



Standard Test Method for Macroetching Metals and Alloys¹

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This standard has been approved for use by agencies of the Department of Defense.

^{e1} NOTE—Table 13 was editorially updated in August 2002.

1. Scope

1.1 These test procedures describe the methods of macroetching metals and alloys to reveal their macrostructure.

1.2 The values stated in inch-pound units are to be regarded as the standard. The SI equivalents of inch-pound units may be approximate.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 6.2, 7.1, 8.1.3, 8.2.1, 8.8.3, 8.10.1.1, and 8.13.2.

2. Referenced Documents

2.1 ASTM Standards:

- E 3 Methods of Preparation of Metallographic Specimens²
- E 381 Method of Macroetch Testing, Steel Bars, Billets, Blooms, and Forgings²

3. Significance and Use

3.1 Applications of Macroetching:

3.1.1 Macroetching is used to reveal the heterogeneity of metals and alloys. Metallographic specimens and chemical analyses will provide the necessary detailed information about specific localities but they cannot give data about variation from one place to another unless an inordinate number of specimens are taken.

3.1.2 Macroetching, on the other hand, will provide information on variations in (1) structure, such as grain size, flow lines, columnar structure, dendrites, etc.; (2) variations in chemical composition as evidenced by segregation, carbide

and ferrite banding, coring, inclusions, and depth of carburization or decarburization. The information provided about variations in chemical composition is strictly qualitative but the location of extremes in segregation will be shown. Chemical analyses or other means of determining the chemical composition would have to be performed to determine the extent of variation. Macroetching will also show the presence of discontinuities and voids, such as seams, laps, porosity, flakes, bursts, extrusion rupture, cracks, etc.

3.1.3 Other applications of macroetching in the fabrication of metals are the study of weld structure, definition of weld penetration, dilution of filler metal by base metals, entrapment of flux, porosity, and cracks in weld and heat affected zones, etc. It is also used in the heat-treating shop to determine location of hard or soft spots, tong marks, quenching cracks, case depth in shallow-hardening steels, case depth in carburization of dies, effectiveness of stop-off coatings in carburization, etc. In the machine shop, it can be used for the determination of grinding cracks in tools and dies.

3.1.4 Macroetching is used extensively for quality control in the steel industry, to determine the *tone* of a heat in billets with respect to inclusions, segregation, and structure. Forge shops, in addition, use macroetching to reveal flow lines in setting up the best forging practice, die design, and metal flow. For an example of the use of macroetching in the steel forging industry see Method E 381. Forging shops and foundries also use macroetching to determine the presence of internal faults and surface defects. The copper industry uses macroetching for control of surface porosity in wire bar. In the aluminum industry, macroetching is used to evaluate extrusions as well as the other products such as forgings, sheets, etc. Defects such as coring, cracks, and porthole die welds are identified.

4. Sampling

4.1 As in any method of examination, sampling is very important. When macroetching is used to solve a problem, the problem itself largely dictates the source of the sample as to the location on the work piece and the stage of manufacture; for example, when looking for pipe, the sample should represent

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²Annual Book of ASTM Standards, Vol 03.01.

the top of the ingot, or when looking for bursts or flakes, the sample should be taken as soon after hot working as possible.

4.2 When macroetching is used as an inspection procedure, sampling ought to be done in an early stage of manufacturing so that if the material proves faulty, no wasteful unnecessary work is done. However, the sample should not be taken so early that further working can introduce serious defects. In the steel industry, for example, the sample is usually taken after ingot breakdown and after most chances of bursts or flakes occurring have passed. Billets or blooms going into small sizes are sampled after initial breakdown. Material going into forging billets or die blocks is sampled near finish size. Sampling may be done systematically or on a random basis.

4.3 Samples may be cold cut from the source by any convenient fashion; saws and abrasive cutoff wheels are particularly effective. The use of torch cutting or hot cutting should be used only when necessary to cut a sample from a large piece. The sample then is sectioned well away from the hot-cut surface. An example of permissible use of torch cutting is the excising of a piece from a large plate and then cutting a sample for macroetching 4 to 5 in. (102 to 127 mm) away from the torch-cut edge.

4.4 Some common methods of sampling, listed by source, are as follows:

4.5 *Billets, Blooms, and Hot-Rolled Products*—Disks are usually cut from these products near the end. Samples cut too close to the end, however, may have false structures because of fish-tailing. Disks from large blooms are sometimes cut into smaller pieces for ease in handling.

4.5.1 *Forgings and Extrusions*—Disks cut transverse to the long dimension will show flakes, bursts, etc. Forgings may also be cut parallel to the long dimension to show flow lines. In complicated forgings, some thought will have to be given to the proper method of cutting so as to show flow lines. Macroetching of an unprepared specimen will show surface defects such as shuts, flats, seams, etc. In extrusions, coring and coarse grain are more commonly found in the back end of the extrusion.

4.5.2 *Sheets and Plates*—A sufficiently large sample should be taken when looking for surface defects. An ideal length would be the circumference of the last roll, but this may be inconveniently long. Several samples totaling some given fraction of the circumference can be used; however, there is always a chance then that a defect arising from faulty rolls would not be detected. When seeking information on laminations, a transverse section is used. In many cases, however, to reduce the size of the specimen, only a section out of the center of the plate may be taken.

4.5.3 *Weldments*—A disk cut perpendicular to the direction of welding will show weld penetration, heat affected zone, structure, etc. Careful preparation is usually rewarded with highly detailed structures giving a large amount of information. Welds involving dissimilar metals will produce problems in etching. The best method is to etch the least corrosion-resistant portion first and the more resistant portion afterwards. Occasionally an intermediary etchant may be required. The boundaries between etched and unetched portion will give an idea of weld penetration and dilution.

