

ETCHING

Metallographic etching encompasses all processes used to reveal particular structural characteristics of a metal that are not evident in the as-polished condition. Examination of a properly polished specimen before etching may reveal structural aspects such as porosity, cracks, and nonmetallic inclusions. Indeed, certain constituents are best measured by image analysis without etching, because etching will reveal additional, unwanted detail and make detection difficult or impossible. The classic examples are the measurement of inclusions in steels and graphite in cast iron. Of course, inclusions are present in all metals, not just steels. Many intermetallic precipitates and nitrides can be measured effectively in the as-polished condition.

In certain nonferrous alloys that have non-cubic crystallographic structures (such as beryllium, hafnium, magnesium, titanium, uranium and zirconium), grain size can be revealed adequately in the as polished condition using polarized light. Figure 30 shows the microstructure of cold-drawn zirconium viewed in cross-polarized light. This produces grain coloration, rather than a “flat etched” appearance where only the grain boundaries are dark.

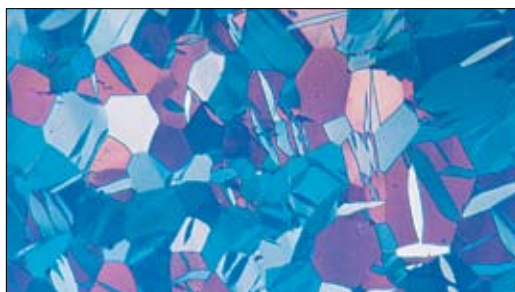


Figure 30. Mechanical twins at the surface of hot worked and cold drawn high-purity zirconium viewed with polarized light (200X).

Etching Procedures

Microscopic examination is usually limited to a maximum magnification of 1000X — the approximate useful limit of the light microscope, unless oil immersion objectives are used. Many image analysis systems use relay lenses that yield higher

screen magnifications that may make detection of fine structures easier. However, resolution is not improved beyond the limit of 0.2-0.3- μm for the light microscope. Microscopic examination of a properly prepared specimen will clearly reveal structural characteristics such as grain size, segregation, and the shape, size, and distribution of the phases and inclusions that are present. Examination of the microstructure will reveal prior mechanical and thermal treatments given the metal. Many of these microstructural features are measured either according to established image analysis procedures, e.g., ASTM standards, or internally developed methods.

Etching is done by immersion or by swabbing (or electrolytically) with a suitable chemical solution that essentially produces selective corrosion. Swabbing is preferred for those metals and alloys that form a tenacious oxide surface layer with atmospheric exposure such as stainless steels, aluminum, nickel, niobium, and titanium and their alloys. It is best to use surgical grade cotton that will not scratch the polished surface. Etch time varies with etch strength and can only be determined by experience. In general, for high magnification examination the etch depth should be shallow; while for low magnification examination a deeper etch yields better image contrast. Some etchants produce selective results in that only one phase will be attacked or colored. A vast number of etchants have been developed; the reader is directed to references 1-3, 9 and ASTM E 407. Table 43 lists some of the most commonly used etchants for the materials described in this book.

Etchants that reveal grain boundaries are very important for successful determination of the grain size. Grain boundary etchants are given in [1-3, 9]. Problems associated with grain boundary etching, particularly prior austenite grain boundary etching, are given in [2, 10 and 11]. Measurement of grain size in austenitic or face-centered cubic metals that exhibit annealing twins is a commonly encountered problem. Etchants that will reveal grain boundaries, but not twin boundaries, are reviewed in [2].

Selective Etching

Image analysis work is facilitated if the etchant chosen improves the contrast between the feature of interest and everything else. Thousands of etchants have been developed over the years, but only a small number of these are selective in nature. Although the selection of the best etchant, and its proper use, is a very critical phase of the image analysis process, only a few publications have addressed this problem [12-14]. Selective etchants, that is, etchants that preferentially attack or color a specific phase, are listed in [1-3, 9, 13 and 14] and illustrated in 13 and 14. Stansbury [15] has described how potentiostatic etching works and has listed many preferential potentiostatic etching methods. The potentiostat offers the ultimate in control over the etching process and is an outstanding tool for this purpose. Many tint etchants act selectively in that they

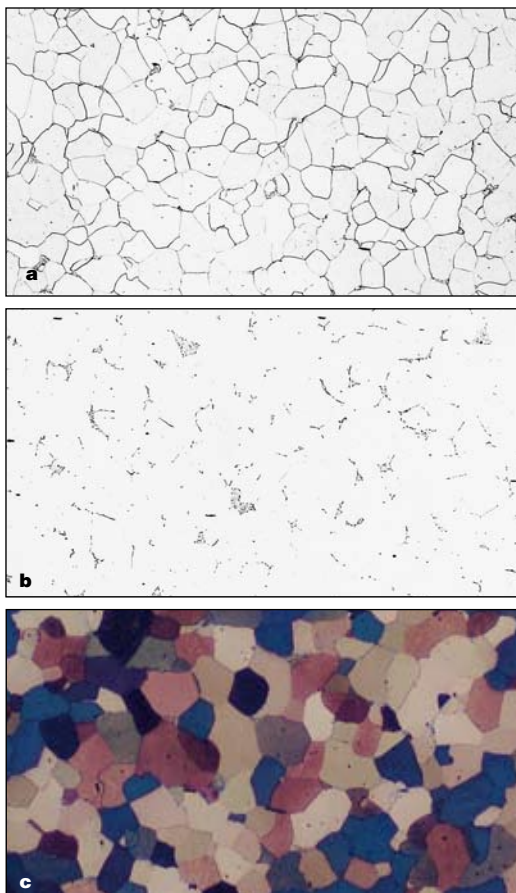


Figure 31. Microstructure of low-carbon sheet steel etched with (a, top) 2% nital, (b, middle) 4% picral; and (c, bottom) Beraha's reagent (100 mL water, 10 g $\text{Na}_2\text{S}_2\text{O}_8$, and 3 g $\text{K}_2\text{S}_2\text{O}_8$) at 100X.

color either the anodic or cathodic constituent in a microstructure. Tint etchants are listed and illustrated in several publications [1-3, 16-21].

