Fe – 0.23% C – 13.4% Co – 11.1% Ni – 3.1% Cr – 1.2% Mo). The grain size was coarsened by the heat treatment (1093 °C, AC, age at 675 °C for 6 h, AC) making it easier to see the lath structure. Etched with aqueous 10% sodium metabisulfite and viewed with polarized light plus sensitive tint. The magnification bar is 100 μm long. AerMet is a trademark of Carpenter Technology Corp., Reading, Pennsylvania.
# Beraha’s Sulfamic Acid Etchants

<table>
<thead>
<tr>
<th>Reagent</th>
<th>H₂O mL</th>
<th>K₂S₂O₅ g</th>
<th>NH₂SO₃H g</th>
<th>NH₄FHF g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>6</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>3</td>
<td>1</td>
<td>0.5 - 1</td>
</tr>
</tbody>
</table>

1 is basic solution for cast iron, carbon and alloy steels. 2 and 3 are faster acting. 4 is for martensitic stainless steel, Mn steels, and tool steels.
Microstructure of a wrought iron Roman-era nail, in the shaft beneath the head, revealing ferrite grains, slag stringers (red arrows), and Neumann Bands (mechanical twins – yellow arrows) etched with Beraha’s sulfamic acid etch (No. 1) and viewed with polarized light plus sensitive tint. The magnification bar is 100 µm long.
Microstructure of an AH-36 ship steel (Fe - <0.18% C – 1.3% Mn – 0.3% Si – 0.03% Nb – 0.03% Al) flux-cored arc weld (gas assisted) tint etched with Beraha’s sulfamic acid reagent (No. 3) and viewed with polarized light plus sensitive tint. The red arrows point to the fusion line. The magnification bar is 200 µm long.
Microstructure of the core of a carburized, heat treated 4118 alloy steel (Fe – 0.2% C – 0.8% Mn – 0.5% Cr – 0.12% Mo) tint etched with Beraha’s sulfamic acid reagent (No. 1) and viewed with polarized light plus sensitive tint revealing a lath martensite structure. The magnification bar is 20 µm long.
Microstructure at the surface of a decarburized, hardened specimen of type 420 martensitic stainless steel (Fe – 0.35% C – 13% Cr) tint etched with Beraha’s sulfamic acid reagent (No. 4) and viewed with polarized light plus sensitive tint. Note the “free ferrite” (arrows) at the surface (complete loss of carbon) and the change in the appearance of the martensite in the partial decarburized zone. The magnification bar is 100 µm long.
Twinned austenitic grain structure of wrought, annealed Fe – 39% Ni tint etched with Beraha’s sulfamic acid solution (No. 3) and viewed with polarized light plus sensitive tint. The magnification bar is 100 µm long.
Twined austenitic grain structure of solution annealed, wrought Hadfield manganese steel (Fe – 1.12% C – 12.7% Mn – 0.31% Si) tint etched with Beraha’s sulfamic acid reagent (100 mL water, 3 g potassium metabisulfite and 2 g sulfamic acid) and viewed with polarized light plus sensitive tint. The magnification bar is 100 µm long.
# Beraha’s Solutions Based on HCl and K$_2$S$_2$O$_5$

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>B0</th>
<th>BI</th>
<th>BII</th>
<th>BIII</th>
<th>BIV</th>
<th>BV</th>
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</thead>
<tbody>
<tr>
<td>HCl (%) in H$_2$O</td>
<td>0.6</td>
<td>16.7</td>
<td>33.3</td>
<td>40</td>
<td>50</td>
<td>66.7</td>
</tr>
<tr>
<td>NH$_4$FHF*</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>2-10</td>
</tr>
<tr>
<td>K$_2$S$_2$O$_5$*</td>
<td>1</td>
<td>0.1-0.6</td>
<td>0.3-0.8</td>
<td>0.3-1.0</td>
<td>0.3-0.8</td>
<td>0.6-1.0</td>
</tr>
<tr>
<td>Na$_2$S**</td>
<td>0</td>
<td>0</td>
<td>0.1-0.25</td>
<td>0.1-0.25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CuCl$_2$**</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>FeCl$_3$**</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1-1.5</td>
<td>1-3</td>
</tr>
</tbody>
</table>