4.5.4 *Castings*—Cut the specimen to display the defect or feature being sought.

4.5.5 *Machined and Ground Parts*—When looking for grinding cracks, etc., the surface itself is used as a sample. Because the machined or ground part is often the finished part, it may be undesirable to immerse the part in acid. In this case, other methods such as dye penetrant methods may be more desirable.

5. Preparation

5.1 Sample preparation need not be elaborate. Any method of presenting a smooth surface with a minimum amount of cold work will be satisfactory. Disks may be faced on a lathe or a shaper. The usual procedure is to take a roughing cut, then a finish cut. This will generate a smooth surface and remove cold work from prior operations. Sharp tools are necessary to produce a good specimen. Grinding is usually conducted in the same manner, using free-cutting wheels and light finishing cuts. When fine detail is required, the specimen should be ground down through the series of metallographic papers (see Methods E 3). Where necessary, details are given in the tabulation of procedures.

5.2 After surface preparation, the sample is cleaned carefully with suitable solvents. Any grease, oil, or other residue will produce uneven attack. Once cleaned, care should be taken not to touch the sample surface or contaminate it in any way.

6. Solutions

6.1 The solutions used for macroetching are given in the tables listed under each alloy. In most cases a good grade of reagent should be used but need not be chemically pure or of analytical quality. The so-called technical grades are usually satisfactory. The solution should be clean and clear, free of suspended particles, scum, etc.

6.2 Caution must be observed in mixing. Many of the etchants are strong acids. In all cases, the various chemicals should be added slowly to the water or solvent while stirring. In the cases where hydrofluoric acid is used, the solution should be mixed and used in polyethylene vessels. (**Warning**—Hydrofluoric acid should not be allowed to contact the skin since it can cause painful serious ulcers if not washed off immediately.)

7. Procedure

7.1 Many of the solutions are aggressive and may give off irritating and corrosive fumes. Etching should be done in a well-ventilated room, preferably under a fume hood. The solution should be mixed and placed in a corrosion resistant tray or dish and brought to the operating temperature. The specimen or specimens should be placed in a tray of stainless steel screen or on some non-reactive support. Glass rods often are placed on the bottom of the acid container and the specimens laid directly on the rods. When etching is completed, remove the specimens from the dish taking great care not to touch the etched surface. When desmutting is required, dip the specimen into a second solution. After rinsing the specimen with hot water, blow dry with clean compressed air.

7.2 In the case of large specimens, such as ingot sections, swabbing may be the only practical method of macroetching.

Saturate a large wad of cotton held in stainless steel or nickel tongs with the etchant and sweep over the surface of the specimen. An effort should be made to wet the entire surface as soon as possible. After the initial wetting, keep the swab saturated with solution and frequently sweep over the surface of the specimen to renew the solution. When the structure has been suitably developed, rinse the specimen, either with a swab saturated with water, or better still, by pouring water over the specimen. After rinsing with hot water, blow the specimen dry with compressed air. Details of the procedure not discussed here are covered in the sections for the various metals and their alloys.

7.3 The times given in individual tabulations are only intended as guides. In fact, the progress of etching should be closely watched and etching stopped when the preferred structural details have been revealed. Specimens should be etched to develop structure. Generally, a light etch is better than a heavy etch; overetching can often lead to misinterpretation. The actual time to develop a structure properly may be quite different from the one suggested.

8. Specific Preparation Procedures and Recommended Solutions

8.1 Aluminum:

8.1.1 The specimens can be cut using common cutting tools, hack saws, band saws, shears, abrasive cutoff wheels, etc. All these methods will cause cold work at the surface and will generate heat. The temperature rise can be enough to cause changes in structure. For these reasons sharp tools and generous lubrication are necessary for sectioning.

8.1.2 The cold-worked surface should be removed by machining the surface. Again sharp tools and copious lubrication are required. If fine detail is required, the machined surface should be ground using silicon carbide paper lubricated with water or kerosine.

8.1.3 Several of the solutions used in macroetching react vigorously with the metal and can overheat the specimen. In these cases the specimen is periodically removed from the solution, cooled in running water, and reimmersed in the etchant. This procedure is repeated until the desired degree of etching is obtained.

8.1.4 Macroetchants for Aluminum and Aluminum Alloys—(Table 1).

8.2 Beryllium:

8.2.1 While beryllium in the massive form is not dangerous, beryllium and its compounds in the finely divided state are extremely poisonous. (**Warning**—Before starting any work involving beryllium, a review of hazards and plans for handling should be made. A number of references on beryllium are available. Particular mention may be made of “Toxicity of Beryllium” ASD-TR-62-7-667, prepared by the Kettering Laboratory for the Air Force.)

8.2.1.1 Generally speaking, beryllium and its alloys have given difficulty in obtaining good macroetched specimens. First, beryllium is a rather brittle metal and sectioning can be difficult. Cut-off wheels with the designation C46FR70 have been the most successful. Secondly, beryllium does not grind easily; hence, specimens should be as small as possible to minimize grinding time. Grinding has been most successful with the entire sequence of wet silicon carbide papers.

8.2.1.2 The etching of fine grained metal may not always be entirely successful, and further preparation will be required. Rough polishing with 15 μm Al_2O_3 suspended in water is performed on a low-nap cloth. Light pressure and frequent change of cutting direction produce the best results. If further polishing is required, 1- μm green Cr_2O_3 in tap water on synthetic suede works best.

