

## 10 Metallography

Metallography is the branch of science dealing with the study of the constitution and structure of metals and alloys, its control through processing, and its influence on properties and behavior. Its original implementation was limited by the resolution of the reflected light microscope used to study specimens. This limitation has been overcome by the development of transmission and scanning electron microscopes (TEM and SEM). The analysis of x-rays generated by the interaction of electron beams with atoms at or near the surface, with wavelength- or energy-dispersive spectrometers (WDS, EDS) with the SEM or the electron microprobe analyzer (EMPA), has added quantitative determination of local compositions, e.g., of intermediate phases, to the deductions based upon observations. Introduction of metallogical and stereological methods, and the development of computer-aided image analyzers, permits measurement of microstructural features. Crystallographic data can be obtained using classic x-ray diffraction methods using a diffractometer, or diffraction analysis can be performed with the TEM using selected area or convergent-beam electron diffraction (SAD and CBED) techniques, and more recently with the SEM with the orientation-imaging (EBSD) procedure. There is a wide variety of very sophisticated electron or ion devices that can be utilized to characterize surfaces and interfaces, but these devices are generally restricted in availability due to their high cost.

Conventional light-optical techniques are still the most widely used and are capable of providing information needed to solve most problems. Examination by light optical microscopy (LOM) should always be performed before use of electron metallographic instruments. LOM image contrast mechanisms are different than EM imaging modes. Natural color can not be seen with EM devices. Microstructures are easier to study at low magnification with the LOM than with the SEM. The LOM examination may indicate the need for SEM or TEM analysis and determine the locations for such work. Interpretation of LOM examination results is enhanced and reinforced by the use of electron metallographic techniques. The SEM has become ubiquitous in the metallographic laboratory.

### 10.1 Macroscopic examination

For examination of large-scale features, known as macrostructure<sup>152</sup> because it is visible with the unaided eye, disks are cut from cast or wrought products (in the case of wrought products, usually before extensive hot deformation is performed). The disks must be representative of the product and are usually taken from prescribed test locations. Mechanical sawing or abrasive sectioning is used to obtain the disk, which may be ground to various surface finish levels, depending upon the nature of the detail that must be observed. The disks are cleaned and hot acid etched to reveal the solidification structure, deformation structure, segregation, soundness, etc. Disks may also be subjected to contact printing methods, such as sulfur printing (see 152, ASTM E 1180 and ISO 4968).

The required disk is obtained by sawing, abrasive sectioning or machining with adequate cooling and lubrication, and is normally finished by grinding. Due to the size of these disks, machine shop grinders are used. In the case of a small section, laboratory practices may be utilized. Grinding on abrasive cloth or paper, such as an “endless belt grinder”, is often used, but the platen beneath the belt must be kept flat. For most macroexamination work, a ground surface is adequate. In a few cases, chiefly dependant upon the nature of the examination and the

desired etchant, a polished surface is required. Conventional metallographic procedures are adequate. The main problem is obtaining flatness over a section area that is rather large compared to standard metallographic specimens. But, with modern grinder/polisher devices, this can be readily accomplished.

Capturing images of macroetched components can be quite difficult due to the need for obtaining proper uniform illumination, especially if the surface is as-polished, as might be the case when documenting porosity, cracks or other voids in sections. Although film-based documentation is becoming less common, compared to digital imaging, film is still preferred at this time in failure analysis work involving litigations. Regardless of the technology used, illumination still must be uniform. With an as-polished surface, “hot spots” and reflections are a major problem that can be overcome by a variety of “tricks” utilizing vertical illumination and passing light through translucent material.

Etching reagents for macroscopic work are given in many national and international standards, such as ASTM E 340, and text books<sup>152</sup>. The commonly used reagents are listed in Table 10.1. Directions for sulfur-printing are given in ISO 4968 and ASTM E 1180. This technique is used to show the distribution of sulfur in steel and is also described in Table 10.1.