* Amount per 100 mL   ** Optional additions, amount per 100 mL
Microstructure of Custom Flo 302-HQ austenitic stainless steel (Fe - <0.08% C – 18% Cr – 9% Ni – 3.5% Cu) in the hot rolled and solution annealed condition after tint etching with Beraha’s BI reagent. The structure is equiaxed, twinned FCC austenite. The faint vertical lines are from alloy segregation (longitudinal direction is vertical). Viewed with polarized light plus sensitive tint. The magnification bar is 100 µm long.
Austenite grains, with annealing twins, in type 316 stainless steel (Fe - <0.08% C - <2% Mn - <1% Si – 17% Cr – 12% Ni – 2.5% Mo) color etched with Beraha’s reagent (modified BI) and viewed in bright field. The magnification bar is 100 µm long.
Austenitic, twinned grain structure of 316L austenitic stainless steel (Fe - <0.03% C – 17% Cr – 12% Ni – 2.5% Mo) that was hot rolled, solution annealed, cold reduced 30% in thickness and solution annealed (1150 °C – 1 hour, water quench). The specimen was tint etched with Beraha’s BII reagent and viewed with polarized light plus sensitive tint. The faint lines, slightly off horizontal, are due to alloy segregation and are parallel to the longitudinal axis. The magnification bar is 200 µm long.
Microstructure of 7-Mo PLUS duplex stainless steel (Fe - <0.03C - <2% Mn – 27.5% Cr – 4.85% Ni – 1.75% Mo – 0.25% N) etched with Beraha’s reagent (15 mL HCl – 85 mL water – 1 g K$_2$S$_2$O$_5$) and viewed with bright field illumination. Ferrite is colored and austenite is unaffected. The magnification bar is 50 µm long.
Microstructure of 7-Mo PLUS duplex stainless steel (Fe - <0.03C - <2% Mn – 27.5% Cr – 4.85% Ni – 1.75% Mo – 0.25% N) welded with Nitronic 50, etched with Beraha’s B1 reagent and viewed with bright field illumination. Ferrite is colored and austenite is unaffected. The magnification bar is 200 µm long.
Microstructure of wrought, solution annealed and double aged (about 42 HRC) Waspaloy, a nickel-based superalloy (Ni – 0.06% C – 19.5% Cr – 4.2% Mo – 13.5% Co – 3% Ti – 1.35% Al – 0.07% Zr – 0.005% B - <2% Fe) tint etched with Beraha’s BIV reagent revealing twinned austenitic grains. Viewed in bright field. The magnification bar is 100 μm long.
Microstructure of Elgiloy, a Co-based alloy used for watch springs (Co – 20% Cr – 15% Fe – 15% Ni – 2% Mn – 7% Mo – 0.05% B – 0.15% C) after hot rolling and solution annealing (1150 °C – 2 hours, water quenched). Note the annealing twins. The specimen was tint etched with Beraha’s IV plus 1 g FeCl₃ per 100 mL. The specimen was viewed with polarized light plus sensitive tint. The magnification bar is 100 µm long.
Lichtenegger and Bloech Tint Etch

100 mL Hot Water (distilled)
20 g NH₄F·HF
0.5 g K₂S₂O₅

Dissolving ammonium bifluoride in water creates a strong endothermic reaction, hence the need to begin with hot water.

Etch for coloring austenite in stainless steels, delta ferrite and carbides are not colored. Etch at 25-30 °C, for 1 to 5 minutes. Use polyethylene containers. Wet etching is preferred.
Microstructure of as-cast ASTM A 890-5A duplex stainless steel (Fe – <0.03% C - <1.5% Mn - <1% Si – 25% Cr – 7% Ni – 4.5% Mo – 0.2% N) in the solution annealed condition. Etched with LB1 (100 mL water – 20 g NH4FHF – 0.5g K2S2O5). Austenite is colored and ferrite is unaffected. Because it is as-cast, there are no annealing twins in the austenite. Compare to images using electrolytic NaOH and with Murakami’s reagents. The magnification bar is 100 µm long.
## Beraha’s CdS and PbS Reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Composition</th>
<th>Uses</th>
</tr>
</thead>
</table>
| PbS | 1000 mL H₂O  
240 g Na₂S₂O₃·5H₂O  
24 g Lead Acetate  
30 g Citric Acid | For Copper-Based Alloys. |
| CdS | 1000 mL H₂O  
240 g Na₂S₂O₃·5H₂O  
20-25g Cadmium Chloride*  
30 g Citric Acid | For Cast Iron, Steels, Ferritic and Martensitic Stainless Steels |