8.2.2 Macroetchants for Beryllium and Beryllium Alloys—(Table 2).

TABLE 1 Macroetchants for Aluminum and Aluminum Alloys

Alloy	Composition		Procedure	Comments
All	NaOH H ₂ O	10 g 100 mL	Immerse sample 5 to 15 min in solution heated to 60 to 70°C (140 to 160°F). Rinse in water, and remove smut in strong HNO ₃ solution. Rinse and repeat etching if necessary.	Good general-purpose etchant, can be used on almost all aluminum alloys. Does not require fine grinding.
3XXX 4XXX 5XXX 6XXX High Si castings	HCl (concentrated) HNO ₃ (concentrated) HF (48 %)	75 mL 25 mL 5 mL	Mix fresh before using. Use at room temperature. May be used as immersion etch or swabbed over specimen surface. Rinse specimen in warm water and dry.	Used to develop grain structure. May be diluted with 25 % water to slow down etching. Does not require fine grinding.
High purity A1 1XXX 3XXX 4XXX 5XXX 6XXX	HCl (concentrated) HNO ₃ (concentrated) HF (48 %) H ₂ O	45 mL 15 mL 15 mL 25 mL	Immerse specimen at room temperature until desired contrast is developed. Rinse in warm water and dry.	Tucker's etch. General purpose etch for revealing microstructure of both cast and wrought aluminum. Does not require fine grinding.
All except high Si castings	HCl (concentrated) HNO ₃ (concentrated) HF (48 %) H ₂ O	15 mL 5 mL 5 mL 75 mL	Same as above.	1 + 2 Tucker's. Same as above, but slower acting.
2XXX High Cu alloys	HCl (concentrated) HF (48 %) H ₂ O	15 mL 10 mL 90 mL	May be used as an immersion etch or swabbed over the specimen surface. When desired contrast is obtained, rinse in water and remove deposits with concentrated HNO ₃ . Rinse in warm water and dry.	Flick's reagent. Best results are obtained with a ground surface. 180 grit will suffice.

TABLE 2 Macroetchants for Beryllium and Beryllium Alloys

Metal	Composition		Procedure	Comments
Be	HCl	10 mL	Either swab or immerse at room temperature for a few minutes, rinse in water and dry.	Works best on coarse grained Be.
	NH ₄ Cl	4 g		
	H ₂ O	90 mL		
Be	HCl	10 mL	As above.	An alternative when No. 1 does not work. Fine-grained metal may not give good results in either case.
	NH ₄ Cl	2 g		
	Picric acid	2 g		
	H ₂ O	90 mL		

8.3 Cobalt and Cobalt Alloys:

8.3.1 Many of the cobalt-base high-temperature alloys can be etched using the same procedures as those for iron- and nickel-base high-temperature alloys. Other cobalt alloys, such as the stellites used as machine tools, require special treatment.

8.3.1.1 The cobalt-base alloys, as a group, are not easily machined. The specimens should be sectioned with abrasive cutoff wheels and ground on wet silicon carbide papers. Because of the rapid work-hardening characteristics of these alloys, fresh paper and copious cooling should be used.

8.3.2 *Macroetchants for Cobalt and Cobalt Alloys* (Table 3).

8.4 Copper and Copper Alloys:

8.4.1 These metals are usually macroetched to bring out the general structure of wire bar and billets as well as variations in grain size in extrusions and forgings.

8.4.1.1 Specimens may be sectioned using common cutting tools. To minimize cold working the tools should be kept sharp.

8.4.1.2 Good results can be obtained by machining a smooth surface in two stages, the first being a heavy cut to remove the cold work from sectioning and the second a fine cut with a V-shaped tool to remove the remaining cold work. Grinding through the series of metallographic papers will give more detailed results. The degree of grinding depends upon the amount of detail required. The etching solutions listed in Table 4 are simple to prepare and their use requires no special technique.

NOTE 1—It should be pointed out that heavy etching often will remove the effect of cold work but at the expense of producing a rough surface. If the specimen is then given light regrinding to remove the rough etched surface, the second etch will provide good results.

8.4.2 *Macroetchants for Copper and Copper Alloys*—(Table 4).

8.5 Iron and Steel:

8.5.1 Macroetching has been most highly developed and is used extensively in the iron and steel industries. In hot-mill products such as bars, billets, sheet, and plate, the disk cut with a parting tool is prepared by facing on a lathe or by grinding. In facing, the first cut is moderately heavy with a sharp tool. The second facing is a light cut with a V-shaped tool run at high speed. Specimens produced in this manner are adequate for general inspection. A better though slower method is to grind the specimen. For inspection purposes, finishing on a 120-grit wheel will be sufficient.

8.5.1.1 When the maximum amount of detail is required, as in weldments, polishing the specimen with the series of metallographic papers gives the best results. When examining for surface defects, the surface itself should be etched directly without much preparation. The only preparation that is advisable is to brush off the loose scale and then to give the specimen a light grinding pass with very coarse abrasive to break through the adherent scale. When etching in 1 + 1 HCl for example, this scale will be removed, exposing the surface underneath. If care has been exercised in the grinding operations, the grinding scratches will not interfere with examination.

8.5.1.2 The most commonly used solutions for macroetching iron and steel are Solution Nos. 1 and 3 in Table 5.

8.5.1.3 Electrolytic etching using a solution of 3 to 6 % concentrated HCl in water at room temperature may be used³. The specimen is immersed in the solution, placed in a carriage, and passed over a cathodic bar at a current of 40 A/in. of specimen width. After etching, the specimen is cleaned by

³ An apparatus for performing this procedure may be obtained from Steltech Ltd., 2800 Speakman Drive, Sheriden Science and Technology Park, Missasauga, Ontario, Canada.

