GUIDE TO

ETCHING SPECIALTY ALLOYS

Specialty alloys with high resistance to corrosion have challenged many laboratories to refine the way they etch alloy samples for microstructural evaluation.
The big problem is that the alloys resist the etchants just as they do the corrosive conditions encountered in service.

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Etching superalloys in preparation for microscopic examination is extremely challenging because of their inherent corrosion resistance. Over the years, Carpenter engineers have developed guidelines for the most effective procedures for etching a wide range of iron-, nickel-, and cobalt-base alloy systems. The following discussion offers guidelines for processing stainless steels, high temperature alloys, tool and alloy steels, and magnetic and expansion alloys.

Etchant selection

Selection of the proper etchant depends largely upon alloy composition, heat treatment, and processing. The etchants for metallographic examination are solutions of acids and other chemicals that are applied selectively to attack a highly polished surface, thus permitting microstructural examination. Three basic methods have been developed to etch alloy samples:

• **Immersion**: The sample is immersed in the etching solution until the preferred structure is developed. Samples may be immersed in stain etchants to highlight specific microstructural features.

• **Swabbing:** The sample is swabbed with cotton that has been immersed in the etchant.

• **Electrolytic etching:** A D.C. source or a rectifier serves as the power supply, and the specimen acts as the anode in the electrolytic cell. Power requirements can be adjusted as needed, depending on sample size, anode-to-cathode spacing, and electrolyte.

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Etchant rules

The following rules should be observed to reveal a true and representative microstructure:

1. If the specimen is mounted, an adherent mount is very important. Separation between the specimen and the mounting compound can result in "bleeding" of the residual etchant or water, and subsequent staining.

2. A good metallographic polish is a *must*. The sample must be free of scratches, disturbed metal, and any kind of embedded contaminants.

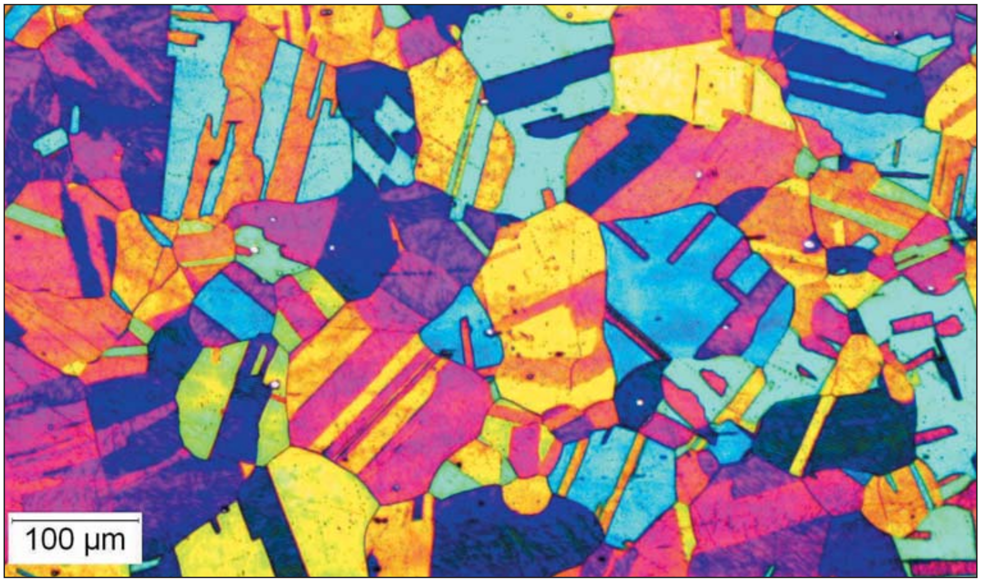
3. The specimen must be thoroughly cleaned and dried before etching. Oil and any polishing compounds must be removed.

4. After etching, the sample should be rinsed in hot water, followed by an alcohol rinse, and should then be dried under hot air. (Note: an alcohol rinse can dull/wash out a stain etch.) Samples with cracks must be thoroughly dried to prevent bleeding.

