

# Etching Steel

## General Consideration

▶ You might have looked at the "[Defect Etching in Silicon](#)" module. If not: now would be a good time to do this. Why? Because etching Si is so much easier than etching steel!

Let's start here by considering what we would like to see after defect-etching (or just etching for short) a polished piece of steel, looking at its surface with a [light microscope](#) or, on occasion (budget permitting), with a [scanning electron microscope](#).

● On second thought, let's start by considering what we will *not* see:

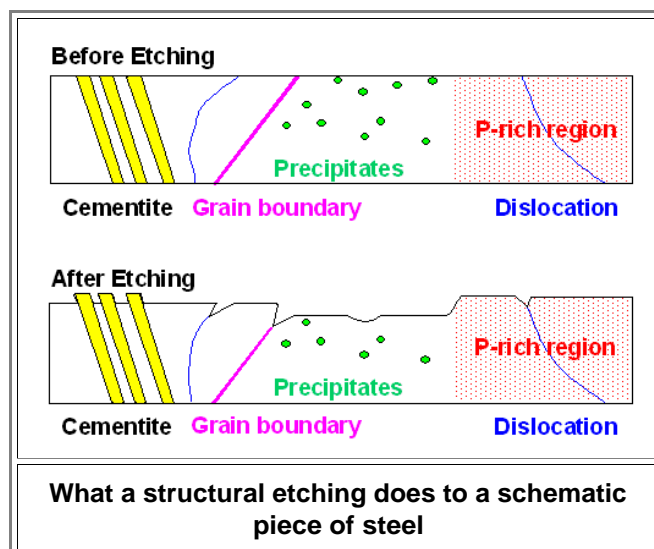
1. Everything inside the bulk of the specimen not intersecting the etched surface.
2. Everything not in your field of view (typically 99.9999.. % of a sword surface considering that you look at a few 100  $\mu\text{m}^2$  at best for one shot).
3. Individual small things with dimensions much smaller than the resolving power of the microscope (at best about 1  $\mu\text{m}$  for the light microscope).
4. Everything not sensitive to the etching medium.
5. Individual big things if they are too close together.
6. In a light microscope: the chemical nature of whatever since you just can't "see" that.

A sobering list! Nevertheless, looking at an *etched* surface by some kind of microscopy is far superior to most other "lookings" where you simply see *nothing*. The exception is an element analysis in a scanning electron microscope with EDX ([here](#) is an example). In doing this, however, you miss other things, not to mention that this is rather tricky and costly.

If we look at bloomery steel (plain carbon steel with small amounts of dissolved impurities and some slag / "dirt" inclusions), what we can see within the limits given above are:

1. Defects in the "parent" phase ferrite: Grain boundaries (including twin boundaries), dislocations if they are revealed by large (typically conical) etch pits, and the remains of not-too-small precipitates formed by dissolved dirt if they are revealed by large (typically shallow) etch pits.
2. Second phases like cementite or martensite.
3. Inclusions that are large enough.
4. Regions with a sufficiently high concentration of "something" (like phosphorous atoms), see below.
5. Regions with a high density of small defects (like lots of little cementite particles close together) that cannot be seen individually but produce a rough (and then dark) surface.

▶ The picture below shows how some of this "works":



● We have used an "etchant" that dissolves ferrite, if ever so slowly, but not cementite. As a first consequence, the cementite will now stick out. Moreover, the etchant dissolves regions with a "high" phosphorous content considerably slower than those with little phosphorous, leading to raised plateaus wherever you have sufficient phosphorous known as "[ghost structure](#)". It also dissolves some (not all) grains faster than others, leading to steps along some (but not all) grain boundaries. Finally, it dissolves regions where a defect ends considerably faster, leading to etch pits for dislocations and precipitates and grooves for grain boundaries.

We produce structure by "**differential dissolution**", by employing a dissolution rate that is different for different structures.

You can see all of that in your light microscope. You only have to be a bit careful in interpreting what you see

because grooves or steps look about the same at high magnification.

Note that in the picture above I omitted martensite, slag inclusions and "[dark etching acicular aggregates](#)" nowadays called bainite, and whatever you might find in more complex steels, so it would not get too complicated.

Now I need to answer your simple question: How does one "design" a proper etchant? The answer is quite simple, too: Nobody really knows. To be sure, I and everybody else who knows something about chemistry in general and the chemistry of iron and steel in particular, would have some idea of how to start but etchant development is still mostly trial and error with a strong touch of "[black art](#)"; see also the module [Sword Polishing and Revealing the Pattern / Structure](#).

Nobody is perfect and that also applies to etchants. That's why we have a lot of steel etchants, each one optimized for some specific purpose.