## **10.2 Microscopic examination**

Metallographic specimens are normally prepared for examination with the light microscope by cutting out the piece to be examined (preferably not more than about 3 cm diam.) using a laboratory abrasive cutoff machine or a precision saw. Sometimes specimens are cut in the shop or in the field using more aggressive methods, such as power hacksaws, dry abrasive cutting, and even by flame cutting. These techniques introduce a great deal of damage into the structure adjacent to the cut. It is generally best to re-section the specimen with a laboratory abrasive cutoff machine rather than to try to grind through the damaged layer. In many cases, the specimen is encapsulated in a polymeric compound, either a compression mounting resin or a castable resin. Larger specimens of uniform shape may be prepared without mounting but the edge retention may not be adequate for examination above 100X. The specimens are then subjected to at least one grinding step and one or more diamond abrasive steps, followed by one or more polishing steps with other abrasives, such as alumina or colloidal silica. But, the steps must be designed to remove the damage from sectioning. However, each abrasive does produce damage proportional to its particle size. So, each step must remove the damage from the previous step so that at the final step the damage depth is so thin that etching will remove it. At the same time, the preparation procedure must keep the specimen surface flat and other problems (e.g., pull out, drag, smear, embedding, etc.) are prevented. The surface must be more than just reflective in nature if the true microstructure is to be revealed.

For some purposes, e.g., the study of slip processes involving individual dislocations using transmission electron microscopical studies of fine structure, and microindentation hardness testing under light loads, electropolishing has been considered in the past to be almost indispensable. In the later case, this is certainly unnecessary today with proper mechanical preparation methods. Preparation of specimens for replica work requires a proper metallographic preparation procedure, but this can be done mechanically. Preparation of TEM thin foils normally employs jet-electropolishing (or similar alternative procedures) to perforate the specimen. But, this is the final step after initial mechanical grinding. Electropolishing does have

certain advantages, but also disadvantages. It is best for single phase metals, particularly for relatively pure metals. In alloys containing two or more phases, the rate of electropolishing varies for each phase and flat surfaces may be difficult to obtain. Even for single phase metals, the surface is often wavy rather than flat which makes high magnification examination difficult or impossible. Electropolishing solutions are often quite aggressive chemically, and may be dangerous, even potentially explosive under certain operating conditions, or under careless operating conditions.

**Table 10.1** ETCHING REAGENTS FOR MACROSCOPIC EXAMINATION

<i>Material</i>	<i>Reagent*</i>	<i>Remarks</i>
<i>A. Aluminium base</i>		
1. Aluminium and its alloys	(a) Concentrated Keller's Reagent Nitric acid (1.40) 100 ml Hydrochloric acid (1.19) 50 ml Hydrofluoric acid (40%) 1 ½ ml	Can be diluted with up to 50ml water,
	(b) Nitric acid (1.40) 30 ml Hydrochloric acid (1.19) 30 ml 2% conc. Hydrofluoric acid 30 ml	Widely applicable, but very vigorous
	(c) Tucker's Reagent Nitric acid (1.40) 15 ml Hydrochloric acid (1.19) 45 ml Hydrofluoric acid (40%) 15 ml Water 25 ml	Use fresh
	(d) 10% sodium hydroxide in water	Use at 60-70°C
2. Unalloyed Aluminium and Al-Cu alloys	(e) Flick's Reagent Hydrochloric acid 15 ml Hydrofluoric acid 10 ml Water 90 ml	Wash in warm water after etching and clear by dipping in concentrated nitric acid
3. Aluminium – silicon	(f) Hume-Rothery's Reagent Cupric chloride 15 g Water 100 ml	For high-silicon alloys, Fine polish undesirable. Immerse specimen. 5-10s, remove, and brush away deposited copper or remove it with 50% nitric acid in water
4. Aluminium – copper	(g) Keller's Reagent 2 ½ % nitric acid (1.40) 1 ½ % hydrochloric acid (1.19) ½ % hydrofluoric acid (40%) Rem. water	More frequently used as micro-etch
5. Aluminium – magnesium	(h) 5% cupric chloride 3% nitric acid (1.40) Rem. water	Clear surface with strong nitric acid
6. Aluminium – copper – silicon	(g) Keller's Reagent (as above) (i) Nitric acid (1.40) 15 ml Hydrochloric acid (1.19) 10 ml Hydrofluoric acid (40%) 5 ml Water 70ml	
7. Aluminium–copper–magnesium–nickel	(j) Zeerleder's Reagent Hydrochloric acid (1.19) 20 ml Nitric acid (1.40) 15 ml Hydrofluoric acid (40%) 5 ml Water 60 ml	