5. If additional etching time is required, the specimen should be re-rubbed for a few seconds on a final polishing wheel. If this is not done, "flashing" can develop in certain alloys, necessitating a complete re-polish. However, flashing does not develop and re-rubbing is not required if the alloy being etched forms no passive oxide layer, or if the specimen is etched electrolytically. Re-rubbing is usually mandatory only with alloys requiring the use of Ralph's, Glyceregia, Acetic Glyceregia, and HCL + H_2O_2 etchants. More-complete specimen preparation instructions are readily available in the literature.

Etchants and alloys

Table 1 lists 28 common etchants, along with their compositions and guidelines. Table 2 lists various specialty alloys, suggested etchants for each, and application notes. These tables can help you to quickly select the appropriate etching procedure for a particular alloy. Additional etchants are reported in ASTM specification E-407-99 "Standard Practice for Microetching Metals and Alloys," and ASM Metals Handbook (Volume 9, *Metallography and Microstructures).*



This photomicrograph shows the microstructure of a sample of Type 330 stainless steel in the annealed condition at 100X magnification. It was etched using a tint etch consisting of a solution of 40 ml hydrochloric acid (HCL) + distilled water (H_2O) + one gram potassium meta bisulfite ($K_2S_2O_5$) + four grams ammonium bifluoride ($NH_4F–HF$) at room temperature.

Table 1 — List of etchants and their chemical composition

Etchant No.	Etchant name	Composition	Remarks
1	Nital, 2%. (ASTM E 407 designation is 74 Nital)	2cc HNO_3 + 98cc Ethyl alcohol	Immersion
3	Picral, 5% (ASTM E 407 designation is 76 Picral)	5gr Picric acid + 100cc Ethyl alcohol	Immersion
4	Oxalic acid	10gr oxalic acid + 10cc H_2O	Electrolytic at 200/400 Ma.
6	Nital, 5% (ASTM E 407 designation is 74 Nital)	5cc HNO_3 + 95cc Ethyl alcohol	Immersion. Do not store
7	HCl in alcohol	15cc HCl + 100cc Ethyl alcohol	Immersion
8	Ferric Chloride	5g Ferric Chloride + 50cc HCl +100cc H_2O	Use fresh swab. Use under hood. Do not store.
9	Marble's Reagent (ASTM E 407 designation is 25 Marble's)	4g $CuSO_4$ + 20cc HCl + 20cc H_2O	Immersion or swab
10	Viella's (ASTM E 407 designation is 80 Vilella's. ASTM contains 1 gr Picric)	5cc HCl + 2gr Picric acid + 100cc Ethyl alcohol	Immersion or swab
11	Aqua Regia in alcohol. (ASTM E 407 designation is 12 Aqua Regia)	100cc HCl + 3cc HNO_3 + 100cc Methyl alcohol	Immersion
12	Chromic acid	10gr CrO_3 + H_2O	Electrolytic at 200/400 Ma
13	2% H_2SO_4	2cc H_2SO_4 + 98cc H_2O	Use electrolytic. Under hood. 200/400 Ma
15	G	12cc H_3PO_4 + 41cc HNO_3 + 47cc H_2SO_4	Use electrolytic. Under hood. 200/400 Ma
18	Acetic Glyceregia (Mixed Acids)	15cc HCl + 10cc HNO_3 + 10cc Acetic Acid + 2/3 Drops Glycerine	Use fresh. Under hood. Swab. Do not store.
19	Waterless Kalling's (ASTM E 407 designation is 95 Kalling's 2)	5gr $CuCl_2$ + 100cc HCl + 100cc Ethyl alcohol	Immersion or swab
22	HF + HNO_3	1 to 3cc HF + 2 to 6cc HNO_3 + 100cc H_20	Swab. Handle with care. HF causes serious burns. Use in plastic container, as HF attacks glass.
23	HNO_3 + H_2O	75cc HNO_3 + 25cc H_20	Use under hood. Electrolytic 5 to 7 amps
26	Glyceregia (ASTM E 407 designation is 87 Glyceregia)	15cc HCl +10cc Glycerol + 5cc HNO_3	Use fresh. Under hood. Swab. Do not store.
28	Ralph's	100cc H_2O + 200cc methyl alcohol + 100cc HCl + 2gr $CuCl_2$ + 7gr $FeCl_2$ + 5cc HNO_3	Swab
29	Special #4	10% Sodium meta-Bisulfate in distilled water	Immersion
30	Special #5	20ml HCl + 4ml H_2O_2 (3%)	Swab