### "Etchants"

First I need to narrow the subject: I'm only looking at rather standardized **structural etchants** here, reagents that reveal the *structure* as outlined above. I am not considering "cosmetic" etchants that give your steel or blade a particular look. Here is why:

<p>etching reagents alum, 8, 10, 23, 30, 147, 253 ammonia, 195 aqua fortis; <i>see</i> nitric acid <i>Bergbutter</i>, 23 copper sulphate, 22, 33, 61, 147, 253 copperas, 22 Dutch mordant, 11 electrolytic, 195 ferric chloride, 11, 195 ferric sulphate, 22, 23, 31 ferrous sulphate, 10, 33, 147 hydrochloric acid, 11, 64, 149, 151, 159–62, 253 lemon juice, 22, 27, 33, 147 mercuric chloride, 10, 163–65, 219 nitric acid, 11, 30, 32, 33, 64, 145–50, 157, 160, 161, 175, 212, 219, 250–53 potassium chlorate, 11 sal ammoniac, 10, 11 salicylic acid, 212 salt, 10, 11, 30, 253 sulphuric acid, 151, 253 tartar, 10 vegetable acids, 8 verdigris, 10, 11, 61 vinegar, 10, 27 vitriol, 10, 33, 61, 147 zag, 22, 23, 27 eutectics, 61, 128, 194, 225</p>
<p><b>Etching reagents mostly for "cosmetic" etching</b> This is "etching reagents" the entry from the index of <a href="#">Cyril Stanley Smith's book</a></p>

Smith lists 26 chemical, several with rather quaint names ("*Bergbutter*"?), that appear on 64 or so pages of his book. They all are more or less intended to enhance or to bring out the structure of pattern welded or wootz blades, to embellish harnesses, etc.

I certainly will not go into that and then run the risk that you blame me because you messed up your wootz blade instead of enhancing its beauty by using one of those concoctions.

So let's get straight to the No. 1 of structural etchants:

**Nital**; short for "**Nitric acid** (HNO<sub>3</sub>) and (ethyl) **Alcohol** C<sub>2</sub>H<sub>5</sub>OH. Methanol (CH<sub>3</sub>OH) is also used.

Mix it in a ratio of acid : alcohol about 3 : 100 and you have Nital. I won't give you precise information because I don't want you to do it if you don't know exactly what you are doing. Nitric acid is dangerous and some mixtures of nitric acid with alcohol are explosive.

If mixed right, etching is quick, less than a minute produces results. It works more or less as shown in the picture above and there are many examples of nital etched steel in the hyperscript; e.g. [here](#).

There are many kinds of steel and there are correspondingly many variations of nital and etching conditions, The temperature, for example, does have some effect, too.

- Nital has many brethren (concoctions with alcohols and other acids like picric acid (explosive!)) and they all work essentially as shown in the schematic picture above.  
The following "etchants" work on a different principle, though.

**Color Etches: Oberhoffer's etch, Stead's etch, Klemm's etch** and so on.

- The principle of structure delineation with those etches - sometimes called "color etches" - is not so much the differential dissolution of the steel, but the *deposition of copper* (Cu) on parts with a low concentration of phosphorous (or arsenic, or....?). The Cu protect the covered areas to some extent from dissolution; the uncovered areas will the get attacked. Since copper has a definite color, the etched surface appears colored.
- You might ask why copper should deposit itself on an iron / steel surface? That is not a good question. The good question is: Why does copper deposit itself *only* on certain parts of iron / steel samples? Any metal **A** in solution will want to deposit itself on a solid metal **B** surface if **A** is "nobler" than **B**. The degree of nobleness is well defined in chemistry. The more you are asocial (no contact / bonding to all those people / atoms around you) and lazy (not doing much that is useful), the nobler you are. Gold is nobler than silver, which is nobler than copper, which is nobler than lead,.... Way down on the scale is iron, aluminum, silicon and carbon, the guys who do the work.