TABLE 3 Macroetchants for Cobalt and Cobalt Alloys

Alloy	Composition		Procedure	Comments
49Co-49Fe-V Some Co-Cr alloys	HCl	50 mL	Immerse specimen in hot solution (140 to 180°F) for 30 to 60 min. Rinse in hot water and dry.	General structure, porosity.
	H ₂ O	50 mL		
25Cr-10Ni-8W 21Cr-20Ni- 3W-3Mo-1Cb	HCl	50 mL	Swab until desired contrast is obtained then rinse in warm water and dry.	Grain size, general structure.
	HNO ₃	10 mL		
	FeCl ₃	10 g		
	H ₂ O	100 mL		
18Cr-10Ni-14W	CuCl ₂ ·2NH ₄ Cl·2H ₂ O	2 g	As above.	As above.
	FeCl ₃	5 g		
	HNO ₃	5 mL		
	HCl	50 mL		
	H ₂ O	80 mL		

TABLE 4 Macroetchants for Copper and Copper Alloys

Alloys	Composition	Procedure	Comments	
Cu and all brasses	HNO ₃ H ₂ O	10 mL 90 mL	Immerse specimen in solution at room temperature for a few minutes. Rinse in water and dry.	Emphasize grains and cracks.
Cu and all brasses	HNO ₃ H ₂ O	50 mL 50 mL	As above.	Brings out grain contrast, pits result unless agitated. Aluminum bronzes may form smut which can be removed by brief immersion in concentrated HNO ₃ .
Cu and all brasses	HCl FeCl ₃ H ₂ O or ethanol	30 mL 10 g 120 mL	As above.	Good grain contrast.
Cu, high Cu alloys, phosphorus, tin bronzes	K ₂ Cr ₂ O ₇ sat soln of NaCl H ₂ SO ₃ H ₂ O	2 g	Immerse specimen in solution at room temperature for 15 to 30 min then swab with fresh solution. Rinse in warm water and dry.	Emphasizes grain boundaries and oxide inclusions.
All	HNO ₃ AgNO ₃ H ₂ O	50 mL 5 g 50 mL	Immerse specimen in solution at room temperature. Rinse in warm water and dry.	Brilliant deep etch.
Brass	20 % acetic acid 5 % chromic acid 10 % FeCl ₃ in H ₂ O	20 mL 10 mL 5 mL	As above.	Strain lines.
Silicon brass or bronze	CrO ₃ NH ₄ Cl HNO ₃ (concentrated) H ₂ SO ₄ (concentrated) H ₂ O	40 g 7.5 g 50 mL 8 mL 100 mL	Immerse specimen in solution at room temperature, rinse in warm water and dry.	

using a vegetable fiber brush and a 10 % sodium citrate solution. The specimen finally is air dried.

8.5.2 Forgings—In addition to the examination for internal structure, surface defects, and structure, closed-die forgings are often sectioned to show flow lines. Etching for flow lines requires extremely careful preparation to provide a smooth surface with a minimum of cold work. Long pieces such as crank shafts are awkward to handle and are best prepared on a grinding machine using successively finer grinding wheels. Sectioning into shorter lengths may be advisable. The specimen should be heavily etched in 1 + 1 HCl or 20 % H₂ SO₄. Contrast can often be increased by wiping the surface lightly with very fine metallographic paper after etching. Examination for structure, defects, etc. is carried out in the same fashion as hotmill products.

8.5.3 Special Tests for Segregation—There are a number of etchants containing copper salts which will reveal segregation. Careful specimen preparation through the metallographic papers is required. Very careful cleaning after grinding is extremely important. When a specimen is immersed in this type of solution, copper plates out onto the specimen by a replacement reaction. The rate of deposition depends on the composition of the steel and the copper plating will cover the segregated regions. Sometimes the specimen can be left in a little longer than recommended and then rubbed lightly with metallographic papers to increase contrast.

8.5.4 Macroetchants for Iron and Steel (Table 5).

8.6 Stainless Steels and High-Temperature Alloys:

8.6.1 These alloys are generally more susceptible to cold working of the surface than are the lower alloy grades of steel. The best method of preparation is to grind the specimens as described for iron and steel. A smut tends to form on the

surface of the steel when immersed in 1 + 1 HCl. This can be prevented by adding a small quantity of HNO₃ to the etching bath. It can also be removed by scrubbing the specimen with a vegetable fiber brush under running warm water or by immersion in warm 20 % HNO₃. Scrubbing will provide a higher contrast for detection of segregation and inclusions. The desmutting either by the addition of HNO₃ to the etching bath or by the secondary rinse in HNO₃ will provide a brighter surface which is suitable for determination of grain size and structure. High-alloy stainless steels and austenitic high-temperature alloys because of their extreme corrosion resistance often will give trouble in etching. Aqua regia, HCl-H₂ O₂, and Marble's reagent are the recommended etchants. All three of these require very careful specimen preparation.

8.6.2 Macroetchants for Stainless Steels and High-Temperature Alloys (Table 6).

8.7 Lead and Lead Alloys:

8.7.1 Lead and its alloys are among the most difficult metals to prepare for macroetching. They are not only very soft and cold work easily, but they (pure lead especially) recrystallize readily at temperatures which can be easily achieved in careless preparation.

8.7.2 For best results in the macroetching of lead, all surfaces other than that to be examined must be masked from the macroetch by the use of several coats of a plastic spray. The surface to be examined should be filed prior to etching. Three 14-in. (360-mm) files⁴ are usually required and used in the

⁴ Nicholson designations. Be sure to preserve the distinction between hand smooth and hand-finishing smooth.