A classic example of the different behavior of etchants is given in Figure 31 where low-carbon sheet steel has been etched with the standard nital and picral etchants, and also a color tint etch. Etching with 2% nital reveals the ferrite grain boundaries and cementite. Note that many of the ferrite grain boundaries are missing or quite faint; a problem that degrades the accuracy of grain size ratings. Etching with 4% picral reveals the cementite aggregates (one could not call this pearlite as it is too nonlamellar in appearance and some of the cementite exists as simple grain boundary films) but no ferrite grain boundaries. If one is interested in the amount and nature of the cementite (which can influence formability), then the picral etch is far superior to the nital etch as picral revealed only the cementite. Tint etching with Beraha's solution (Klemm's I could also be used) colored the grains according to their crystallographic orientation. With the development of color image analyzers, this image can now be used quite effectively to provide accurate grain size measurements since all of the grains are colored.

Figure 32 shows a somewhat more complex example of selective etching. The micrograph shows the ferrite-cementite-iron phosphide ternary eutectic in gray iron. Etching sequentially with picral and nital revealed the eutectic, Figure 32a, surrounded by pearlite. Etching with boiling alkaline sodium picrate, Figure 32b, colored the

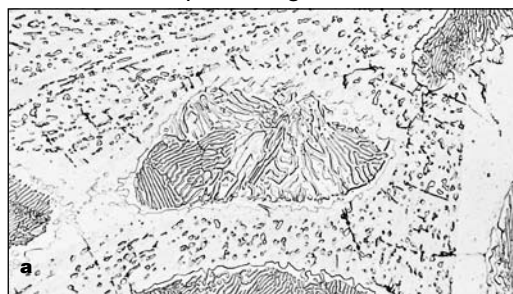


Figure 32a. The ternary eutectic ($\alpha\text{-Fe,C-Fe,P}$) in gray cast iron revealed by etching (a, top) in picral and nital to "outline" the phases

cementite phase only, including in the surrounding pearlite (a higher magnification is required to see the very finely spaced cementite that is more lightly colored). Etching with boiling Murakami's reagent, Figure 32c, colors the iron phosphide

lightly color the cementite after prolonged etching. The ferrite could be colored preferentially if Klemm's I was used.

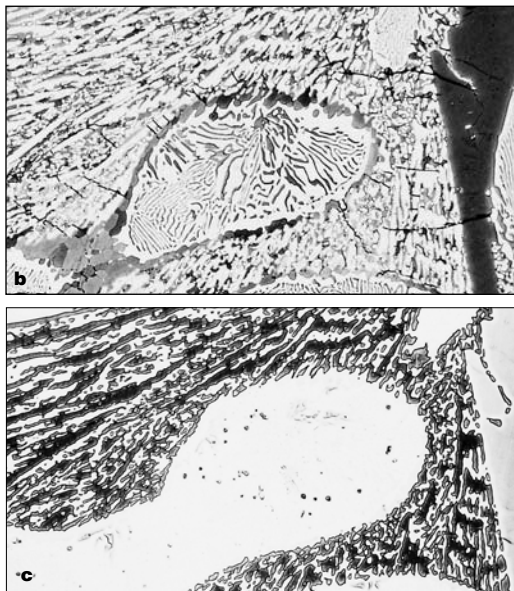


Figure 32b. (top) boiling alkaline sodium picrate to color the cementite. Figure 32c. (bottom) boiling Murakami's reagent to color the phosphide (200X).

Selective etching has been commonly applied to stainless steels for detection, identification and measurement of delta ferrite, ferrite in dual phase grades, and sigma phase. Figure 33 shows examples of the use of a number of popular

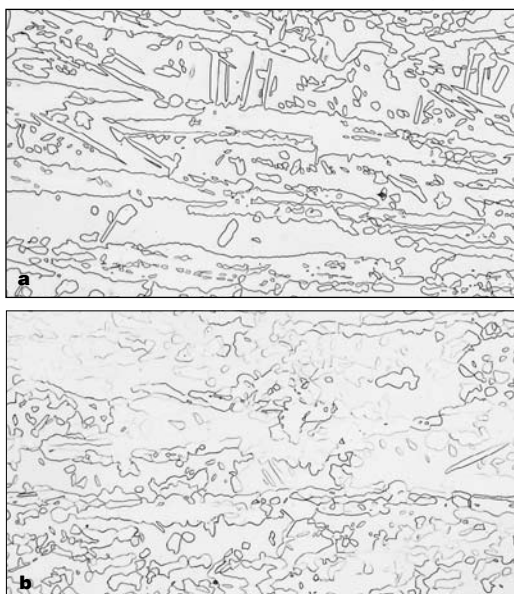


Figure 33. Microstructure of a duplex stainless steel revealed using (a, top) alcoholic 15% HCl by immersion (30 min.); and, with (b, bottom) glyceresia by swabbing (2 min.) at 200X.

etchants to reveal the microstructure of a dual phase stainless steel in the hot rolled and annealed condition. Figure 33a shows a well delineated structure when the specimen was immersed in ethanolic 15% HCl for 30 minutes. All of the phase boundaries are clearly revealed, but there is no discrimination between ferrite and austenite. Twin boundaries in the austenite are not revealed.