Dissolve in order listed. Age in dark bottle, 24 h minimum. For CdS, filter excess precipitates in 50-100 mL before use; do not filter PbS solution before use. Store in dark place. *Can substitute cadmium acetate or cadmium sulfate.
Microstructure of pearlitic ductile iron revealed by tint etching with Beraha’s CdS reagent and viewed with polarized light plus sensitive tint. Polarized light reveals the growth structure of the graphite nodules, which are surrounded by ferrite (magenta color is from the sensitive tint filter). The matrix is fine, unresolved pearlite. The magnification bar is 20 µm long.
As-cast Ni-hard cast iron (Fe – 2.98% C – 0.64% Mn – 0.85% Si – 4.4% Ni – 2.34% Cr) containing cementite (white), retained austenite (light brown), manganese sulfides (gray particles) and plate martensite “needles” (light blue and medium blue) after tint etching with Beraha’s CdS reagent and viewing with polarized light plus sensitive tint. The magnification bar is 10 µm long.
Microstructure of austempered ductile iron tint etched with Beraha’s CdS reagent containing large graphite nodules (arrow), bainite (blue and brown) and retained austenite (white) when viewed with polarized light plus sensitive tint. Original at 500X.
Martensitic microstructure of Project 70 416 stainless steel (Fe - >0.15% C - >0.15% S – 13% Cr) in the wrought heat treated condition (about 98 HRB) tint etched with Beraha’s CdS reagent. The white grains are delta ferrite and the elongated gray particles are manganese sulfides. The longitudinal direction is horizontal. The magnification bar is 200 µm long.
Microstructure of wrought, annealed OFHC copper (oxygen-free, high-conductivity) etched with Beraha’s PbS reagent revealing a twinned, FCC, alpha grain structure. The specimen was viewed with polarized light and had a hardness of 85 HV. The magnification bar is 100 µm long.
Microstructure of cold drawn tough-pitch arsenical copper (Cu – 0.4% As) tint etched with Beraha’s PbS reagent revealing a slightly elongated twinned, FCC alpha grain structure. The structure was imaged with polarized light plus sensitive tint. The magnification bar is 100 µm long.
Microstructure of aluminum brass, Cu – 22% Zn – 2% Al, that was cold drawn and annealed at 750 °C after etching with Beraha’s PbS reagent revealing a coarse alpha FCC grain structure with annealing twins. The grain size is ASTM 0.8 and the hardness is 61 HV. The magnification bar is 200 µm long.
# Beraha’s Selenic Acid Etch for Steels and Superalloys

<table>
<thead>
<tr>
<th>Etch</th>
<th>Ethanol (mL)</th>
<th>HCl (mL)</th>
<th>H$_2$SeO$_4$ (mL)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>2</td>
<td>0.5</td>
<td>For cast iron and steels. Immerse up to 6 min. Cementite colored red-violet, ferrite unaffected, phosphide colored blue-green.</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5-10</td>
<td>1-3</td>
<td>For stainless steels. Immerse at room temperature until surface is colored.</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>20-30</td>
<td>1-3</td>
<td>For corrosion- and heat-resistant alloys. Wet etch, immerse 1-4 min. Colors carbides and gamma prime. Austenite unaffected.</td>
</tr>
</tbody>
</table>

Store in dark bottle. Etch by Immersion.
Microstructure of chilled gray iron revealed using Beraha’s selenic acid etch (No. 1). Cementite was colored and ferrite is white. The image was viewed with bright field illumination. The magnification bar is 50 µm long.
Beraha’s Sodium Molybdate Etch for Steels