\*Acids are concentrated, unless otherwise indicated, e.g. with specific gravity.

*B. Copper base*

1. Copper and copper alloys generally	(a) Alcoholic ferric chloride Ethyl alcohol 96 ml Ferric chloride (anhydrous) 59 g Hydrochloric acid (1.19) 2 ml	Avoid use of water for washing or staining may result. Use alcohol or acetone instead. Grain contrast
	(b) Acid aqueous ferric chloride Ferric chloride 25 g Hydrochloric acid (1.40) 25ml Water 100 ml	(a) and (b) require moderately high standard of surface finish
	(c) Concentrated nitric acid (1.40) 50 ml Nitric acid (1.40) 50 ml Water 10 ml	A rapid etch, suitable for roughly prepared surfaces. Addition of a trace of silver nitrate (5%) enhances contrast
	(d) 10% ferric chloride in water 10 ml 5% chromium trioxide in 10 ml	To reveal strains in brasses

		saturated brine		
		20% acetic acid in water	20 ml	
	(e)	A. 1% mercuric nitrate in distilled water		Time required to induce cracks is indication of residual stress
		B. 1% nitric acid (1.40) in water		
		Mix A and B in equal proportions		
	(f)	Chromium trioxide	40 g	Good for alloys with silicon and silicon bronzes
		Ammonium chloride	7.5 g	
		Nitric acid (1.40)	50 ml	
		Sulphuric acid (1.84)	8 ml	
		Distilled water	100 ml	
C.	<i>Iron and steel</i>			
	(a)	50% hydrochloric acid in water		Use hot (70-80°C) for up to 1 h. Shows segregation porosity, cracks useful for examination of welds for soundness
	(b)	20% sulphuric acid in water		Use hot (80°C) for 10-20 min. Scrub lightly to remove carbonaceous deposit. Purpose as (a). Mixtures of (a) and (b) are also used similarly
	(c)	25% nitric acid in water		Purposes as (a) and (b). May be used cold if more convenient
	(d)	10% ammonium persulphate in water		Grain contrast etch. Apply with swab. Reveals grain growth and recrystallization at welds.
	(e)	Stead's Reagent Cupric chloride Magnesium chloride Hydrochloric acid (1.19) Alcohol to 1 litre	10 g 40 g 20 ml	For revealing phosphorus segregation and primary dendritic structure of cast steels. Dissolve the salts in the acid with addition of a minimum of water. Phosphorus segregate unattacked, also eutectic cells in cast iron
	(f)	Fry's Reagent Cupric chloride Hydrochloric acid Water	90 g 120 ml 100 ml	To reveal strain lines in mild steel. Heat to 150-250°C for 15-30min before etching specimen. Etch for 1-3min while rubbing with a soft cloth. Rinse with alcohol.
	(g)	Humphrey's Reagent Copper ammonium chloride Hydrochloric acid (1.19) Water	120 g 50 ml 1 litre	Reveals dendritic structure of cast steels. First treat surface with 8% copper ammonium chloride solution and then with (g) for ½ - 1 ½ h. Remove copper deposit (loosely adherent), dry and rub surface lightly with abrasive
	(h)	5-10% nitric acid in alcohol		Etch for up to ½ h. Reveals cracks and carbon segregation. More controlled than aqueous acids
	(j)	Sulphur-printing 3% sulphuric acid in water		Soak photographic printing paper in the acid and remove surplus acid with blotting paper. Lay paper face down on the clean steel surface and

\*Acids are concentrated, unless otherwise indicated, e.g. , with specific gravity.