TABLE 5 Macroetchants for Iron and Steel

Alloys	Composition	Procedure	Comments
Plain and alloy steels, high-speed and tool steels, cutlery (12–14 % Cr) and stainless steels	HCl (concentrated) 50 mL H ₂ O 50 mL	Immerse specimen in solution heated to 160 to 180°F for 15 to 30 min. Desmut by vigorous scrubbing with vegetable fiber brush under running water. Stainless steels may be desmuted by dipping in a warm 20 % HNO ₃ to give a bright finish.	General purpose.
High-alloy steels	HCl (concentrated) 50 mL HNO ₃ (concentrated) 25 mL H ₂ O 25 mL	Immerse specimen for 10 to 15 min in solution at room temperature. Rinse in warm water and dry.	Ratio HCl:HNO ₃ runs 2:1 to 3:1.
Plain and alloy steels, cutlery steels	HCl (concentrated) 38 mL H ₂ SO ₄ (concentrated) 12 mL H ₂ O 50 mL	Immerse specimen for 15 to 45 min in solution heated to 160 to 180°F. Rinse in warm water and dry.	Works well on 12 % Cr steel.
High-alloy steels	HNO ₃ (concentrated) 10 mL HF (48 %) 4 mL H ₂ O 87 mL H ₂ O 87 mL to HNO ₃ (concentrated) 40 mL HF (48 %) 10 mL H ₂ O 50 mL	Immerse specimen in solution heated to 160 to 180°F until desired etch is obtained and rinse in warm water and dry.	Ratio HNO ₃ -HF varies.
Stainless steels, high-alloy steels	HCl (concentrated) 50 mL H ₂ O 50 mL H ₂ O ₂ (30 %) 20 mL	Mix HCl and water then heat to 160 to 170°F. Immerse specimen and add H ₂ O ₂ in several parts. Do not mix. Make each subsequent addition after foaming from previous addition has stopped.	Produces bright finish.
Austenitic stainless steels	HCl (concentrated) sat soln 50 mL CuSO ₄ in H ₂ O 25 mL	Immerse specimen in solution which may be heated or not depending upon alloy. Time also depends on alloy. Rinse in warm water and dry.	Marble's reagent. Light etch, good for structure.
Plain and low-alloy steels	(NH ₄) ₂ S ₂ O ₈ (ammonium persulfate) 10 g H ₂ O 100 mL	Swab solution at room temperature over specimen. Rinse and dry.	Grain size, weldments.
Plain and alloy steels	CuCl ₂ 2.5 g MgCl ₂ 10 g HCl (concentrated) 5 mL Alcohol—up to 250 mL	Immerse in solution at room temperature until a coppery sheen appears. Rinse thoroughly and dry.	Stead's reagent. Salts dissolved in HCl with minimum of hot water. To bring out P-rich areas and P banding.
Mild steel, Bessemer and high N ₂ steel	CuCl ₂ 90 g HCl (concentrated) 120 mL H ₂ O 100 mL	The surface should be rubbed with cloth soaked in etching solution. Wash in alcohol or rinse in HCl (1 + 1) after etching to prevent deposition of copper.	Fry's reagent. Before etching, sample should be heated to 200 to 250°C (302 to 482°F) for 5 to 30 min depending on condition of steel. To show strain lines due to cold work.
Plain and alloy steels	CuCl ₂ 45 g HCl (concentrated) 180 mL H ₂ O 100 mL	As above.	Modified Fry's reagent. Same as for reagent No. 9 but modified by Wazau, may give more contrast specimen can be washed in water without depositing copper.
Stainless and high-Cr steels	HCl 10 mL Alcohol 100 mL Picric acid 1 g	Immerse specimen in solution at room temperature until desired contrast is obtained. Rinse and dry.	Vilella's reagent.
Plain and alloy steels	HCl (concentrated) 6 to 12 mL H ₂ O 100 mL	Electrolytic, 5 to 10 A per square inch, specimen vertical, rinse, brush, and dry.	Small specimens, <20 in. ² area.
Plain and alloy steels	HCl (concentrated) 6 mL H ₂ O 100 mL HBO ₃ 1 g	Electrolytic, specimen moves past a cathode bar, 30 to 40 A per inch of specimen width, rinse, brush, and dry.	For specimens over 20 in. ² area, blooms, billets, and slabs.

following order: (1) aluminum, Type A, (2) hand smooth, and (3) hand-finishing smooth.

8.7.3 The file is usually held in a fixture and the specimen is drawn over the file proceeding from the point of the file to the tang. Remove the filings after each pass of the specimen with a few short strokes of a brass file brush in the direction of the

last cut of the file. The molybdate etch listed in Table 7 is used in the removal of worked metal and also to reveal the structure of lead of low-alloy content. The preparation of the solution is of paramount importance.

8.7.4 *Macroetchants for Lead and Lead Alloys* (Table 7).