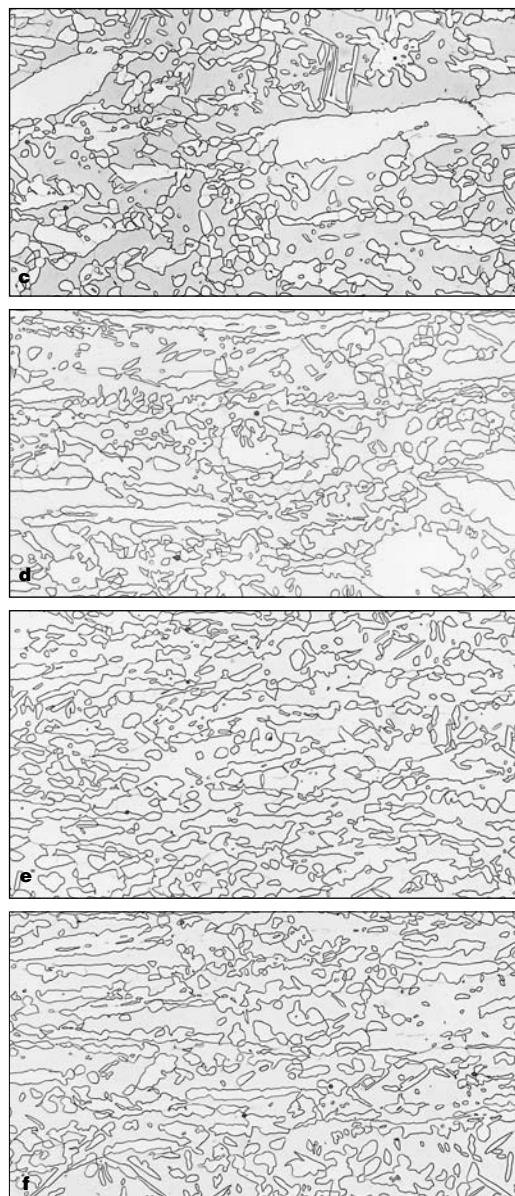


Figure 33. Microstructure of a duplex stainless steel revealed by electrolytic etching with (c) aqueous 60% HNO₃ (1 V dc, 20 s); with (d) aqueous 10% oxalic acid (6 V dc, 75 s); with (e) aqueous 10% CrO₃ (6 V dc, 30 s); and, with (f) aqueous 2% H₂SO₄ (5 V dc, 30 s) at 200X.

Glyceregia, a etchant for stainless steels, was not suitable for this grade, Figure 33b, as it appears to be rather orientation sensitive. Many electrolytic etchants have been used for etching stainless steels, but only a few have selective characteristics. Of the four shown in Figures 33c to f, only aqueous 60% nitric acid produced any gray level discrimination between the phases, and that was weak. All revealed the phase boundaries nicely, however. Two electrolytic reagents, shown in Figures 33g and h, are commonly used to color ferrite in dual phase grades and delta ferrite in martensitic grades. Of these, aqueous 20% sodium hydroxide, Figure 33g, usually gives more uniform coloring of the ferrite. Murakami's and Groesbeck's reagents have also been used for this purpose. Tint etchants have been developed by Beraha that color the ferrite phase nicely, as demonstrated in Figure 33i.

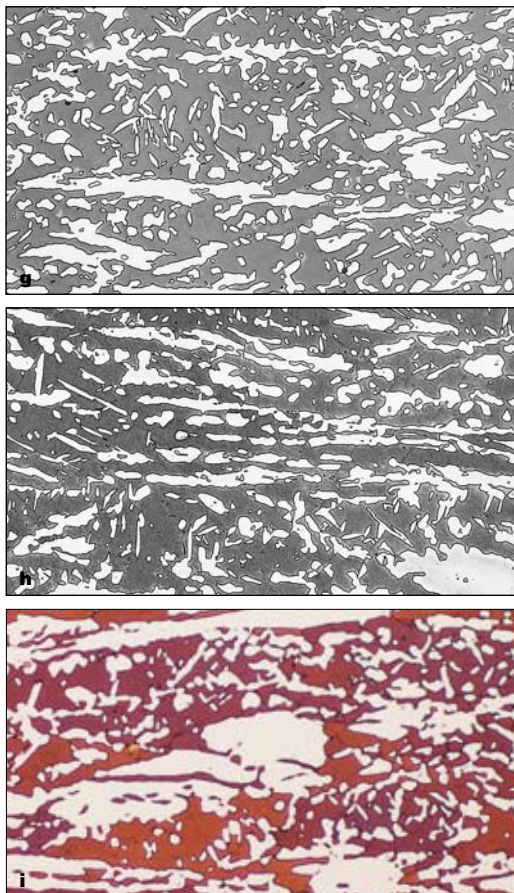


Figure 33. Selective coloring of ferrite in a duplex stainless steel by electrolytic etching with (g) aqueous 20% NaOH (4 V dc, 10 s) and with (h) aqueous 10 N KOH, (3 V dc, 4 s); and by immersion color etching (i) with Beraha's reagent (100 mL water, 10 mL HCl and 1 g $K_2S_2O_8$) at 200X.