C.	<i>Iron and steel – Continued</i>			'squeegee' into close contact. After 2 min remove paper, wash it and fix in 6 % sodium thiosulphate in water. Brown coloration on the paper indicates local segregation of sulphides
	(k)	Dithizone process for lead distribution		See p. 10.38, <i>Lead in steels</i> . Analogous to sulphur-printing
	(l)	Marble's Reagent Hydrochloric acid (1.19) Saturated aqueous solution of cupric sulphate	50 ml 25 ml	Austenitic steels. High temperature steels. Fe-Cr-Ni casting alloys. Also shows depth of nitriding
	(m)	Oberhoffer's Reagent Hydrochloric acid (1.19) Ferric chloride Stannous chloride Water Ethanol (acid added last) Rinse in 20% hydrochloric acid in ethanol	42 ml 30 g 0.5 g 500 ml 500 ml	Good surface preparation needed. Steel castings. Darkens Fe-rich areas, reveals segregation and primary cast structure
	(n)	Klemm's Reagent Saturated aqueous solution of sodium thiosulphate Sodium metabisulphite (can be increased for contrast)	50 ml 1 g	Phosphorus distribution in cast steel and cast iron. Grain contrast.

D. *Lead base*

Lead and lead alloys generally	(a)	Russell's Reagent A. 80 ml nitric acid (1.40) in 220 ml water B. 45 g ammonium molybdate in 300 ml water		Grain contrast etch; removes deformed layer Mix equal parts of A and B immediately before use. Swab for 10-30 s. Rinse in water
	(b)	Ammonium molybdate Citric acid Water	10 g 25 g 100 ml	Bright etch revealing grain structure, defects, etc.
	(c)	Worner and Worner's Reagent Acetic acid, glacial '100 vol.' hydrogen peroxide	75 ml 25 ml	Chemical polish revealing defects, etc. Specimen must be dry and water content of solution as low as possible <i>N.B.</i> – Avoid all heating, as lead alloys recrystallize very readily
	(d)	Nitric acid (1.40) Water (distilled)	20 ml 80 ml	Immerse 5-10 min. Grain contrast, laminations, welds. Up to 50% nitric acid can be used
	(e)	Glacial acetic acid Nitric acid (1.40) Glycerol	20 ml 20 ml 80 ml	Macrostructure of alloy with Ca, Sb and Sri. Use fresh only. Several minutes needed
	(f)	Glacial acetic acid Nitric acid (1.40) Hydrogen peroxide (30%) Water (distilled)	20 ml 20 ml 20 ml 50 ml	2-10s by swabbing. Good for alloys with Bi, Te or Ni
E. Magnesium base	(a)	Picric acid (64%) saturated in ethanol (96%) Glacial acetic acid Distilled water	50 ml 20 ml 20 ml	Grain size. Flow lines in forging (wash precipitate in hot water). Etch for up to 3 min
	(b)	Ammonium persulphate Distilled water	2 ml 98 ml	Flow lines in forgings
	(c)	Nitric acid (1.40) Water Glacial acetic acid Water	20 ml 80 ml 10 ml 90 ml	Internal defects in casts. Useful for Mg-Mn and Mg-Zr. Etch for up to 3 min General defects; flow lines, segregation. Etch for up to 3 min
F. Nickel base	(a)	Nitric acid (1.40) Acetic acid	50 ml 50 ml	Welds, Ni-Cr-Fe alloys
	(b)	Aqua regia Nitric acid (1.19) Hydrochloric acid (1.19)	25 ml 75 ml	As (a) <i>See also</i> ref. 1. p. 10.69
G. Tin base	(a)	Sat. soln of ammonium polysulphide in water (wipe off surface film)		Grain structure; suitable most tin alloys (etching time 20-30 min)
	(b)	FeCl Hydrochloric acid (1.18) Water	10 g 2 ml 100 ml	Sn-Sb alloys (up to 3 min)
H. Zinc base Zinc and zinc alloys Zinc-rich alloys	(a)	Concentrated hydrochloric acid (1.19)		Good grain contrast
	(b)	5% hydrochloric acid in alcohol		HCl can be increased to 50 % Wash under running water to remove reaction product
	(c)	Sodium sulphate (3.5 g if hydrated) Chromium trioxide Water	1.5 g 20 g 100 ml	Better than above for Zn-Cu alloys
I. Other metals Many of these require etching in aggressive solutions comprising various mixtures of HCl, HNO <sub>3</sub> and HF.  Nitric acid/HF etches: These do not appear to be very sensitive to composition. HF should be 5-10%. Heating to 60-80°C will accelerate etching, e.g. for Ti. Aqueous HCl HNO <sub>3</sub> etches. The reactivity can be reduced by adding water. Acidified hydrogen peroxide etch  Nitric acid in alcohol	(a)	Hydrochloric acid (1.18) Nitric acid (1.40) Hydrofluoric acid (40%)	50 ml 20 ml 30 ml	Platinum metals group, especially. Ru, Os, Rh
	(b)	Hydrochloric acid (1.19) Nitric acid (1.40) Hydrofluoric acid (40%)	30 ml 15 ml 30 ml	Cr, Mo, W, V, Nb, Ta
	(c)	Nitric acid (1.40) Hydrofluoric acid (40%) Water	30-45 ml 10 ml 60-45 ml	Highly alloyed Ti, Hf, Zr; also Cr, W, Mo, V
	(d)	Hydrochloric acid (1.19) Nitric acid (1.40)	66 ml 34 ml	Gold, platinum, palladium. Used for cobalt alloy if added to 34 ml water
	(e)	Hydrofluoric acid Hydrogen peroxide (30%) Water	10 ml 45-60 ml 45-30 ml	Dilute Ti, Hf, and Zr alloys
	(f)	Nitric acid (1.40)	10 ml	Silver. ( <i>Note:</i> for safety methanol must be used. It