8.8 *Magnesium*:

TABLE 6 Macroetchants for Stainless Steels and High-Temperature Alloys

Alloys	Composition		Procedure	Comments
Stainless steels and iron-base high-temperature alloys	HCl (concentrated) H ₂ O	50 mL 50 mL	Immerse specimen in solution heated to 160 to 180°F for 30 min. Desmut by vigorous scrubbing with vegetable brush under running water. Stainless steels may be desmutted by dipping in warm 20 % HNO ₃ to give bright finish. Dropwise or slow addition of H ₂ O is often effective in accelerating etching.	General purpose.
Iron-, cobalt-, and nickel-base high-temperature alloys	HCl (concentrated) HNO ₃ (concentrated) H ₂ O	50 mL 25 mL 25 mL	Immerse specimen in solution at room temperature for 10 to 30 min. Rinse and dry.	Ratio HCl + HNO ₃ runs 2 + 1 to 3 + 1
Stainless steels and high-temperature alloys	HNO ₃ HF (48 %) H ₂ O to HNO ₃ (concentrated) HF (48 %) H ₂ O	10 mL 3 mL 87 mL 40 mL 10 mL 50 mL	Immerse specimen in solution heated to 160 to 180°F until desired contrast is obtained. Rinse and dry.	Ratio HNO ₃ -HF varies.
Austenitic stainless steels and nickel base alloys	I (NH ₄) ₂ SO ₄ H ₂ O II FeCl ₃ HCl (concentrated) III HNO ₃ (concentrated)	15 g 75 mL 250 g 100 mL 30 mL	Combine I and II then add III. Immerse specimen in solution at room temperature until desired contrast is obtained.	Lepito's etch. I, mix fresh, grain structure.
Austenitic stainless steels and high-temperature alloys	HCl (concentrated) H ₂ O H ₂ O ₂ (30 %)	50 mL 50 mL 20 mL	Mix HCl and water then heat, immerse specimen and add H ₂ O ₂ in several parts. Do not mix. Make each subsequent addition after foaming from previous addition has stopped.	
Austenitic stainless steels and high-temperature alloys	HCl (concentrated) Sat soln of CuSO ₄ in H ₂ O	50 mL 25 mL	Immerse specimens in solution which may be heated up to 170°F until desired contrast is obtained. Rinse and dry.	Marble's reagent. Light etch, good for structures. Amount of CuSO ₄ solution may be increased to 1 + 1 ratio for difficult alloys.

TABLE 7 Macroetchants for Lead and Lead Alloys

Alloy	Composition		Procedure	Comments
Lead and lead alloys	A. H ₂ O NH ₄ OH (sp gr 0.90) HNO ₃ (concentrated) Molybdc acid (85 %) B. H ₂ O HNO ₃ (concentrated) C. Glacial acetic acid	250 mL 140 mL 60 mL 100 mL 960 mL 400 mL 100 mL	Add A to B and let precipitate redissolve. If B is added to A an insoluble precipitate forms. Add C to mixture of A and B after precipitate has redissolved. Swab surface of the specimen with mixed solution until desired contrast is obtained. Rinse and dry.	
Antimonial lead	A. Glacial acetic acid HNO ₃ (concentrated) H ₂ O B. Glacial acetic acid H ₂ O A. HNO ₃ (concentrated) H ₂ O B. (NH ₄) ₂ MoO ₄ H ₂ O A. (NH ₄) ₂ MoO ₄ Citric acid H ₂ O A. Acetic acid H ₂ O ₂	30 mL 40 mL 16 mL 1 mL 400 mL 80 mL 220 mL 45 g 10 g 25 g 100 mL 75 mL 25 mL	Prepare surface on silk velvet wheel with Al ₂ O ₃ abrasive at 150 rpm. Etch with solution A at 42°C then repolish until bright. Reetch with B at room temperature for 1 to 2 h. Mix equal quantities of A and B immediately before use. Immerse specimen in solution at room temperature until desired contrast is obtained. Rinse and dry. Immerse specimen in solution at room temperature until desired contrast is obtained, then rinse and dry. Immerse dry specimen in solution at room temperature until desired contrast is obtained, then rinse and dry.	Grain structure Bright etch, grain structure, defects. Chemical polish-etch.

8.8.1 Features detected by macroetching are grain size, segregation of intermetallic compounds, coring, cracks, porosity, laps, germinations, surface burning, and tears.

8.8.2 Cast or wrought magnesium alloys are prepared in a similar manner to aluminum or copper and brass; however, a final facing with a 0.005-in. (0.127-mm) radius V-shaped tool fed at a rate of 0.002 to 0.003 in. (0.508 to 0.762 mm) is often sufficient. For some applications, the specimen may be finished on a 400-grit wet wheel. To resolve small detail, additional polishing with a water suspension of 600-grit Alundum or further with alpha alumina may be necessary.

8.8.3 The finely divided magnesium as chips or swarf is highly combustible and precautions against it catching fire should be taken.

8.8.4 *Macroetchants for Magnesium and Magnesium Alloys*—(Table 8).

8.9 *Nickel and Nickel Alloys:*

8.9.1 Nickel alloys cold work easily and their preparation is not always easy. Grinding produces the best specimens. Low-nickel and cobalt alloys of basically pure metal can be etched

with Marble's reagent or strong HNO₃ solutions. The high-temperature alloys are difficult to etch. First of all, they are subject to cold-working problems, and secondly, the alloys are extremely corrosion resistant. Best results have been obtained with aqua regia, modified Marble's reagent, or HCl-H₂O₂ solutions.

8.9.2 *Macroetchants for Nickel and Nickel Alloys* (Table 9).

8.10 *Noble Metals—Ag, Au, Ru, Rh, Pd, Os, Ir, and Pt:*

8.10.1 These metals, in general, are soft and ductile. Because of their expense, usually specimens for macroetching will be small and can be handled the same as microspecimens. Care should be used to avoid cold work. Well-lubricated metallographic papers are recommended. Some of the platinum group metals, notably osmium and rhodium, are more abrasion resistant than their hardness would indicate and, therefore, will require long grinding time.

8.10.1.1 Except for silver, all of these metals are corrosion resistant and require the use of strong etchants. Etching should be done under a fume hood, with the proper precautions for the use of HF.