Selective etching techniques are not limited to iron-based alloys, although these have more thoroughly developed than for any other alloy system. Selective etching of beta phase in alpha-beta copper alloys has been a popular subject. Figure 34 illustrates coloring of beta phase in Naval Brass (UNS 46400) using Klemm's I reagent. Selective etching has a long historical record for identifica-

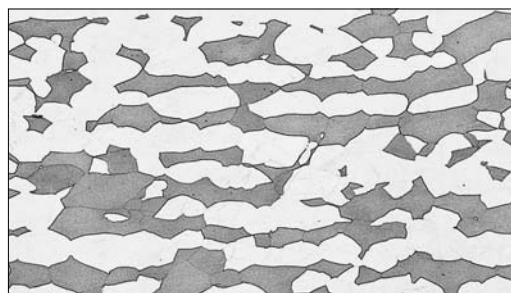


Figure 34. Beta phase colored in Naval Brass (Cu-39.7% Zn-0.8% Sn) by immersion color etching with Klemm's I reagent (200X).

tion of intermetallic phases in aluminum alloys. This method was used for many years before the development of energy-dispersive spectroscopy. Today, it is still useful for image analysis work. Figure 35 shows selective coloration of theta phase, $CuAl_2$, in the Al-33% Cu eutectic alloy. As a final example, Figure 36 illustrates the structure of a

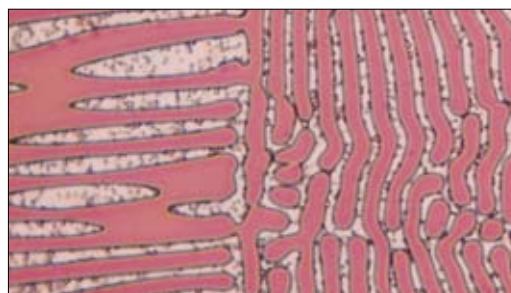


Figure 35. Theta phase, $CuAl_2$, colored in the α -Al/ $CuAl_2$ eutectic in an as-cast Al-33% Cu specimen by immersion color etching with the Lienard and Pacque etch (200 mL water, 1 g ammonium molybdate, 6 g ammonium chloride) at 1000X.

simple WC-Co sintered carbide, cutting tool. In the as-polished condition, Figure 36a, the cobalt binder can be seen faintly against the more grayish tungsten carbide grains. A few particles of graphite are visible. In Figure 36b, light relief polishing has brought out the outlines of the cobalt binder phase, but this image is not particularly useful for image analysis. Etching in a solution of hydrochloric acid saturated with ferric chloride, Figure 36c, attacks the cobalt and provides good uniform contrast for measurement of the cobalt

ing this with Murakami's reagent at room temperature reveals the edges of the tungsten carbide grains, useful for evaluation of the WC grain size, Figure 36d.

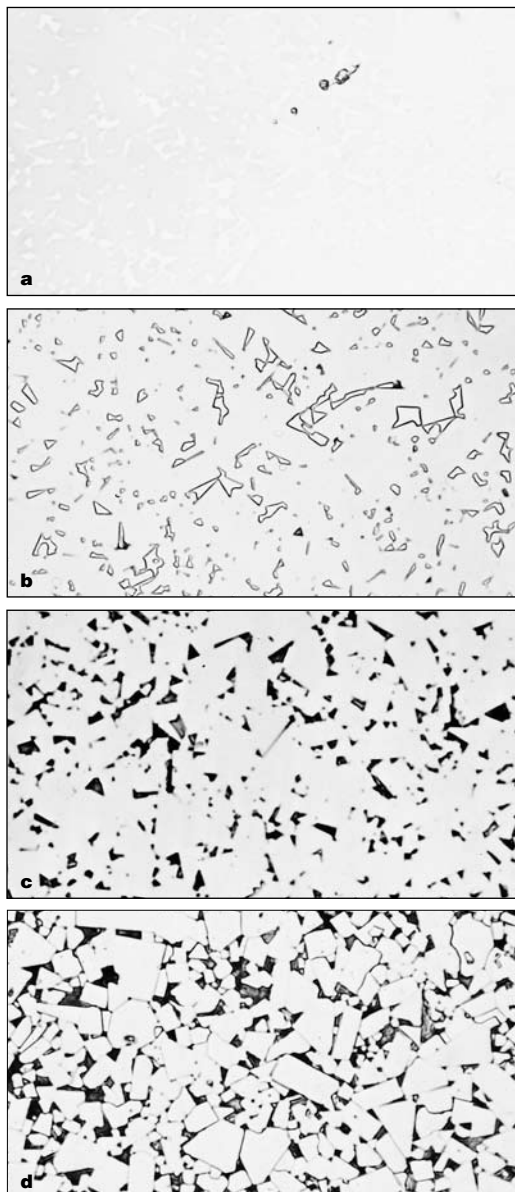


Figure 36. Microstructure of WC-Co cutting tool: a) as-polished revealing graphite particles; b) relief polished revealing the cobalt binder phase; c) after immersion in Chaporova's etch (HCl saturated with FeCl_3) to attack and "darken" the cobalt; and, d) after (c) plus Murakami's reagent to outline the WC grains (1000X).

Electrolytic Etching and Anodizing

The procedure for electrolytic etching is basically the same as for electropolishing except that voltage and current densities are considerably lower. The specimen is made the anode, and some relatively insoluble but conductive material such as stainless steel, graphite, or platinum is used for the cathode. Direct current electrolysis is used for most electrolytic etching. Electrolytic etching is commonly used with stainless steels, either to reveal grain boundaries without twin boundaries, or for coloring ferrite (as illustrated) in Figure 33, delta ferrite, sigma or chi phases. Anodizing is a term applied to electrolytic etchants that develop grain coloration when viewed with crossed-polarized light, as in the case of aluminum, tantalum, titanium, tungsten, uranium, vanadium and zirconium [2]. Figure 37 shows the grain structure of 5754 aluminum revealed by anodizing with Barker's reagent, viewed with crossed-polarized light. Again, color image analysis makes this image useful now for grain size measurements.