Note: Please see ASTM for proper handling of all chemicals.

Table 2 — List of alloys and etchants

Type	Etchant	Applications
Martensitic stainless		
403, 405, 410, 420, TrimRite®, Trinamet™ stainless	10, 28, 19	General structure - grain size, carbides, martensite and ferrite
440A, 440B, 440C	10, 26	General structure - grain boundaries, carbides and martensite
416	10, 19	General structure - grain size, carbides, martensite, and ferrite
	28	Excellent sulfide retention
Austenitic stainless		
304, 304L, 309, 310, 316, 347	10, 26, 4, 12, 28	General structure - grain boundaries, grain size, carbide precipitation
20Cb-3® stainless	10, 26, 4	General structure - grain boundaries, grain size, carbide precipitation
303	28	General structure - grain boundaries, grain size. Excellent sulfide retention.
	26, 10	Similar to #11 but sulfides attacked
Ferritic stainless		
430F, 430FR	10, 19, 18	General structure
430	6, 26, 10	General structure - grain boundaries and grain size
Chrome Core® 18-FM, Chrome Core 12-FM, Chrome Core 13-FM, Chrome Core 13-XP	19, 26	General structure
PH stainless		
Custom 450®, Custom 455®, Custom 465®, Custom 475®, Custom 630, 15Cr-5Ni, Carpenter 13-8	28	General structure - martensite and austenite
Nitrogen-strengthened austenitic stainless		
21Cr-6Ni-9Mn, 22Cr-13Ni-5Mn	28, 19, 26	General structure - grain boundaries, grain size, carbide precipitation
High-temperature alloys		
Pyromet® A-286, Pyromet V-57	19, 26, 9	General structure, including size and grain boundaries
	13	Gamma prime precipitates - banding anddepletion
NCF 3015(1), Nickel 200/201, Thermo-Span, Pyromet 720, Carpenter Alloy 925	19, 26	General structure including grain size and grain boundary precipitate.
Pyromet 706, 718, and 901	19. 26	General structure including grain size and grain boundary precipitate.
	13	Gamma prime precipitates - banding anddepletion
Pyromet 860	19, 26, 15	General structure, including size and grain boundaries
	13	Gamma prime precipitates - banding anddepletion
Waspaloy	19, 26, 15	General structure, including size and grain boundaries. Note: Generally 19 is more effective for aged material and 15 for solution treated material for general structure and grain size.
	13	Gamma prime precipitates - banding and depletion
Pyromet® 680	19, 26, 18	General structure. Note: Use 18 in the annealed condition
Pyrowear® 675	10	General structure

The etchants for each alloy are presented in order of preference as the result of experience. In general, the most benign etchant is shown first, followed by progressively more aggressive formulations. If a weaker etchant is tried first and it does not yield satisfactory results, the investigator need only buff the surface slightly to return a good polish for examination with a stronger etchant.

On the other hand, if the first etchant attempted is too strong, far more preparation is required to restore the surface to a workable condition. Therefore, it is usually good practice to start with the weakest solution.

Reasons for etching

If the intent is to evaluate nonmetallic inclusions and sulfide distribution/morphology, the sample is best examined in the as-polished condition. The reason is that etching can remove various inclusions and attack structures such as ferrite stringers in an austenitic matrix.