<table>
<thead>
<tr>
<th>Etch</th>
<th>Water (mL)</th>
<th>Na$_2$MoO$_4$·2H$_2$O (g)</th>
<th>NH$_4$F·HF (g)</th>
<th>pH</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1</td>
<td>-</td>
<td>2.5 – 3.0</td>
<td>For cast iron. Acidify with nitric acid to pH range. Ferrite unaffected, phosphide and cementite yellow-orange.</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1</td>
<td>0.1 – 0.5</td>
<td>2.5 – 3.5</td>
<td>For cast iron, carbon, alloy and tool steels. Acidify with nitric acid to pH range. Ferrite white-yellow, carbides brown-yellow. Phosphides and carbides in cast iron blue-violet.</td>
</tr>
</tbody>
</table>
Cementite in white cast iron (Fe – 3.11% C – 1.05% Si – 0.41% Mn – 0.12% S – 0.052% P) colored with Beraha’s sodium molybdate tint etch. The specimen was viewed with bright field illumination. The magnification bar is 20 µm long.
Cementite in an as-hot rolled Fe – 1% C binary alloy revealed by tint etching with Beraha’s sodium molybdate tint etch. The arrow points to proeutectoid cementite that precipitated in a prior-austenite grain boundary. The etch also colored the cementite in the pearlite. The specimen was viewed in bright field illumination. The magnification bar is 20 μm long.
Spheroidize annealed microstructure of type W1 carbon tool steel (Fe - 1.05% C – 0.25% Mn – 0.2% Si) etched with Beraha’s sodium molybdate reagent which colored both the cementite particles (brownish red) and the ferrite matrix. The magnification bar is 5 µm long.
Beraha’s Selenic Acid Etch for Copper

300 mL Ethanol
2 mL HCl
0.5 – 1 mL Selenic Acid
Store in dark bottle. Etch by Immersion.
Annealed and cold drawn Naval Brass (Cu – 39.7% Zn – 0.8% Sn) viewed with polarized light on a transverse plane after etching with Beraha’s selenic acid reagent, which colors the alpha phase (note annealing twins) and the beta phase (color is non-uniform). The magnification bar is 50 µm long.
Microstructure of hot extruded and cold drawn Muntz metal, Cu – 40% Zn, tint etched with Beraha’s selenic acid reagent for copper which colored the twinned FCC alpha grain structure shades of yellow and red and non-uniformly colored the beta phase (note light blue border around the beta phase). Viewed in bright field. The magnification bar is 20 μm long.
The microstructure of hot worked, annealed and cold drawn Monel 400 (Ni – 32% Cu - <0.3% C - <2% Mn - <0.5% Si) revealed using Beraha’s selenic acid etch for copper (longitudinal axis is horizontal). Monel alloys are very difficult to color etch, especially wrought alloys (as-cast alloys are easier). Bright field revealed a weak image as the interference film produce is thin (inclusions, arrows, can be seen). When this occurs, polarized light will often enhance the image quality dramatically (the sensitive tint filter enhances coloration), as shown. Note the deformed, twinned FCC alpha grain structure. The magnification bars are 50 µm long.
Weck’s Reagent for Aluminum

4 g Potassium permanganate
1 g sodium hydroxide
100 mL water
Immersion at room temperature
(Works well with cast alloys)
As-cast (concast) 1100 Al (>99% Al) tint etched with Weck’s reagent revealing a dendritic solidification structure. Unlike anodizing with Barker’s reagent, the tint etch reveals the segregation (“coring”) within the dendrites. Magnification bar is 200 µm long. Viewed with crossed polarized light plus sensitive tint.
As-cast (concast) 3004 aluminum (Al – 1.25% Mn – 1.05% Mg) tint etched with Weck’s reagent and viewed with crossed polars plus sensitive tint. Magnification bar is 50 \( \mu \text{m} \) long. Reveals segregation ("coring") within the dendrites and intermetallics between the dendrites.
Microstructure of as-cast 206 grade aluminum (Al – 4.4% Cu – 0.3% Mg – 0.3% Mn) after tint etching with Weck’s reagent, which revealed a dendritic structure containing segregation (constitution supercooling or “coring”) within the dendrites and intermetallic phases in the interdendritic regions. The magnification bar is 50 µm long.
As-cast Al – 7.3% Si – 0.4% Mg tint etched with Weck’s reagent and viewed with crossed polarized light plus sensitive tint. Original at 100X. Note coring segregation in the primary alpha dendrites.
Weck’s Reagent for Titanium

100 mL Water
50 mL Ethanol
2 g Ammonium bifluoride

Immerse at room temperature

This produces etch artifacts, which can be eliminated by using 25 mL ethanol, per J. M. Radzikowska
Microstructure of CP Ti, ASTM F 67, Grade 2 (longitudinal plane) prepared using the three-step method, etched with Mod. Weck’s reagent, and viewed with crossed polarized light plus sensitive tint to reveal the grain structure. Original images are at 100X. Magnification bars are 100 µm long. The images show the interior (left) and subsurface (right) regions. The later was apparently affected by mill sectioning, probably with a power hacksaw.
Color Etch for Molybdenum