\*Acids are concentrated, unless otherwise indicated, e.g. with specific gravity.

		<i>Methanol</i>	90 ml	is dangerous to add more than 5% nitric acid to ethanol)
Hydrochloric acid etches	(g)	Hydrochloric acid (1.19)	10ml	Be and its alloys, especially for large grain sizes
		Water	90ml	
		Ammonium chloride	4 g or 2 g	
		Picric acid	2 g	
	(h)	Hydrochloric acid (1.19)	50ml	Cobalt alloys
		Water 60-80°C for 30-60 min	50 ml	

\* Acids are concentrated, unless otherwise indicated, e.g., with specific gravity.

The most frequent problems are: failure to completely remove the distorted metal produced at the original cut surface; alteration of the structure by overheating the specimen; contamination of the succeeding steps by carrying abrasives over, due to poor cleaning practices, from a coarse stage of polishing, to a finer one; and, the development of false structures by staining through faulty drying after etching or bleed out from shrinkage gaps between specimen and mounting material. Preparation of an unfamiliar material should be guided by checking the progress of the grinding and polishing steps during the preparation sequence to determine if the scratches from the previous step have been removed and to detect any problems, such as pull out, drag, embedding, and so forth. After the preparation has been completed through to about a 1- $\mu$ m abrasive size, the specimen can be etched (or examined with polarized light if it is an optically anisotropic metal) to examine the development of the structure. This will aid the metallographer in determining if the preparation sequence has been adequate. Hard metals and ceramics or sintered carbides can often be adequately examined after preparing down to only a 1- $\mu$ m finish, although going to a finer abrasive size will yield improved results.