However, if the search is designed to examine grain structure, precipitation, or cold-work de-

Type	Etchant	Applications
Ti base alloys		
Ti Base Alloys	22, 23	General structure
Medical/high corrosion resistant alloys		
MP35N(2), Alloy 2 (AMS 5842)(3), MP35N LTi	30	General structure
BioDur Carpenter CCM®, BioDur CCM Plus® alloy	30	General structure. Note: Fresh sample needed. Should prepare one sample at a time. Use of Differential Interference Contrast (DIC) would help.
Pyromet 625/Custom Age 625 PLUS®	26, 18, 19	General structure. Note: Fresh sample needed. Should prepare one sample at a time. Use of Differential Interference Contrast (DIC) would help.
BioDur® 108	26	General structure
Nickel Copper 400	28	General structure
Maraging steels		
Nimark® 200/250/300, Carpenter Ferrium S53(4)	28	General structure
AerMet® 310/340	19, 29	General structure
AerMet 100	19, 29	General structure
18Ni - 200 Maraging Steel, 18Ni - 250 Maraging Steel, 18Ni - 300 Maraging Steel	12	Prior austenitic grain boundaries
Controlled expansion alloys		
Cr-Fe, Glass Sealing 18, Glass Sealing 27, 430F, 446	11, 26, 28, 7, 8	General structure, grain size
Kovar® alloy	28, 26, 19	General structure
Magnetic alloys		
Core irons	6, 11, 7	General structure
Fe and Si core irons	11, 7	General structure
Ni-Cr-Fe - 22-3, 45-5, 42-6	28, 26, 19	General structure
Co-Fe Hy-Sat alloy 27, Co-Fe-V Remendur, Hiperco® 50	26, 28, 19	General structure
Fe-Cr-Al, No. 1 JR® alloy Types 1 and 2	7, 11, 28, 26, 19	General structure
Tool steels		
W1, O2, L6, D3, A2, A6, D2, T1, M2, M4, M42, H11, H12, H13, H21, M50	1, 6, 3, 11	General structure
	10	Prior austenitic grain boundaries
52100	1	General structure

NOTE: Etchants listed in order of preference. All Etchants should be used on a freshly polished surface.
(1) Manufactured and sold under license from Hitachi.
(2) Registered trademark of SPS Technologies, Inc.
(3) Also known as MP159N, a trademark of SPS Technologies Inc.
(4) Manufactured and sold under license from QuesTek Innovations LLC. Ferrium is a registered trademark of QuesTek Innovations LLC.

formation, the sample must be etched.

The condition of an alloy and its heat treatment also must be considered in the selection and application of etchants. Therefore, even if the alloy grade and analysis are known, it is important to know whether it has been annealed, aged, cold worked, tempered, and/or is in the as-hardened condition.

Corrosion-resistant alloys

Special techniques are required to effectively prepare highly corrosion resistant alloys for microstructural examination. Prominent in this group are alloys such as BioDur CCM Plus Alloy, MP35N Alloy (MP35N is a registered trademark of SPS Technologies Inc.) and Custom Age 625 Plus Alloy (UNS N07716).

Because these nickel-base and cobalt-base alloys have superior corrosion resistance, they should be etched with Waterless Kalling's, Glyceregia, Acetic Glyceregia, or Ralph's. If these do not work, HCL + H_2O_2 may be suitable. In any case, these alloys usually should be etched slowly.

All require a fresh polish to avoid "flashing," which would require a complete re-polish. Best results are achieved by lightly re-rubbing one or two samples at a time on the final polishing wheel (normally a 0.05-micron alumina slurry).

The challenge with these alloys is to offset their natural tendency to self-passivate rapidly in the presence of oxygen. Therefore, to effectively process these grades, specimens must be etched immediately after final polishing. They should be rinsed, dried, and etched without delay.