70 mL water
20 mL H₂O₂ (30% Conc.)
10 mL H₂SO₄

Immerse about 3 minutes

(Developed at Oak Ridge National Laboratory)
Microstructure of cold worked pure molybdenum (longitudinal direction horizontal) tint etched with the ORNL solution and viewed with polarized light plus sensitive tint revealing highly elongated BCC alpha grains containing substantial deformation. The magnification bar is 20 µm long.
Color Due to Heat Tinting

• Colors Due to Interference Effects Due to Oxide Film Formed by Heating in Air
  • Cannot Use Mounted Specimens
• Heat Must Not Cause Phase Changes, Precipitation, etc.
• Colors Can Be Enhanced Using Polarized Light and Sensitive Tint Filter
Microstructure of CP Ti, ASTM F 67, Grade 4 (transverse plane, specimen was annealed) prepared using the three-step method, heat tinted on a laboratory hot plate, and viewed with polarized light plus sensitive tint to reveal the grain structure.
Comparison of Etchants - Examples
Wrought cartridge brass, Cu – 30% Zn, cold reduced 50%, and annealed at 704 °C (1300 °F) – 30 minutes produced a fully recrystallized, coarse grained, equiaxed FCC grain structure with annealing twins. The specimen was tint etched with Klemm’s I reagent for 3 minutes producing a lightly colored image in bright field. The structure was imaged with polarized light and sensitive tint (which dramatically improved the color contrast). The magnification bar is 200 µm long.
Wrought cartridge brass, Cu – 30% Zn, cold reduced 50%, and annealed at 704 °C (1300 °F) – 30 minutes produced a fully recrystallized, coarse grained, equiaxed FCC grain structure with annealing twins. The specimen was tint etched with Klemm’s II reagent for 2 minutes. This version line etches many of the alpha grains. Imaged with polarized light plus sensitive tint. The magnification bar is 200 µm long.
Wrought cartridge brass, Cu – 30% Zn, cold reduced 50%, and annealed at 704 °C (1300 °F) – 30 min produced a fully recrystallized, coarse grained, equiaxed FCC grain structure with annealing twins. The specimen was tint etched with Klemm’s III reagent for 3 minutes. It was imaged with polarized light and sensitive tint. The magnification bar is 200 µm long.
Wrought cartridge brass, Cu – 30% Zn, cold reduced 50%, and annealed at 704 °C (1300 °F) – 30 minutes to produce a fully recrystallized, coarse grained, equiaxed FCC grain structure with annealing twins. Tint etched with Beraha’s PbS. Viewed with polarized light and sensitive tint. The magnification bar is 200 µm long.
Microstructure of an as-rolled, continuously cast HSLA steel (Fe – 0.19% C – 1.24% Mn – 0.37% Si – 0.08% V) containing segregation (and some cracks – yellow arrows at left) etched with nital (left in bright field) and aqueous 10% Na$_2$S$_2$O$_5$ (right in polarized light plus sensitive tint). The normal structure is ferrite and pearlite but bainite (yellow-green arrows, both images) is observed in the segregated regions (greater hardenability). Average hardness values were 180, 260 and 325 HV for the ferrite, pearlite and bainite streaks, respectively. The magnification bars are 50 µm.
Microstructure of an as-rolled, continuously-cast HSLA steel (Fe – 0.19% C – 1.24% Mn – 0.37% Si – 0.08% V) containing segregation etched with Beraha’s “10/3” etch (left) and with Klemm’s I (right), both images in polarized light plus sensitive tint. The normal structure is ferrite and pearlite but bainite (yellow-green arrows, both images) is observed in the segregated regions. The segregated regions are hard to detect using Klemm’s I as it darkens the ferrite in the bainite as heavily as the matrix ferrite. The magnification bars are 50 µm long.
Microstructure of an as-rolled, continuously-cast HSLA steel (Fe – 0.19% C – 1.24% Mn – 0.37% Si – 0.08% V) containing segregation etched with Beraha’s sulfamic acid etch (No. 1) and viewed with polarized light plus sensitive tint. The normal structure is ferrite and pearlite but bainite (yellow-green arrows) is observed in the segregated regions. The segregated regions are easier to detect with this etch than using Klemm’s I (previous slide), but 10% sodium metabisulfite and Beraha’s “10/3” reagents were better. The magnification bar is 50 µm long.

Aqueous 3% K$_2$S$_2$O$_5$ + 1% H$_2$NSO$_3$H