TABLE 8 Macroetchants for Magnesium and Magnesium Alloys

Alloy	Composition	Procedure	Comments	
ZK60A	Glacial acetic acid H ₂ O	5 mL 95 mL	Immerse specimen in solution at room temperature for ½ to 8 min until desired contrast is obtained. Desmut with 50 % HF (48 %) in water. Rinse in rapidly flowing water and dry.	Flow lines in forgings.
AZ61A	Glacial acetic acid	10 mL	As above but for ½ to 5 min.	Grain size, surface casting defects.
AZ80A	H ₂ O	90 mL		
AZ31B	Glacial acetic acid	20 mL	As above but for ¼ to 5 min.	Flow pattern in forgings. Surface casting defects. Glycolic acid may be substituted for acetic acid.
AZ61A AZ80A	NaNO ₃ H ₂ O	5 g 80 mL		
AZ31B	HNO ₃ (concentrated) H ₂ O	10 mL 90 mL	As above but for ½ to 5 min.	Flow pattern in forgings. Internal defects in cast slabs and ingots.
	Na ₂ Cr ₂ O ₇ HNO ₃ (concentrated) H ₂ O to make	180 g 180 mL 1000 mL	As above but rinse in hot water.	General etch for defects in sand and die castings.
	CrO ₃ HNO ₃ (concentrated) HF (48 %) H ₂ O to make	280 g 25 mL 10 mL 1000 mL	As above.	Germination on sand cast surfaces. Surface defects of die castings.
AZ61A AZ80A	6 % picric acid in alcohol H ₂ O Glacial acetic acid	100 mL 10 mL 5 mL	As above for ½ to 3 min or may be swabbed.	Grain size and flow patterns of both cast and wrought forms. Requires fine finish (600 grit).
AZ21 AZ31	6 % picric acid in alcohol H ₂ O Glacial acetic acid	70 mL 10 mL 10 mL	As No. 7.	Grain size. Specimen should be finished on 600-grit paper.
ZK60A	6 % picric acid in alcohol H ₂ O Glacial acetic acid	50 mL 20 mL 20 mL	As No. 7.	Flow pattern and grain size of homogeneous alloy. Increase water to increase strain contrast. Specimen should be finished on 600-grit paper.
	4 % picric acid in alcohol H ₃ PO ₄	100 mL 0.7 mL	Immerse specimen in solution at room temperature repeatedly until desired stain is obtained, rinse and dry.	Segregation of intermetallic compounds and associated cracks. Specimen should be finished on 600-grit paper.

TABLE 9 Macroetchants for Nickel and Nickel Alloys

Alloy	Composition	Procedure	Comments
Ni	CuSO ₄ 10 g HCl 50 mL H ₂ O 50 mL	Immerse specimen in solution at room temperature until desired contrast is obtained. Rinse and dry.	Marble's reagent, for grain structure.
Low-Ni alloys	HNO ₃ 20 mL H ₂ O 10 mL CuSO ₄ 10 g	Immerse specimen in solution at room temperature for 20 to 30 min, rinse and dry.	Grain structure.
High-Ni alloys	HNO ₃ (concentrated) 50 mL H ₂ O 50 mL	As above.	Porosity and flowlines.
Alloys containing Cr, Fe, and other elements	HNO ₃ 50 mL Acetic acid 50 mL	Immerse specimen in hot solution. Rinse in hot water and dry.	Grain structure.
	Acetic acid 50 mL HNO ₃ 50 mL	Swab	Lepito's reagent II, etchant for nickel welds.
	Sat soln of CuSO ₄ in H ₂ O 50 mL	Swab etchant.	Modified Marble's reagent.
	HCl 100 mL H ₂ O 100 mL H ₂ O ₂ (30 %) 40 mL	Mix HCl and water, then heat, immerse specimen, and add H ₂ O ₂ in several parts. Do not mix. Make subsequent additions after foaming from the previous addition has stopped.	

8.10.2 *Macroetchants for the Noble Metals* (Table 10).

8.11 *Refractory Metals—Cr, Mo, W, V, Cb, and Ta:*

8.11.1 The above six metals, the refractory metals, are found in Group V-B (V, Cb, Ta) and Group VI-B (Cr, Mo, W) of the periodic table. (Some tables list them as V-A and VI-A.) In general, these metals are soft and ductile in the pure state, but in the form usually encountered are hard and brittle. Consequently, these metals and their alloys must be carefully ground before macroetching. The abrasives must be of sufficient hardness, and particles on the laps must be sharp. Wet silicon carbide papers have proved satisfactory provided they are used with sufficient pressure to effectively cut the sample and are not used after they become dull or worn. Longer grinding times than would be expected from the hardness of these metals and alloys are needed. The solutions listed in Table 11 used for the metals specified will reveal defects, general structure, grain size, and segregation.

8.11.2 *Macroetchants for the Refractory Metals* (Table 11).

8.12 *Tin and Tin Alloys:*

8.12.1 Tin and its alloys, like lead, are difficult to prepare. Because these metals cold work easily and recrystallize at room temperature, false structures are easily produced. The best method of preparation for macroetching is the same as for microetching. The specimen should be cut carefully and then ground gently on lubricated silicon carbide paper. This may be followed by polishing with 6- μ m diamond paste on a moderately nappy wheel.

8.12.2 Precision cast tin-base bearing alloys may be etched directly without preparation.

8.12.3 *Macroetchant for Tin and Tin Alloys* (Table 12).