When etching these highly resistant alloys, the etchant should be prepared in advance of the polishing process. This advance planning will minimize the length of time between polishing and etching, thus permitting a more effective microstructural evaluation.

Stainless steels

Austenitic, ferritic, precipitation hardenable, and martensitic stainless steels should be etched with various reagents to reveal features of interest.

• **Austenitic:** When etching austenitic stainless steels (particularly annealed material that contains few grain boundary precipitates), DIC illumination better shows the grain structure and helps find cold-work deformation. Waterless Kalling's reagent reveals the general structure of many austenitic stainless alloys.

Other agents, such as Glyceregia or Acetic Glyceregia, may be required to reveal retained ferrite and carbide precipitation.

If the only goal is to determine grain structure in an austenitic stainless, the etching process should start with a more aggressive etchant. However, if features other than grain boundaries, such as carbides, ferrite stringers, second phases, and duplex structures are to be examined, then Glyceregia should be applied, and for a shorter time.

• **Ferritic:** Ralph's reagent normally provides a good etch for general structures in ferritic stainless steels. Waterless Kalling's and Glyceregia also can yield good results. Even after a good polish, scratches may still be visible. They may or may not be a problem.

• **Precipitation hardenable:** Ralph's is usually best for the precipitation hardenable stainless steels; however, Vilella's reagent will work fine if a light etch is preferred. Etching time varies because the alloy in the aged condition reacts more quickly to the etchant. The higher the aging temperature, the quicker the response. An alloy aged at 1100°F (590°C) etches darker and more quickly than one aged at 900°F (480°C).

The annealed structure in PH stainless steels requires either an aggressive etchant for a short

Microscopy methods

Five light microscopy methods of illumination are suitable for microstructural examination (Table 3):

- **Brightfield illumination**
- **Darkfield illumination**
- **Oblique illumination**
- **Differential interference-contrast (DIC)**
- **Polarized light**

DIC, using brightfield microscopes that change the way light is deflected, gives a three-dimensional image. The brightfield image is changed by inserting a beam splitting prism, polarizer + analyzer to separate and recombine the image to provide a three-dimensional effect.

This is the ultimate in light optical microscopy, showing grain boundaries very clearly in highly corrosion-resistant alloys. It is the most effective means of showing relief in structures, and is capable of identifying the effects of cold work and mechanical damage. Compared with the other methods, DIC provides increased image contrast. The well-equipped laboratory should have all five because their capabilities are complementary. Their role in microstructural evaluation cannot be overestimated.

Darkfield, oblique, and differential interference-contrast illumination methods can aid in delineating grain boundaries and other microstructural features that are only weakly visible in bright field illumination. A polarizing filter can be used in conjunction with a stain etch to enhance color contrast.

In darkfield microscopy, the grain seen is dark and the grain boundaries light. With the brightfield microscope, the grain is light and the boundaries dark. Oblique illumination shines light at an angle on the surface, producing shadows on microstructural features.

Table 3 — Light optical microscopy methods

Method	Description
Brightfield illumination	The most commonly encountered method of illumination, in which the light reflection is perpendicular to the specimen being viewed. Generally, microstructural features such as grain boundaries are dark and matrix regions are bright.
Darkfield illumination	The light is obliquely reflected back through the objective, so that what appears bright and dark in brightfield illumination is reversed in darkfield illumination.
Oblique illumination	The illustration source is de-centered at an oblique angle, producing shadows on microstructural features. This method is extremely helpful if the operator knows the illumination direction; thereby knowing which features are raised and which are recessed by the shadow orientation.
Differential interference-contrast (DIC)	A beam-splitting prism, polarizer, and analyzer are inserted into the light path producing shadowing variations that reveal height differences in the microstructural features.
Polarized light	The light is passed through a polarizing filter and can be adjusted to enhance the color contrast obtained with stain etchants.

time, or a less aggressive etchant for a longer time. For example, Ralph's reagent would etch in a few seconds, or Vilella's, which is less aggressive, would etch more slowly.