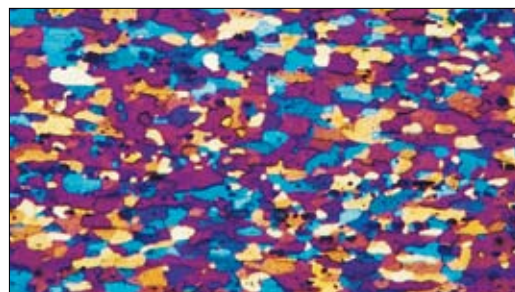


Figure 37. Grain structure of annealed 5754 aluminum sheet revealed by anodizing with Barker's reagent (30 V dc, 2 min.) and viewing with polarized light plus sensitive tint (100X).

Heat Tinting

Although not commonly utilized, heat tinting [2] is an excellent method for obtaining color contrast between constituents or grains. An unmounted polished specimen is placed face up in an air-fired furnace at a set temperature and held there as an oxide film grows on the surface. Interference effects, as in tint etching, create coloration for film thicknesses within a certain range, about 30-500 nm. The observed color is a

function of the film thickness. Naturally, the thermal exposure cannot alter the microstructure. The correct temperature must be determined by the trial-and-error approach, but the procedure is reproducible and reliable. Figure 38 shows the grain structure of CP titanium revealed by heat tinting.

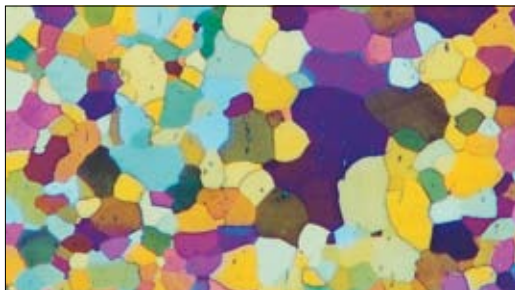


Figure 38. Grain structure of annealed CP titanium revealed by heat tinting on a hot plate (100X, polarized light plus sensitive tint).

Interference Layer Method

The interference layer method [2], introduced by Pepperhoff in 1960, is another procedure for obtaining a film over the microstructure that generates color by interference effects. In this method, a suitable material is deposited on the polished specimen face by vapor deposition to produce a low-absorption, dielectric film with a high refractive index at a thickness within the range for interference. Very small differences in the natural reflectivity between constituents and the matrix can be dramatically enhanced by this

method. Suitable materials for the production of evaporation layers have been summarized in [22,23]. The technique is universally applicable, but does require a vacuum evaporator. Its main weakness is difficulty in obtaining a uniformly coated large surface area for image analysis measurements.



HELPFUL HINTS FOR ETCHING

Many etchants can be used by swabbing or by immersion.

Swabbing is preferred for those specimens that form a tight protective oxide on the surface in air, such as Al, Ni, Cr, stainless steels, Nb (Cb), Ti and Zr. However, if the etchant forms a film, as in tint etchants, then immersion must be used as swabbing will keep the film from forming. Keller's reagent reveals the grain size of certain aluminum alloys by forming a film. This will not occur if the etch is used by swabbing.

Many etchants, and their ingredients, do present potential health hazards to the user. ASTM E 2014, Standard Guide on Metallography Laboratory Safety, describes many of the common problems and how to avoid them.

Table 43. Commonly Used Etchants for Metals and Alloys³.**LIGHT METALS - Aluminum and Alloys**

Composition	Comments
1. 95 mL water 2.5 mL HNO ₃ 1.5 mL HCl 1.0 mL HF	Keller's reagent, very popular general purpose reagent for Al and Al alloys, except high-Si alloys. Immerse sample 10-20 seconds, wash in warm water. Can follow with a dip in conc. HNO ₃ . Outlines all common constituents, reveals grain structure in certain alloys when used by immersion.
2. 90-100 mL water 0.1-10 mL HF	General-purpose reagent. Attacks FeAl ₃ , other constituents outlined. The 0.5% concentration of HF is very popular.
3. 84 mL water 15.5 mL HNO ₃ 0.5 mL HF 3 g CrO ₃	Graff and Sargent's etchant, for grain size of 2XXX, 3XXX, 6XXX, and 7XXX wrought alloys. Immerse specimen 20-60 seconds with mild agitation.
4. 1.8% fluoboric acid in water dc. For most alloys and tempers, 20 seconds at 1 A/in ² and 30 V dc at 20 °C not needed. Rinse in warm water, dry. Use polarized	Barker's anodizing method for grain structure. Use 0.5-1.5 A/in ² ; 30-45 V is sufficient. Stirring light; sensitive tint helpful.

Magnesium and Alloys

Composition	Comments
5. 25 mL water 75 mL 3-5 ethylene glycol 1 mL HNO ₃	Glycol etch, general purpose etch for pure Mg and alloys. Swab specimen seconds for F and T6 temper alloys, 1-2 minutes for T4 and 0 temper alloys.
6. 19 mL water 60 mL ethylene glycol 20 mL acetic acid 1 mL HNO ₃	Acetic glycol etchant for pure Mg and alloys. Swab specimen 1-3 seconds for F and T6 temper alloys, 10 seconds for T4 and 0 temper alloys. Reveals grain boundaries in solution-treated castings and most wrought alloys.
7. 100 mL ethanol 10 mL water 5 g picric acid	For Mg and alloys. Use fresh. Immerse specimen for 15-30 seconds. Produces grain contrast.