8.12.4 *Preparation of Ammonium Polysulfide*—Pass H₂ S gas into 200 mL of NH₄ OH (sp gr 0.9) until saturated. The solution should be kept in an ice bath during this operation. Add an additional 200 mL of NH₄ OH (sp gr 0.9) and dilute

TABLE 10 Macroetchants for the Noble Metals

Metal	Composition of Solution	Condition of Use	Comments and Use
Ag	HNO ₃ 10 mL	RT, few minutes.	Grain contrast.
	Methyl alcohol 90 mL		
Au Pt alloys Pd alloys	HCl 66 mL	Hot, few minutes.	Grain contrast.
	HNO ₃ 34 mL		
Ru and alloys Os and alloys Rh and alloys	Lactic acid 50 mL	RT, few minutes.	Grain contrast.
	HNO ₃ 20 mL		
	HF 30 mL		
As above	HCl 30 mL	RT, few minutes.	Grain contrast.
	HNO ₃ 15 mL		
	HF 30 mL		
Pt and alloys	Sat solution of NaCl in H ₂ O 80 mL	Electrolytic, 6V, few minutes.	Grain contrast.
	HCl 20 mL		

TABLE 11 Macroetchants for the Refractory Metals

Metal	Composition of Solution	Temperature	Time	Comments
Mo, W, V, Cb, and Ta	HCl (concentrated)	30	RT	5 to 20 min
	HNO ₃ (concentrated)	15		
	HF (48 %)	30		
Mo, W, and V	HF (48 %)	15	RT	10 to 20 min
	HNO ₃ (concentrated)	35		
	H ₂ O	75		
W, V, Cb, and Ta	HF (48 %)	10	RT	Too fast for Mo, 1 to 5 s
	HNO ₃ (concentrated)	30		
	Lactic acid (85 %)	50		
Cr	H ₂ SO ₄	10	Boiling	2 to 5 min
	H ₂ O	90		

TABLE 12 Macroetchant for Tin and Tin Alloys

Composition of Solution	Procedure	Comments
Saturated ammonium polysulfide	Immerse specimens in full strength solution at room temperature for 20 to 30 min. Do not swab surface during etching.	Grain structure

with water to make 1 L. Add 100 g of sulfur. Stir occasionally over a period of 1 h, then filter and use.

8.13 Titanium, Zirconium, Hafnium and Their Alloys:

8.13.1 Titanium, zirconium, and hafnium, the reactive metals, are macroetched for general structure, grain size, and segregation of impurities. They require extreme care in preparation. Sharp tools and fresh grinding paper are required to prevent cold work from blurring the structure. The best results are obtained by grinding. These metals grind slowly and require sharp, fresh abrasives. The recommendations of grinding wheel manufacturers should be followed closely for rough grinding. Silicon carbide papers, usually run wet, will give a fine finish. Papers should be discarded frequently to prevent loading. Chemical polishing preparations, while relatively untried, may have decided advantages in handling these materials.

8.13.2 Solutions in Table 13 are not difficult to prepare but involve the use of hydrofluoric acid. This acid can give extremely serious, very painful burns. The HCl-HF solution requires desmutting. The specimen should be rinsed between etching and desmutting. (Table 13)

8.14 Zinc and Zinc Alloys:

8.14.1 Zinc and its alloys cold work rapidly and recrystallize at low temperatures, thus allowing false structures to form easily. Coarse-grained zinc and zinc alloys are more prone to cold work than some of the fine grained die-casting alloys. A good test for the presence of cold work, especially in coarse-grained samples, is the appearance of twinning after etching.

8.14.2 Samples should be cut with a sharp saw and ground on well-lubricated silicon carbide papers at slow speeds.

8.14.3 Macroetchants for Zinc and Zinc Alloys (Table 14).

TABLE 13 Macroetchants for Titanium, Zirconium, Hafnium and Their Alloys

Alloy	Solution Composition	Procedure	Comments
Ti alloys	HCl (concentrated)	20 mL	Immerse specimen in solution heated to 120 to 150°F for 20 to 30 min. Rinse. If smut forms immerse in 30 % H ₂ SO ₄ for 3 min. Rinse and dry.
	HF (48 %)	40 mL	
	H ₂ O	40 mL	
7Al-4Mo alloys	HNO ₃ (concentrated)	42 mL	As above.
	HF (48 %)	8 mL	
	H ₂ O	50 mL	
Zr, Hf, and low alloys	H ₂ O ₂ (30 %)	45 mL	Swab specimen with solution at room temperature. Rinse 10 s after yellow fumes form, then dry.
	HNO ₃ (concentrated)	45 mL	
	HF (48 %)	10 mL	
Zr, Hf, and high alloys	H ₂ O	45 mL	As above.
	HNO ₃	45 mL	
	HF	10 mL	
1.5Sn-0.15Fe-0.10Cr, and Hf	H ₂ O	70 mL	As above.
	HNO ₃ (concentrated)	30 mL	
	HF (48 %)	5 mL	
Iodide Ti	H ₂ O ₂ (30 %)	60 mL	Swab with solution at room temperatures until desired contrast is obtained. Rinse in cold water and dry.
	H ₂ O	30 mL	
	HF (48 %)	10 mL	

TABLE 14 Macroetchants for Zinc and Zinc Alloys

Alloy	Solution Composition		Procedure	Comments
Cu-free zinc alloys	HCl (concentrated) H ₂ O	50 mL 50 mL	Immerse in solution for about 15 sec. Remove smut by wiping under running water. Repeat until desired contrast is obtained, then dry.	Grain structure.
Zn alloys containing Cu	CrO ₂ Na ₂ SO ₄ or Na ₂ SO ₄ ·10H ₂ O H ₂ O	20 g 1.5 g 3.4 g 100 mL	Immerse in solution until good contrast is obtained. Rinse in running water and dry. Repeat if necessary.	Grain structure.

9. Keywords

9.1 alloys; etchants; etching; macroetching; macroetchant; macrostructure; metals

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