Many metals and alloys can be prepared with essentially the same procedure with more than adequate results. However, there are many metals and alloys, and nonmetallic materials, that do require quite different preparation approaches. These will be described in the text where appropriate. Etching, however, is quite specific to the metal under examination and the feature of the structure to be investigated. There are no truly universal etchants, although a few have wide applicability. However, because of the specific corrosion aspects of different metals and alloys, it is unlikely that any universal etch would produce optimal results for more than a very limited range of compositions.

## MOUNTING

Specimens of irregular shape, or are fragile or small in size are best encapsulated or “mounted” in polymeric materials. Several specimens, if of similar materials, may be prepared in the same mount, with a saving of time, although etching may become a problem. In general, it is best to prepare as small a specimen as feasible, for example a 1-cm square area is ideal. With the introduction of automated equipment, specimen sizes have gradually become larger due to the ease of preparation compared to manual preparation. To obtain flatness out to the extreme edge, e.g., for examination of platings, coatings and other surface treatments, mounting is required. The preparation process can be optimized for obtaining good edge retention (“edge preservation”). Compression mounting resins, particularly thermosetting resins, yield best results. A modern press that cools the specimen automatically to near ambient temperature after polymerization has been completed, yields much better results than the former “hot ejection” method because shrinkage gaps are reduced. If a shrinkage gap is formed between specimen and mounting compound, a “free edge” exists and it will become beveled by abrasives getting into the gap. This is one reason why a protective plating, such as electroless nickel, is effective in

providing good edge retention. Modern automated polishing devices yield better edge retention than manual polishing. Rigid grinding disks used with coarse diamond abrasives and hard, woven, napless clothes for the subsequent polishing steps, yield much better flatness than the older clothes, such as canvas, felt or billiard cloth.

Modern mounting presses have the heating elements and cooling channels built in so that one no longer needs to remove the heating element from around the mold cylinder after the polymerization cycle has been completed (thermosetting resin) or after the resin melts (thermoplastic resin) and place copper chill blocks around the cylinder, required for a thermoplastic resin, for cooling the polymer to below 70 °C under pressure. These presses were introduced in the mid 1970's, chiefly to facilitate molding of thermoplastic resins. It was not until the 1990's that metallographers realized that cooling a thermosetting mount, already polymerized, towards ambient temperature under pressure helped reduce shrinkage gap formation which greatly improved edge retention.

To mount a specimen, the specimen is placed on the lower ram which is lowered into the cylinder about an inch (25 mm). The desired powdered resin (see Table 10.2) is added to a depth of at least 1 - 1.5 inches (25 - 37 mm). The ram is lowered all the way to the bottom and the top ram is placed into the cylinder hole and pushed downward and locked in place. The press is then turned on. Modern presses recognize the mold size (1, 1.25, 1.5 or 2 inches, or 25, 30, 40 or 50 mm in diameter) and are set to the required pressure and temperature for either thermosetting or thermoplastic resins. Further, many can be set to have a pre-heat cycle where the temperature is brought up to the set point without applied pressure. This is helpful for more delicate specimens that might be folded over or bent by the initial application of pressure. The cooling cycle is controlled by either setting a cooling time, or a desired final temperature. Upon reaching this temperature, the cooling will be stopped, a bell rings, and the press is turned off automatically.

*It is essential to verify that the structure of the metal will not be materially affected by any heat and pressure applied in forming the mount.* In cases where the temperature of molding, typically about 150 °C, cannot be tolerated (e.g., low-melting point metals and alloys, alloys where aging will occur, etc.), the so called "cold" mounting resins are used. It must be pointed out that obtaining a very low exotherm (from the heat of polymerization) is not automatic when using these resins. Acrylic resins are widely used because they are very inexpensive and they cure very quickly, usually in 5 – 8 minutes. However, they can generate considerable heat during polymerization, enough to burn your hand. Polyester materials are not utilized much in metallography. Cast epoxy resins are quite popular due to several characteristics, although they are relatively expensive and do have a shelf life of about a year. The shelf life can be improved by storing resin and hardener in a refrigerator (but do not freeze the resin or hardener). It is best to buy only a quantity that you expect to use in about six months. The epoxy resin and hardener are mixed, usually on a weight basis (more accurate than by volume), stirred gently for about a minute, then poured into a mold in which the specimen resides face down. Molds can be made of plastic, phenolic ring forms, silicone rubber, glass or metal. The phenolic ring forms are usually allowed to adhere to the polymer, while the others are coated with a mold release agent and removed after the mount cures. Low viscosity epoxy can be drawn into cracks and voids in specimens under vacuum. This greatly facilitates specimen preparation as the voids are supported by the epoxy and liquids cannot enter the openings and bleed out later.