LOW MELTING POINT METALS - Sb, Bi, Cd, Pb, Sn and Zn

Composition	Comments
8. 100 mL water 30 mL HCl 2 g FeCl ₃	For Sb, Bi and alloys. Immerse specimen up to a few minutes.
9. 100 mL water 25 mL HCl to a 8 g FeCl ₃	For Sb-Pb, Bi-Sn, Cd-Sn, Cd-Zn, and Bi-Cd alloys. Immerse specimen up few minutes.
10. 95-99 mL ethanol 1-5 mL HNO ₃ Pb and alloys, if a stain forms, wash in 10% alcoholic HCl.	For Cd, Cd alloys, Sn, Zn alloys, Pb and alloys, Bi-Sn eutectic alloy and Bi-Cd alloys. Can add a few drops of zephiran chloride. Immerse sample.
11. 100 mL water 10 g ammonium molybdate 10 g citric acid	Pollack's reagent for Pb and alloys. Immerse specimen 15-30 seconds. Other compositions used are: 100 mL: 9 g: 15 g and 100 mL: 10 g: 25 g.
12. 100 mL water 2 mL HCl 10 g FeCl ₃	For Sn-based babbitt metal. Immerse specimen up to 5 minutes.
13. 200 mL water 40 g CrO ₃ 3 g Na ₂ SO ₄	Palmerton reagent for pure Zn and alloys. Immerse specimen up to 3 minutes. Rinse in 20% aqueous CrO ₃ .
14. 200 mL water 10 g CrO ₃ 1 g Na ₂ SO ₄	Modified Palmerton reagent for Zn die-casting alloys. Immerse specimen for several seconds, rinse in 20% aqueous CrO ₃ .

³When water is specified, always use distilled water. It is best to use reagent grade chemicals. Etchants can be quite dangerous and it is advisable to consult with a chemist when dealing with new etchants that may be potentially dangerous. ASTM E 2014, Standard Guide on Metallographic Laboratory Safety, is a valuable reference.

Table 43. Commonly Used Etchants for Metals and Alloys^a.**REFRACTORY METALS: Ti, Zr, Hf, Cr, Mo, Re, Nb, Ta, W and V**

Composition	Comments
15. 100 mL water 1-3 mL HF 2-6 mL HNO ₃	Kroll's reagent for Ti alloys. Swab specimen 3-10 seconds or immerse specimen 10-30 seconds.
16. 200 mL water 1 mL HF	For Ti, Zr and alloys. Swab or immerse specimen. Higher concentrations can be used but are prone to staining problems.
17. 30 mL lactic acid 15 mL HNO ₃ 30 mL HF	For Ti alloys. Swab specimen up to 30 seconds. Decomposes, do not store. Good for alpha-beta alloys.
18. 30 mL HCl 15 mL HNO ₃ 30 mL HF	For Zr, Hf, and alloys. Swab specimen 3-10 seconds, or immerse specimen up to 120 seconds.
19. 45 mL H ₂ O (H ₂ O ₂ or glycerol) 45 mL HNO ₃ 8-10 mL HF 20	Cain's chemical polish and etch for Hf, Zr, and alloys. Can dilute aqueous solution with 3-5 parts water to stain the structure (swab specimen) after chemical polishing. Chemically polish and etch specimen by swabbing 5-seconds. Use polarized light.
20. 60 mL HCl 20 mL HNO ₃	Aqua regia. For Cr and alloys. Immerse or swab specimen up to 1 minute. Use under a hood with care, do not store.
21. 30 mL HCl 45 mL glycerol 15 mL HNO ₃	Modified "Glyceregia". For Cr and alloys. Immerse specimen up to a few minutes.
22. 100 mL water 10 g KOH or NaOH 10 g K ₂ Fe(CN) ₆	Murakami's reagent. For Cr, Mo, Re, Ta-Mo, W, V and alloys. Use fresh, can immerse sample for up to 1 minute.
23. 70 mL water 20 mL H ₂ O ₂ (30%) 10 mL H ₂ SO ₄	For Mo alloys. Immerse specimen 2 minutes. Wash with water and dry; immersion produces colors, swabbing produces grain-boundary etch.
24. 10-20 mL glycerol 10 mL HNO ₃ 10 mL HF	For Mo and Mo-Ti alloys. Immerse specimen for up to 5 minutes.
25. 100 mL water 5 g K ₂ Fe(CN) ₆ 2 g KOH	For Mo-Re alloys. Use at 20 °C by immersion.
26. 50 mL acetic acid 20 mL HNO ₃ 5 mL HF	For Nb, Ta and alloys. Swab specimen 10-30 seconds.
27. 50 mL water 14 mL H ₂ SO ₄ 5 mL HNO ₃	DuPont Nb reagent. For Nb-Hf and Nb alloys.
28. 50 mL water 50 mL HNO ₃ 1 mL HF	For Nb-Zr and Nb-Zr-Re alloys. Swab specimen.
29. 30 mL lactic acid 10 mL HNO ₃ 5 mL HF	For Re and W-Re alloys. Swab specimen.
30. 10 mL HF 10 mL HNO ₃ 10-30 mL glycerol	For V and alloys; grain-boundary etch for Ta alloys. Swab specimen. Equal parts used for Ta and high Ta alloys.

IRON and STEEL

Composition	Comments
31. 90-99 mL methanol or ethanol 1-10 mL HNO ₃ structures. The 2% solution is most common, 5-10% used for high alloy	Nital. Most common etchant for Fe, carbon and alloy steels, cast iron. Reveals alpha grain boundaries and constituents. Excellent for martensitic steels (do not store). Use by immersion or swabbing of sample for up to about 60 seconds.

Table 43. Commonly Used Etchants for Metals and Alloys^a.