• **Martensitic:** Vilella's reagent is preferred for martensitic stainless steels. Etching time and response vary depending on whether the alloy has been annealed, hardened, or tempered. Annealed samples usually require the longest etching time, because everything is in solution, with not much to be seen.

It is best to stop etching while the specimen is still on the light side. Etching has gone too long when the sample starts going black. A little experience will help the examiner to stop etching at the right time. Hardened and tempered samples usually require less etching time than annealed stock.

High-temperature alloys

Etching procedures for high-temperature alloys can vary greatly depending on condition of the material and what type of evaluation is required. High-temperature alloys are typically more difficult to etch than austenitic stainless steels because they exhibit different aging conditions with a range of aging responses, phases, and precipitates.

If uncertain about which etchant to use, start with Glyceregia and increase in severity until the required structure is revealed. This procedure requires only the final polishing step between etchants, instead of a complete re-polish. Glyceregia should be mixed at time of use, as it becomes more aggressive with the passage of time.

Waterless Kalling's, another choice, works well with alloys such as Waspaloy (UNS N07001), Pyromet Alloy 718 (UNS N07718), and Pyromet Alloy A-286 (UNS K66286). It can be stored, and is thus more convenient than Glyceregia.

Stain etchants and electrolytic etchants can show specific aspects of structure in high-temperature alloys. Stain etchants, used with immersion techniques, have been effective in highlighting structural features such as second phases.

If the etchants for high-temperature alloys do not work, HCL + H_2O_2 may be suitable, just as they are for stainless steels. Precipitation can be evaluated via brightfield microscopy, but DIC is better for showing grain structure.

Other alloy families

• **Tool and alloy steels:** Nital (2 to 5%) is useful for showing carbide structure in tool and alloy steels, but re-etching the treated sample afterward with Vilella's darkens the matrix and provides a clearer view of the microstructure. Many times, samples can be etched with Nital, examined, and then etched with Vilella's, without re-polishing. Alloy condition will determine etching time.

• **Magnetic and expansion alloys:** Most magnetic and expansion alloys can be treated as suggested for one of the stainless steel families, or the tool and alloy steels. For example, Ni-Fe alloys should be prepared by the procedures for austenitic stainless steels. Many of the alloys exploited for their D.C. magnetic properties (such as stainless Type 430F) can be etched via procedures for ferritic stainless steels. Others, such as Fe and Si Core Irons, can be etched like low alloy steels with Nital.

General tips

Some etchants, such as Waterless Kalling's, can be made in bulk and stored. Other reagents, such as Glyceregia and Acetic Glyceregia, must be prepared each time they are needed. Both Glyceregia solutions undergo a continuous chemical reaction as they age, becoming very aggressive in less than one hour. Special care must be taken then, because the aggressive solution can affect etching time and procedure. Generally, it is a good idea to use the solution as soon as possible after mixing.

As shown in Tables 1 and 2, many different etchants can be successful for specific alloys and special circumstances when examining basic microstructure. However, the choice of reagent does not have to be difficult.

With a little experience and a good understanding of what features need to be evaluated, the examiner may find that a few etchants will serve the intended purpose the majority of the time. In order of increasing strength, those etchants are: Nital, Villelas, Ralph's, Glyceregia, Acetic Glyceregia, Waterless Kalling's, and Hydrochloric Acid + Hydrogen Peroxide.

Health and safety

All the referenced etchants are designed to attack the surface of the steels and alloys being analyzed. Therefore, all the etchants contain chemicals that are hazardous to handle, store, use, and discard.

The user of these etchants is responsible for developing appropriate procedures to address all hazardous aspects as required by appropriate health, safety, and environmental practices and regulations. Individual chemical Material Safety Data Sheets (MSDS) should be consulted as a starting source for information. Users are further cautioned that mixtures of the individual chemicals may result in different and possibly more significant risks, which they are obliged to assess prior to application. Standard etchant texts contain additional safety and use information.

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