Some plastics used for encapsulation, and their characteristics, are listed in Table 10.2.

Table 10.2 PLASTIC USED FOR MOUNTING

<i>Plastics</i>	<i>Type</i>	<i>Remarks</i>
Phenolic	Thermosetting	Needs controlled heat and pressure. Sufficiently inert to most solvents. Normal grades good for general-work but have high shrinkage; mineral-filled type preferable for edge-sections. If curing insufficient, e.g., too low a temperature, the mount is soft and is attacked by acetone. Badly degraded by high temperature etchants. Least expensive thermosetting resin.
Epoxy resin	Thermosetting	Cures under heat and pressure yielding excellent mounts with superior edge retention and resistance to solvents and boiling reagents. Good polishing characteristics, low shrinkage.
Methyl methacrylate	Thermoplastic*	Needs controlled heat and pressure. Gives clear mount. Attacked by acetone. Rather soft
Acrylic resins	“Cold setting”	Mix resin and hardener; cures very quickly (<10 min.). Cheap but poor edge retention.
Polyester	“Cold” setting	Several ingredients to be mixed for each batch. Not used commonly today. Inert to usual solvents.
Epoxy resins	“Cold” setting	Liquid resin and hardener are mixed; gives good mounts without heat or pressure. Inert to usual solvents, although the surface can become sticky in alcohol.
Diallyl phthalate	Thermosetting	Needs controlled heat (130-140°C) and pressure. Low shrinkage good polishing characteristics <sup>3</sup> Expensive resin, provides only marginal improvement over phenolics.

\* Must be cooled under pressure to low temperature to solidify before ejection.

Thermoplastics, such as methyl methacrylate, and thermosetting resins, such as phenolic, are convenient for routine work because they are available as powders immediately ready for use, but they require a press, and normally only one size of cylindrical mold may be available. On some presses, it is rather simple to change molds, while on others it may take more time and effort. Cold-setting resins may be formed simply in a container consisting of a short piece of tube standing on a glass plate, and are therefore suitable for occasional use and odd shapes and sizes.

To examine a surface edge on a cross section, use the best mounting compound (thermosetting epoxy containing a filler, e. g., Epomet® resin). The edge can be protected by plating (e.g., with copper or electroless nickel) or, if that is not possible, by applying an evaporated coating before mounting. Mount specimens with a press that incorporates water cooling after the polymerization cycle to minimize or eliminate shrinkage gaps between specimen and mount. If a “cold” mounting compound must be used, use epoxy, never an acrylic or a polyester. Use a slow curing epoxy, rather than a fast curing epoxy. Soft (about 750-800 HV) ceramic shot (“Flat-Edge Filler” shot) can be added to the epoxy at the polishing face to reduce shrinkage and help support the edge. Hard ceramic shot, such as made from alumina, is incompatible in grinding and polishing characteristics with metals and should be avoided. Use automated grinding/polishing equipment with central force loading, use “hard” napless cloths or pads or rigid grinding disks (usually with coarse diamond abrasive sizes), and use proper loads and times. Do not use napped cloths, especially with diamond abrasive, except in the final step with a very fine abrasive.

Conductive mounting resins have also been developed to simplify electrolytic polishing and etching and for SEM or EMPA work. Copper-filled resins have been used for some time, although they are rather expensive. Probemet™ conductive resin consists of very fine thermosetting epoxy with a silica filler mixed about equally with very fine copper flake. