Metallographic Procedures for Cast Irons

George F. Vander Voort
Director, Research and Technology
Buehler Ltd.
Lake Bluff, Illinois 60044
Preparation of Cast Iron Specimens

- Grind with 220-320 grit SiC (P240-P400), 240-300 rpm, 6 lbs/specimen, complementary rotation, until all samples in holder are co-planar

- Polish with 9-µm Metadi Supreme Diamond on an Ultra-Pol psa cloth, at 150 rpm, comp. rotation, 5 minutes

- Polish with 3-µm Metadi Supreme Diamond on a Texmet 1000 psa cloth at 150 pm, comp. rotation, 4 minutes

- (Optional) Polish with 1-µm Metadi Supreme Diamond on a Trident psa cloth at 150 rpm, comp. rotation, for 3 minutes

- Final polish with 0.05-µm Masterpolish alumina suspension on Microcloth psa pad, 120-150 rpm, contra rotation, for 2 minutes
Etchants for Cast Iron

2 mL HNO₃ in 98 mL Ethanol (Nital)

4 g Picric Acid in 100 mL Ethanol (Picral)

2 g Picric Acid, 25 g NaOH in 100 mL Water
Use Boiling by Immersion, or Electrolytically at 6 V dc to Color Cementite (Alkaline Sodium Picrate)
## 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 K$_2$S$_2$O$_5$ | Cast Iron, Steels, β in Brass, Cu Alloys, Zn and Alloys |
| II      | 50 mL Stock Solution  
5 g K$_2$S$_2$O$_5$ | Alpha Brass, Sn, Mn Steels |
| III     | 5 mL Stock Solution  
45 mL Water  
20 g K$_2$S$_2$O$_5$ | Bronze, Monel |

**Stock Solution:** Water Saturated with Na$_2$S$_2$O$_3$
Beraha’s “10/3” Version of Klemm’s I

100 mL Water
10 g Na₂S₂O₃
3 g K₂S₂O₅

Immerse at room temperature.
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
# Beraha’s CdS and PbS Reagents

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

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.
### 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.
# Beraha’s Selenic Acid Etch for Steels and Superalloys

<table>
<thead>
<tr>
<th>Etc h</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.*
## 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>
Graphite is the most stable form of carbon in Fe-based alloys, but it is normally present only in cast irons with high carbon and silicon contents. In cast irons, graphite shape may be controlled to produce a variety of shapes from flakes to nodules.
Examples of Flake Graphite and Gray Iron
Well-formed flakes of graphite in gray cast iron. As-polished; original at 200X.
Primary alpha dendrite in hypoeutectic gray iron with well-formed graphite flakes. As polished; original at 100X.
Primary, secondary and tertiary alpha dendrite arms in gray cast iron. As polished; original at 500X. Undesirable flake shape.
Example of undercooled graphite in gray cast iron (Fe – 3.58% C – 1.65% Si – 0.51% Mn – 0.014% S – 0.15% P – 0.22% Ti) in the as-polished (left) and etched (right, with 2% nital) conditions. The magnification bars are both 50 µm long.
Compacted and nodular graphite in blast furnace pig iron etched with 10% sodium metabisulfite and viewed with polarized light plus sensitive tint. The matrix contains pearlite and ferrite. The magnification bar is 100 µm long.
PEARLITE

A metastable lamellar aggregate of ferrite and cementite due to transformation of austenite above the bainite region.

The eutectoidal transformation product in steels and cast irons.
Microstructure of Flake Gray Iron
Microstructure of pearlitic gray cast iron tint etched with Beraha’s CdS reagent. Original at 500X.
Pearlitic gray iron microstructure revealed using Beraha’s CdS reagent and viewed with bright field (left) and with polarized light plus sensitive tint (right). Different fields are shown. The magnification bars are both 20 µm long.
Microstructure of pearlitic gray cast iron revealed using Beraha’s sulfamic acid reagent and viewed with polarized light plus sensitive tint. The magnification bar is 20 µm long.
Examples of fully pearlitic gray irons (high strength) with well-formed flakes. The specimen on the right has a slightly coarser interlamellar spacing. The specimens were etched with 2% nital (left) and 4% picral (right) and the magnification bars are 20 and 10 µm long, respectively.
Examples of pearlitic gray irons with small amounts of ferrite (1.5% at left and 18% at right). Both specimens were etched with 2% nital. The magnification bar lengths are 50 and 20 μm, left and right.
Examples of ferritic gray irons specimens, both are etched with 2% nital. The specimen at left has 30% pearlite while the specimen at right is fully ferritic. The magnification bar lengths are 100 and 20 µm, left and right.
Examples of Nodular Graphite
Well-formed spheroidal graphite nodules in ductile cast iron. As polished. Viewed with crossed polars + sensitive tint. Original at 200X.
Two clusters of spheroidal graphite nodules in austempered ductile iron. Viewed with crossed polars + sensitive tint. Original at 500X.
Fine, well-formed spheroidal graphite nodules in ductile cast iron. As polished; original at 200X.
Larger, well-formed spheroidal graphite nodules in ductile cast iron. As-polished; original at 200X.
Examples of poorly formed graphite nodules. At left (arrow), one particle is rectangular in appearance on the plane of polish. At right, the arrows point to examples of “exploded” graphite nodules. Both are as-polished and the magnification bars are both 20 µm long.
Example of a ductile iron specimen with numerous vermicular-graphite shaped particles (arrows). The specimen is as-polished and the magnification bar is 100 µm in length.
Microstructure of Ductile Iron
Microstructure of pearlitic ductile iron revealed using Beraha’s CdS tint etch. Note the ferrite rings (“bull’s eyes”) around the nodules or nodule clusters. Viewed with polarized light plus sensitive tint. Original at 500X.
Microstructure of pearlitic ductile iron containing cementite (white) revealed using Beraha’s CdS reagent and viewed with polarized light plus sensitive tint. Original at 500X.
Examples of nearly fully pearlitic ductile iron specimens containing some pearlite with observable lamellae. At right, the classic ferrite “bulls eye” or “halo” is illustrated. Both specimens were etched with 2% nital and both magnification bars are 10 µm long.
Microstructures of pearlitic ductile iron specimens containing 16% ferrite (left) and 40% ferrite (right). Both were etched with 2% nital and both magnification bars are 100 µm in length.
Examples of the microstructures of ferritic ductile irons containing 18% pearlite (left) and 4% pearlite (right). Both specimens were etched with 2% nital and both magnification bars are 100 µm in length.
Microstructure of a fully ferritic ductile iron specimen. The specimen was etched with 2% nital and the magnification bar is 100 µm long.
Malleable Iron
Temper nodules of graphite in malleable cast iron after a ferritizing anneal. The ferrite matrix was colored using Beraha’s sulfamic acid reagent (original at 500X in crossed polarized light plus sensitive tint). Magnification bar is 20 µm long.
Example of temper carbon nodules in ferritize-annealed malleable cast iron. The specimen is as-polished and the magnification bars are 100 and 20 µm (left and right) in length.
Examples of different matrix microstructures in malleable iron: left) coarse lamellar pearlitic matrix; right) spheroidized carbides (a few manganese sulfide inclusions can be seen in each image). Both specimens were etched with 2% nital. The magnification bars are 20 (left) and 10 (right) µm long.
Poorly annealed blackheart malleable cast iron etched with nital. The magnification bar is 50 μm long.
Microstructure of Austempered Ductile Iron, ADI
Microstructure of austempered ductile iron tint etched with Beraha’s CdS reagent containing large graphite nodules (arrow), bainite (blue and brown), also called “ausferrite” and retained austenite (white) when viewed with polarized light plus sensitive tint. Original at 500X.
Microstructure of austempered ductile iron containing “ausferrite” needles and retained austenite. The specimen was etched with aqueous 10% sodium metabisulfite and the magnification bar is 10 µm long.
Microstructure of austempered ductile iron (Fe – 3.6% C – 2.5% Si – 0.7% Cu) austenitized at 900 °C and transformed at 280 °C for 2 h (left) and at 380 °C for 2 h (right) revealed by nital. Note the substantial difference in appearance of the structure. The arrow at right points to a patch of martensite. The magnification bars are both 10 µm long. The matrix hardness was 525 and 310 HV, respectively.
Compacted Graphite
Compacted graphite cast iron, in the as-polished condition. The magnification bar is 100 µm long.
Compacted graphite in CG cast iron. As-polished; original at 200X.
LEDEBURITE

The eutectic of the iron-carbon system, austenite and cementite. Upon further cooling, the austenite decomposes into the eutectoid, ferrite and cementite.
Ledeburite in white cast iron (Fe – 4% C – 0.3% Si – 0.11% Mn – 0.96% Cr) revealed using nital. The magnification bar is 100 µm long.
Microstructure of pearlitic ductile iron containing cementite (C) particles and cementite in Ledeburite (L) which will harm machinability. Note the ferrite “halos” (FH) are the nodules. The specimen was etched with 2% nital and the magnification bar is 20 µm long.
Microstructure of Ni-Hard cast iron (Fe – 3.3% C – 0.9% Mn – 0.9% Si – 1.8% Cr – 4.4% Ni – 0.4% Mo) revealing massive cementite (C), ledeburite (arrows) and patches of plate martensite and retained austenite. Etched with aqueous 10% Na₂S₂O₅. Original at 200X. Ledeburite is a eutectic of cementite and austenite where, with cooling, the austenite transforms to ferrite and cementite in the form of pearlite.
Microstructure of Ni-Hard cast iron (Fe – 3.3% C – 0.9% Mn – 0.9% Si – 1.8% Cr – 4.4% Ni – 0.4% Mo) revealing massive cementite (C), ledeburite (arrows) and patches of plate martensite and retained austenite. Etched with aqueous 10% Na₂S₂O₅. Original at 500X. Ledeburite is a eutectic of cementite and austenite where, with cooling, the austenite transforms to ferrite and cementite in the form of pearlite. Some graphite (G) is also present.
STEADITE

A pseudo-binary or ternary eutectic of ferrite and iron phosphide or ferrite, iron phosphide and cementite, respectively, that can form in mottled iron or gray iron with a phosphorous content > 0.06%. Small amounts of Cr and V promote the ternary eutectic. The presence of cementite depends upon how much of the carbon is present as graphite.
Ternary Steadite in gray iron

Picral/Nital to reveal the microstructure

Alkaline sodium picrate to color cementite

Murakami’s (100 °C – 2 min) to color Fe₃P
Ternary Steadite in pig iron revealed using 2% nital and then Murakami’s reagent (20 °C – 2 min). The magnification bar is 10 µm long.
Ternary eutectic, Steadite, in blast furnace pig iron (pearlitic matrix) revealed by tint etching with Beraha’s CdS reagent. Original at 500X.
CEMENTITE

A compound of iron and carbon, also called iron carbide, with the approximate formula $\text{Fe}_3\text{C}$ and an orthorhombic crystal structure. Other elements, such as Mn and Cr, will substitute for Fe. Cementite is present in white cast iron and mottled cast iron and may be observed in gray or ductile iron.
Microstructure of white cast iron revealed using 2% nital and consisting of lamellar pearlite and cementite (white). Original at 1000X.
White cast iron etched with 4% picral revealing a network of massive cementite (white) and a martensitic matrix.
Cementite colored in white cast iron (Fe – 3.11% C – 1.05% Si – 0.41% Mn) revealed using alkaline sodium picrate (90 °C – 2 min). The magnification bar is 20 µm long.
Cementite colored in chill cast hypoeutectic gray iron using Beraha’s selenic acid reagent (bright field). The magnification bar is 100 µm long.
Cementite colored orange using Beraha’s selenic acid reagent (bright field). Note the ferrite dendrites. The magnification bar is 50 µm long.
Alloyed Cast Irons
Microstructure of acicular gray cast iron (Fe – 3.25% C – 2.63% Si – 0.78% Mn – 2.2% Ni – 1.48% Mo) after heat treatment revealed with Beraha’s CdS reagent. The magnification bar is 20 µm long.
Microstructure of 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) etched with Groesbeck’s reagent (80 °C – 30 sec) to color the massive cementite (light brown). Note the gray graphite particles. Original at 200X.
Microstructure of 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) etched with alkaline sodium picrate reagent (100 °C – 7 min.) to color the massive cementite (light brown). Note the gray graphite particles. Original at 200X.
Beraha’s selenic acid reagent was used to color cementite orange in this NiHard specimen (bright field). The magnification bar is 50 µm long.
Alloyed white cast iron (Fe – 2.2% C – 0.9% Mn – 0.5% Si – 12.7% Cr – 0.4% Mo – 0.1% V) with a martensitic matrix and a network of eutectic alloy carbides (white). Etched with Vilella’s reagent. Original at 200X.
Alloyed white cast iron (Fe – 2.2% C – 0.9% Mn – 0.5% Si – 12.7% Cr – 0.4% Mo – 0.1% V) with a martensitic matrix and a network of eutectic alloy carbides (colored). Etched with Groesbeck’s (80 °C – 30 sec) reagent to color the alloy carbides. Original at 200X.
Alloyed white cast iron (Fe – 3.1% C – 0.8% Mn – 1% Si – 18.6% Cr – 2% Mo) with a martensitic matrix and a network of eutectic alloy carbides (white). Etched with Vilella’s reagent. Original at 200X.
Alloyed white cast iron (Fe – 3.1% C – 0.8% Mn – 1% Si – 18.6% Cr – 2% Mo) with a martensitic matrix and a network of eutectic alloy carbides (colored). Etched with Groesbeck’s (80 °C – 30 sec) reagent to color the alloy carbides. Original at 200X.
MARTENSITE

Generic term for microstructures that form by diffusionless transformation, where the parent and product phases have a specific crystallographic relationship.
Heat treated ductile cast iron tint etched with Beraha’s CdS film reagent and viewed with crossed polars and sensitive tint. Note the oddly-shaped graphite nodule (bottom, center) and the white (not colored) cementite particles. The martensite is colored blue and brown and there are small patches of (white) retained austenite between martensite “needles”. Original at 1000X.
Microstructure of Ni-Hard cast iron (Fe – 3.3% C – 0.9% Mn – 0.9% Si – 1.8% Cr – 4.4% Ni – 0.4% Mo) revealing massive cementite (C) and patches of plate martensite and retained austenite. Originals at 1000X. Some graphite (arrows) is also present.
As-cast Nihard 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. Original at 1000X.
Examples of heat treated cast iron specimens containing coarse plate martensite and retained austenite in gray iron (left) and ductile iron (right). Both specimens were etched with 2% nital and both magnification bars are 10 µm in length.
Eutectic Cells

When gray iron solidifies, solidification begins at nucleation sites and grows outward. The graphite is interconnected and in flake form. When the growing cells impinge upon each other, they create a boundary area. The graphite within one cell is not interconnected to graphite in other cells. Cell size has the same influence on as-cast properties as dendrite spacings.
Dendrite cell boundaries in gray cast iron revealed using Klemm’s I tint etch and by viewing with polarized light plus sensitive tint. Original at 50X.
Primary alpha dendrites in hypoeutectic gray iron. The specimen was etched with 2% nital and the magnification bar is 100 µm long.
Shrinkage Cavities

Shrinkage cavities in white cast iron, structure revealed using nital. The magnification bar is 50 µm long.