32. 100 mL ethanol 4 g picric acid chloride improves etch rate and uniformity.	Picral. Recommended for structures consisting of ferrite and carbide. Does not reveal ferrite grain boundaries. Addition of about 0.5-1% zephiran
33. 100 mL ethanol 5 mL HCl 1 g picric acid in stainless steels. Good for tool steels and martensitic stainless steels.	Vilella's reagent. Good for ferrite-carbide structures. Produces grain contrast for estimating prior austenite grain size. Results best on martensite tempered at 572-932 °F (300-500 °C). Occasionally reveals prior-austenite grain boundaries in high alloy steels. Outlines constituents
34. Saturated aqueous picric acid solution grain plus small amount of a wetting agent at 20-100 °C. Swab or immerse sample for 2-60 minutes. Etch in ultrasonic 219-223). Additions of 0.5g CuCl ₂ per 100mL steels to common. Lightly back	Bechet and Beaujard's etch, most successful etchant for prior-austenite boundaries. Good for martensitic and bainitic steels. Many wetting agents have been used, sodium tridecylbenzene sulfonate is one of most successful (the dodecyl version is easier to obtain and works as well). Use cleaner (see ref.2, pg. solution or about 1% HCl have been used for higher alloy produce etching. Room temperature etching most polish to remove surface smut.
35. 150 mL water 50 mL HCl 25 mL HNO ₃ 1 g CuCl ₂	Modified Fry's reagent. Used for 18% Ni maraging steels, martensitic and PH stainless steels.
36. 100 mL water 25 g NaOH 2 g picric acid high carbon steels when no apparent grain boundary film is present.	Alkaline sodium picrate. Best etch for McQuaid-Ehn carburized samples. Darkens cementite. Use boiling for 1-15 minutes or electrolytic at 6 V dc, 0.5 A/in ² , 30-120 seconds. May reveal prior-austenite grain boundaries in
37. 3 parts HCl 2 parts glycerol 1 part HNO ₃	"Glyceregia". For austenitic stainless steels. Reveals grain structure, outlines sigma and carbides. Mix fresh, do not store. Use by swabbing.
38. 100 mL ethanol 100 mL HCl 5 g CuCl ₂	Kalling's no. 2 ("waterless" Kalling's) etch for austenitic and duplex stainless steels. Ferrite attacked readily, carbides unattacked, austenite slightly attacked. Use at 20 °C by immersion or swabbing. Can be stored.
39. 15 mL HCl 10 mL acetic acid 5 mL HNO ₃ 2 drops glycerol	Acetic glyceregia. Mix fresh; do not store. Use for high alloy stainless steels.
40. 100 mL water 10 g K ₂ Fe(CN) ₆ 10 g KOH or NaOH ferrite yellow to yellow-brown, austenite unattacked. Do not always get uniform etching.	Murakami's reagent. Usually works better on ferritic stainless grades than on austenitic grades. Use at 20 °C for 7-60 seconds: reveals carbides si sigma faintly attacked with etching up to 3 minutes. Use at 80°C (176°F) to boiling for 2-60 minutes: carbides dark, sigma blue (not always attacked),
41. 100 mL water 10 g oxalic acid outlined after 6 seconds. 1-3 V also used. Dissolves carbides, sigma moderately attacked, ferrite unattacked.	Use for stainless steels at 6 V dc. Carbides revealed by etching for 15-30 seconds, grain boundaries after 45-60 seconds, sigma strongly attacked, austenite
42. 100 mL water 20 g NaOH and colored tan.	Used to color ferrite in martensitic, PH or dual-phase stainless steels. Use at 3-5 V dc, 20 °C, 5 seconds, stainless steel cathode. Ferrite outlined
43. 40 mL water 60 mL HNO ₃ preferred to stainless steel. Use at 1.4 V dc, 2 minutes (see ref. 2, pgs. 235,	Electrolytic etch to reveal austenite boundaries but not twin boundaries in austenitic stainless steels (304, 316, etc.). Voltage is critical. Pt cathode 238 and 239).

COPPER, NICKEL and COBALT: Copper and Alloys

Composition	Comments
44. 25 mL NH ₄ OH 25 mL water (optional) 25-50 mL H ₂ O ₂ (3%)	General purpose grain contrast etch for Cu and alloys (produces a flat etch for some alloys). Use fresh, add peroxide last. Use under a hood. Swab specimen 5-45 seconds.
45. 100 mL water 10 g ammonium persulfate orientation.	General purpose etch for Cu and alloys. Immerse or swab for 3-60 seconds. Reveals grain boundaries but is sensitive to crystallographic

Table 43. Commonly Used Etchants for Metals and Alloys^a.

46. 100 mL water 3 g ammonium persulfate 1 mL NH_4OH	General purpose etch for Cu and alloys, particularly Cu-Be alloys.
47. 70 mL water 5 g $\text{Fe}(\text{NO}_3)_3$ 25 mL HCl	Excellent general purpose etch, reveals grain boundaries well. Immerse specimen 10-30 seconds.

Nickel and Alloys

Composition	Comments
48. 5 g FeCl_3 2 mL HCl 99 mL ethanol	Carapella's etch for Ni and Ni-Cu (Monel) alloys. Use by immersion or swabbing.
49. 40-80 mL ethanol 40 mL HCl 2 g CuCl_2	Kalling's no.2 etch ("waterless" Kalling's) for Ni-Cu alloys and superalloys. Immerse or swab specimen up to a few minutes.
50. 50 mL water 50 mL HCl 10 g CuSO_4	Marble's reagent for Ni, Ni-Cu, and Ni-Fe alloys and superalloys. Immerse or swab sample 5-60 seconds. Reveals grain structure of superalloys.
51. 15 mL HCl 10 mL glycerol 5 mL HNO_3	"Glyceregia", for superalloys and Ni-Cr alloys. Swab specimen for 5-60 seconds. Mix fresh. Do not store. Use under a hood.
52. 60 mL glycerol 50 mL HCl 10 mL HNO_3	Modified Glyceregia for superalloys. Reveals precipitates. Use under hood; do not store. Add HNO_3 last. Discard when dark yellow. Immerse or swab specimen 10-60 seconds.

Cobalt and Alloys

Composition	Comments
53. 60 mL HCl 15 mL water 15 mL acetic acid 15 mL HNO_3	For Co and alloys. Mix fresh and age 1 hour before use. Immerse specimen for up to 30 seconds. Do not store.
54. 200 mL ethanol 7.5 mL HF 2.5 mL HNO_3	General etch for Co and alloys. Immerse specimen 2-4 minutes.
55. 50 mL water 50 mL HCl 10 g CuSO_4	Marble's reagent, for Co high temperature alloys. Immerse or swab specimen for up to 1 minute.
56. 80 mL lactic acid 10 mL H_2O_2 (30%) 10 mL HNO_3	For Co alloys. Use by swabbing.

PRECIOUS METALS: Au, Ag, Ir, Os, Pd, Pt, Rh and Ru

Composition	Comments
57. 60 mL HCl 40 mL HNO_3	For gold, silver, palladium and high noble metal alloys. Use under hood. Immerse specimen up to 60 seconds. Equal parts of each acid also used.
58. 60 mL HCl 20 mL HNO_3	Aqua regia for pure gold, Pt and alloys, some Rh alloys. Use boiling for up to 30 minutes.
59. 1-5 g CrO_3 100 mL HCl	For Au, Ag, Pd and alloys. Swab or immerse specimen up to 60 seconds.
60. 30 mL water 25 mL HCl 5 mL HNO_3	For pure Pt. Use hot, immerse specimen up to 5 minutes.
61. Conc. HCl	For Rh and alloys. Use at 5 V ac, 1-2 minutes, graphite cathode, Pt lead wires.

Table 43. Commonly Used Etchants for Metals and Alloys^a.

62. Solution a 100 mL water 40 g NaCl Solution b Conc. HCl	For Ru. Mix 4 parts solution a to 1 part solution b, use 5-20 V ac, 1-2 minutes, graphite cathode, Pt-lead wires.
63. 50 mL NH ₄ OH 20 mL H ₂ O ₂ (3%) fine silver, use 30% conc. hydrogen peroxide.	For pure Ag, Ag solders, and Ag-Pd alloys. Mix fresh. Swab specimen up to 60 seconds. Discard after etching. Use a 50:50 mix for sterling silver; for fine silver, use 30% conc. hydrogen peroxide.
64. Solution a 10 g NaCN 100 mL water Solution b H ₂ O ₂ (30%)	For gold alloys up to 18 karat. Mix equal amounts of a and b directly on the specimen using eye droppers. Swab and replenish the etchants until the desired etch level is obtained. If a brown stain forms, swab with a to remove it.

SINTERED CARBIDES

Composition	Comments
65. 100 mL water 10 g KOH or NaOH 10 g K ₃ Fe(CN) ₆ Normally used at 20 °C.	Murakami's reagent, for WC-Co and complex sintered carbides. Immerse specimen seconds to minutes. Use 2-10 seconds to identify eta phase (colored). Longer times attack eta. Reveals phase and grain boundaries.
66. 97 mL water 3 mL H ₂ O ₂ (30%)	For WC, MO ₂ C, TiC, or Ni in sintered carbides. Use boiling for up to 60 seconds. For coarse carbides or high Co content, use short etch time.
67. 15 mL water 30 mL HCl 15 mL HNO ₃ 15 mL acetic acid	For WC, TiC, TaC, and Co in sintered carbides. Use at 20 °C for 5-30 seconds.
68. 100 mL H ₂ O 3 g FeCl ₃	To darken Co (or Ni) binder phase. Mix fresh. Swab 10 seconds.

CERAMICS and NITRIDES

Composition	Comments
69. Phosphoric acid for up to a few minutes for Al ₂ O ₃ or up to 15 minutes for Si ₃ N ₄ .	For alumina, Al ₂ O ₃ , and silicon nitride, Si ₃ N ₄ . Use by immersion at 250 °C
70. 100 mL water 15 mL HNO ₃	For magnesia, MgO. Use by immersion at 25-60 °C for several minutes.
71. 100 mL water 5 g NH ₄ FHF 4 mL HCl	For titania, TiO ₂ . Immerse up to a few minutes.
72. 50 mL water 50 mL H ₂ SO ₄	For zirconia, ZrO ₂ . Use by immersion in boiling solution for up to 5 minutes.
73. HCl	For calcia, CaO, or MgO. Immerse for up to 6 minutes.
74. HF	For Si ₃ N ₄ , BeO, BaO, MgO, ZrO ₂ and Zr ₂ O ₃ . Immerse for up to 6 minutes.

PLASTICS and POLYMERS

Composition	Comments
75. 100 mL water 60 g CrO ₃	For polypropylene (PP). Immerse for up to several hours at 70°C.
76. HNO ₃	For polyethylene (PE). Immerse for up to a few minutes.
77. Xylol 70 °C.	Reveals spherulites in polyethylene (PE). Immerse for up to a few days at
78. 70 mL water 30 mL HCl	For polyoxymethylene (POM). Immerse up to 20 seconds.
79. Xylene	For polyamid (PA) and polyethylene (PE). Use at 70 °C for 60 seconds. For Nylon 6, use at 65-70 °C for 2-3 minutes. For Nylon 6, use at 75 °C for 3-4 minutes.