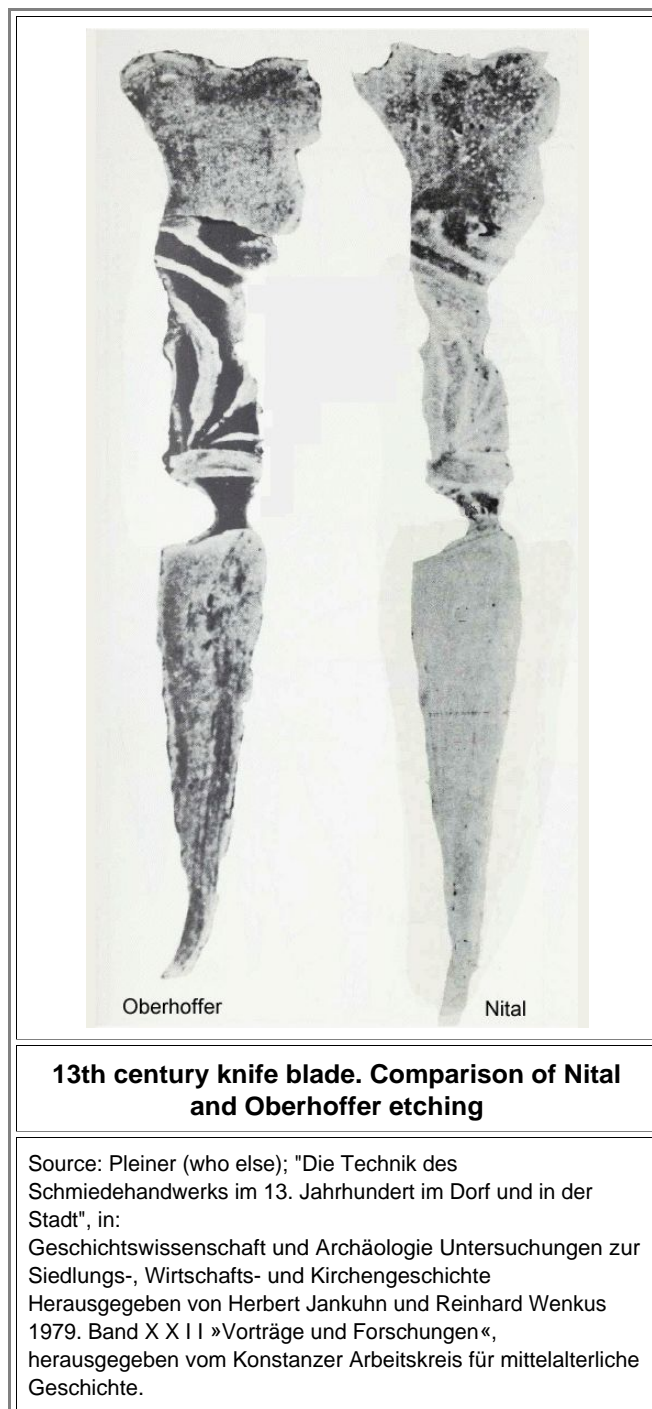
So copper should deposit itself everywhere on an iron / steel surface. Yes, indeed, but copper deposition is not the only reaction that can occur if you throw you iron / steel sample into in a more complex "etchant" that does not only contain dissolved copper salts but also *eye of newt and toe of frog, wool of bat and tongue of dog* or something else to this effect. Then several reactions might be possible besides copper deposition, for example iron oxidation or dissolution. You then have a competition of the various processes, and which one wins will depend on the local peculiarities of your sample, in particular if you add some hard-to-get scale of dragon, tooth of wolf, witches' mummy, maw and gulf.

Here are two compositions of color etches:

Oberhoffer's Etchant	Stead's Etchant
100 cm <sup>3</sup> water - H <sub>2</sub> O	10g copper(II)-chloride (CuCl <sub>2</sub> * 2H <sub>2</sub> O)
100 cm <sup>3</sup> alcohol (C <sub>2</sub> H <sub>5</sub> OH)	40g magnesium chloride (MgCl <sub>2</sub> )
3 cm <sup>3</sup> hydrochloric acid - HCl	20ml hydrochloric acid (conc.) (HCl)
0,2 g copper(II)-chloride (CuCl <sub>2</sub> * 2 H <sub>2</sub> O)	Alcohol to 1L (C <sub>2</sub> H <sub>5</sub> OH)
3 g iron(III)-chloride (FeCl <sub>3</sub> * 6 H <sub>2</sub> )	Room temperature
0,1 g tin(II)-chloride (SnCl <sub>2</sub> * 2 H <sub>2</sub> O)	Duration for up to 3 hrs
Room temperature	
Duration about (1 - 3) minutes	
<b>Two recipes</b>	

- You get the idea. Etching is serious stuff that needs some experience not only with the chemistry but also in the preparation of the specimens before your etch (perfect polishing is needed) and the interpretation of what you see after the etch.

Here is a direct comparison of the two most prominent etches, Nital and Oberhoffer, applied to the same specimen (probably front and backside of a thin cross-sections through a knife)):



- The color etchants (Oberhoffer, Stead, ...) selectively deposit copper on *low* phosphorus/arsenic areas, leaving the high phosphorus/arsenic areas appearing *white*. The reason might be - my guess - that the oxide on the phosphorous-rich areas is just a little bit more stable than in the other regions and that prevents Cu deposition. The Oberhoffer etch does make the P-poor or rich areas better visible than the Nital etch. Even in black-and-white. A picture with color can be found [here](#). Looking at higher magnification would reveal more details (in particular for the Nital) but it is clear that revealing the phosphorous distribution is best done with one of the "color etches.

▸ This is black art, indeed. So in our modern times with fancy scanning electron microscopes at our disposal (provided you can cough up at least half a million) we do not need to resort to those archaic techniques any more. Not so. Proper "color etching" has two huge advantages to about anything else:

1. It is dirt-cheap in comparison
2. In the hand of a (typically female) expert, it is far more sensitive than X-ray techniques, i.e. it can detect phosphorous at very low concentrations.

- There is also a big catch, however:

- The color etches cannot distinguish between phosphorous (P) and arsenic (As) and ?
- No problem if you know you have only phosphorous. That is certainly the standard case but arsenic keeps coming up here and there and appears to be more important than thought some years ago.

Structure etching is here to stay. As long as we use it we run the risk of missing something or interpreting something not quite correctly. One should be aware of this but there is simply no viable alternative