Hints for IMAGING PHASES IN STEELS

Some techniques learned from experience can help metallographers identify certain phases in steels.

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The microstructure of metals and alloys can be quite complex, particularly in certain alloy systems such as iron-based alloys. A good understanding of physical metallurgy, the role of composition and processing on structure formation and modification, and an idea of the approximate expected hardness of different phases or constituents will help narrow the range of possible phases that might be present.

However, this knowledge is sometimes not enough to enable even skilled metallographers to reveal and identify important phases. For example, the polishing response of certain constituents is an indicator of the identity of various phases. Illumination techniques other than the standard bright field illumination can also be quite helpful. Finally, selective etchants offer another very useful tool.

These procedures, although not especially arcane or difficult, are not well known and are not commonly taught. This article discusses methods learned from experience, and presents a number of hints and “tricks” to make the metallographer’s job easier and more precise. It covers ways to improve the visibility and hence the identification of so-called “white-etching phases” in steels (ferrite, delta ferrite, cementite, and retained austenite) etched with standard reagents where the matrix can vary considerably.

Etching is critical

Metallographers generally rely upon the light microscope to characterize microstructures, and success depends on correct specimen preparation. However, in many cases, preparation involves more than sectioning, mounting, grinding, and polishing. Unless the specimen is properly etched, all the prep time is for naught.

In other words, the key to seeing the true microstructure is to choose the etchant that best reveals the phases or constituents in the material. Because the phases depend on composition and processing conditions, knowing what phases to look for is not a simple task. Furthermore, the number and variety of etchants available grows every day, and the applicability of the etchants may not be well documented. The table shows the composition of the etchants discussed here.

In well-characterized alloy systems, the metallographer can examine the microstructure and compare it to published images to identify phases and constituents. However, in less well-studied systems, phase identification is more challenging.

Etching for ferrite

Ferrite is a very low hardness (“soft”) phase in steels. Low-carbon sheet steels are nearly 100% ferrite. Because ferrite is soft, polishing scratches can be difficult to remove. Identification can be challenging because various etchants have different effects on ferrite. For example:

• Nital and picral: Nital attacks ferrite at a rate that varies with the crystal orientation of each grain relative to the plane of polish, while picral is insensitive to crystal orientation. Consequently, nital reveals the ferrite grain boundaries while picral does not. However, because nital is orientation-
sensitive, not all of the grain edges are visible. If cementite is present, and this is quite common in sheet steels, it can be hard to see using nital, as many particles will be in the grain boundaries. However, picral does not reveal the ferrite grain boundaries, making it easy to observe cementite particles. Neither etch darkens either ferrite or cementite, and both appear white in bright field (BF) illumination. Figure 1 shows the microstructure of sheet steel etched with nital and with picral to illustrate this difference in visibility.

Thus, if you want to see where the carbides are located, use picral. The eye and brain can see the cementite well, as nothing else is visible, other than inclusions and possibly nitrides.

Neither etchant provides a positive identification of either the cementite particles or the ferrite matrix. However, several etchants do preferentially color ferrite and cementite.

- *Klemm’s I* colors ferrite strongly. It also colors martensite and bainite, but not cementite or retained austenite. Figure 2 shows a low-carbon steel weld etched with 2% nital and with Klemm’s I. Note the vivid and distinct rendering of the ferrite grains compared to nital, along with positive identification.

- Beraha’s sulfamic acid reagent no. 4. Colors phases in highly alloyed tool steels and martensitic stainless steels. Use by immersion only, 30-180 s, usually. Mix fresh.

Sometimes ferrite is observed in the martensitic matrix of heat-treated alloy steels, either due to under-austenitization or lack of hardenability (ferrite can also be seen at a decarburized surface). Figure 3 shows the microstructure of under-

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**Etchants described in the text**

<table>
<thead>
<tr>
<th>Number</th>
<th>Composition</th>
<th>Comments</th>
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<tbody>
<tr>
<td>1</td>
<td>99-90 mL ethanol 1-10 mL HNO₃</td>
<td>Nital, the most common etchant for steels. Do not stock nital with &gt;3% nitric acid in ethanol. Use by immersion or swabbing (light pressure).</td>
</tr>
<tr>
<td>2</td>
<td>100 mL ethanol 4 g picric acid</td>
<td>Picral, better than nital for annealed microstructures. Does not reveal ferrite grain boundaries. Etch by immersion or swabbing.</td>
</tr>
<tr>
<td>3</td>
<td>100 mL ethanol 5 mL HCl 1 g picric acid</td>
<td>Vilella’s reagent, good for higher alloyed steels, tool steels, and martensitic stainless steels. Etch by immersion or swabbing.</td>
</tr>
<tr>
<td>4</td>
<td>85 mL ethanol 15 mL HCl</td>
<td>Etch for duplex stainless steels developed by Carpenter Technology. Immerse specimens 15-45 min (time is not critical) to reveal the grain and phase boundaries in duplex stainless steels.</td>
</tr>
<tr>
<td>5</td>
<td>50 mL stock solution* 1 g K₂S₂O₅ * water saturated with Na₂S₂O₅</td>
<td>Klemm’s I tint etch. It colors ferrite strongly; also colors martensite and bainite, but not carbides or retained austenite. Use by immersion only until the surface is colored.</td>
</tr>
<tr>
<td>6</td>
<td>100 mL water 25 g NaOH 2 g picric acid</td>
<td>Alkaline sodium picrate, used 80-100°C by immersion only. Colors cementite (Fe₃C) and M₆C carbides.</td>
</tr>
<tr>
<td>7</td>
<td>100 mL water 20 g NaOH</td>
<td>Electrolytic etch for stainless steels. Use at 3 V dc, 10 s to color ferrite (usually tan or light blue) and sigma (orange), but not austenite. Mix fresh.</td>
</tr>
<tr>
<td>8</td>
<td>100 mL water 10 g NaOH (or KOH) 10 g K₃Fe(CN)₆</td>
<td>Murakami’s reagent. Used to color ferrite and sigma (80-100°C for up to 3 min) in stainless steels. At room temperature, it will not color ferrite but will color certain carbides. At high temperature it colors ferrite, sigma, and carbides, but not austenite.</td>
</tr>
<tr>
<td>9</td>
<td>100 mL water 3 g K₂S₂O₅ 2 g sulfamic acid 0.5 - 1 g NH₄F·HF</td>
<td>Beraha’s sulfamic acid reagent no. 4. Colors phases in highly alloyed tool steels and martensitic stainless steels. Use by immersion only, 30-180 s, usually. Mix fresh. Best to use a plastic beaker and plastic tongs.</td>
</tr>
<tr>
<td>10</td>
<td>85 mL water 15 mL HCl 1 g K₂S₂O₅</td>
<td>Beraha-type etch for duplex stainless steels (similar to BI). Mix fresh. Use by immersion until the surface is colored. Colors ferrite but not austenite.</td>
</tr>
</tbody>
</table>
austenitized 4140 alloy steel where ferrite is present in a martensitic matrix.

Etching with nital reveals the structure, but are the white-etching grains ferrite, retained austenite, or possibly cementite? Etching with Klemm’s I tint etch reveals that the white phase is colored and is ferrite. Magnification bar is 10 µm long.

Finding delta ferrite
Martensitic and precipitation-hardenable stainless steels, as well as high-chromium tool steels, can exhibit the high-temperature form of ferrite known as delta ferrite. Ferrite may also be seen in lean austenitic stainless steels and is deliberately stabilized at room temperature in duplex stainless steels. Weld compositions in austenitic stainless steels are deliberately adjusted to precipitate at least 5% ferrite to prevent hot cracking.

As a result, many metallographers encounter delta ferrite in their work. However, in some alloys it may be difficult to differentiate delta ferrite from the other phases present. Several etchants color delta ferrite under specific conditions. Electrolytic aqueous 20% NaOH (3 V dc, 10 s) colors delta ferrite very well. Murakami’s reagent and several of its modifications color delta ferrite (and certain carbides) when used between 80 and 100°C, but not at room temperature.

Figure 4 shows the microstructure of a Russian martensitic stainless steel (similar to type 422). It is used in land-based gas turbine disks and blades for electric power generation in Russia. The specimen had 140,000 hours of service at a nominal temperature of about 350°C (660°F). Etching with Vilella’s reagent, standard procedure for martensitic stainless steels, revealed what looked like patches of delta ferrite. However, the specimen was re-polished and etched with Murakami’s reagent (90°C, 60 s), which colored the delta and more clearly revealed carbides that precipitated during service at the delta ferrite-martensite interface. These carbides were not easily observed with Vilella’s reagent.

Figure 5 shows a 312 stainless steel weld (base metal not shown) that contains ferrite and austenite. Vilella’s reagent reveals the ferrite, although not as crisply as we’d like. On the other hand, etching with boiling Murakami’s reagent produces a better image of the delta ferrite and gives positive identification.

Figure 6a shows the microstructure of a plate of 7 Mo Plus duplex stainless steel etched with 15% HCl in ethanol (immersion for 15 minutes), which clearly reveals the grain and phase boundaries. But which areas are austenite and which are ferrite? Several etchants can help answer that question, including the previously mentioned electrolytic NaOH and Murakami’s.

Figure 6b shows a Beraha-type etchant, similar to his BI reagent, that colors ferrite but not austenite. In addition, certain tint etches color the austenite preferentially. See the article on “Color Metallography” in the new edition of the ASM Handbook, Volume 9, Metallography and Microstructures, for more details.

Seeing cementite
Sometimes a given alloy contains a small amount of a “white-etching” phase, and this can be quite common in carbon and alloy steels with >0.5% carbon. However, this can be confusing, because the phase could be ferrite, undissolved cementite, or possibly retained austenite if it was hardened. Cementite, or Fe₃C, is a carbide and is much harder than ferrite.

The hardness of cementite can vary between about 800 and 1500 HV, with hardness increasing as other elements such as manganese and chromium substitute for iron. Compare this with the hardness of ferrite, which may be as low as 100 HV, although it can be strengthened substantially by elements such as silicon and nickel.

If the carbon content and heat treatment details
If the alloy is hypereutectoid, the white phase could be cementite or retained austenite, unless it is located at a decarburized surface, where it probably is ferrite. Furthermore, because of the hardness difference, polishing scratches are far more likely to be present in ferrite than in cementite.

Figure 7 shows the microstructure of an as-hot-rolled bar of a 1.31% carbon water-hardening tool steel that has both intergranular and intragranular cementite in a very fine pearlitic matrix. Etching with either nital or picral is inadequate to see the intergranular cementite, although the intragranular cementite is more easily observed. However, etching with alkaline sodium picrate near the boiling point darkens the cementite very well.

This etch will also color M6C carbide, but such a carbide is observed only in alloys with substantial molybdenum and tungsten, such as high speed steels. Retained austenite is never observed in such morphologies, but only as small, angular patches between martensite platelets (or “needles,” although this term is inaccurate).

Figure 8 shows the microstructure of white cast iron, in which primary cementite is formed during the eutectic reaction and pearlite is formed by the lower-temperature eutectoid reaction. Etching with picral reveals the pearlite nicely and outlines the cementite. Etching with alkaline sodium picrate, near boiling, darkens the cementite, which is seen to be the continuous phase.

Many other etchants will color, outline, or attack various other carbide types in alloy steels, but space prohibits a complete listing of these etchants and their behavior.

Analyzing austenite
Retained austenite is another “white-etching” phase that can be encountered in steels. However, it is only observed in as-hot-rolled steels, as-carburized steels, and steels that have been heat treated in an effort to form martensite. Furthermore, retained austenite is only observed with the light microscope when the carbon content is high, generally > 0.6%.
peratures at which martensite starts to form (Ms) and the temperature at which formation is complete (Mf).

Although carbon has the strongest influence on these temperatures, dissolving greater amounts of alloying elements in austenite will also suppress these temperatures. If the Mf is below room temperature, austenite will be retained after quenching, unless quenching is continued to temperatures below ambient. Excessive amounts of unstable retained austenite are considered to be very detrimental to the performance of tool steels, but substantial amounts are beneficial to the performance of carburized gears. This difference arises from the nature and magnitude of the stresses involved in these applications, and the toughness or brittleness of the overall component.

Retained austenite cannot be observed with the light microscope when there is less than about 10% present. Very low levels can be observed under TEM examination, but dark field illumination is required.

X-ray diffraction can detect amounts as low as 0.5%, and perhaps even less under ideal conditions, although 2% is often listed as the minimum detectable amount. When amounts are >15%, retained austenite can be seen in the light microscope, but image analysis measurements of retained austenite will be substantially lower than the true level determined by XRD.

Figure 9 shows light microscope BF images of carburized specimens of 8720 alloy steel that were studied first by XRD to determine the retained austenite content, which turned out to be 25.4, 19.7, and 16.2%. Image analysis results are signif-
icantly lower than the true values, and 2% nital gave the poorest results.

Addition of a wetting agent, benzalkonium chloride, to nital gave much better results, but the measurements (13.3, 8.5, and 1.2%, respectively) are more than 10% below the XRD values. This is due to the fineness of the retained austenite when in low concentrations.

Unfortunately, no simple means has been developed to preferentially color retained austenite, particularly when in small amounts in alloy steels. **If retained austenite is in larger amounts,** or is the major phase, it can be colored by a complex tint etch, as shown in Fig. 10. Here, 440C martensitic stainless steel was over-austenitized at progressively higher temperatures, creating a nearly fully austenitic structure at the highest temperature (note the annealing twins). **Beraha’s sulfamic acid reagent** (No. 4) colored both martensite and retained austenite, but not the M₇C₃ carbides.

**The list goes on**

These examples have been chosen to help the metallographer better reveal and identify “white-etching” phases in steels – ferrite, cementite, and retained austenite. Specimens must be properly prepared if they are to reveal the true structure. However, selection of the best etchant to clearly identify the constituents is not simple. In many cases, the standard nital etchant is adequate to reveal the structure, but other etchants can almost always be found that are far better. Many etchants produce selective attack or coloring of specific phases, and these etchants are extremely valuable as an aid to phase identification.

Unfortunately, only a limited number of examples can be shown here. The *ASM Handbook, Volume 9, Metallography and Microstructures*, which is now available, is an excellent source for this type of information.

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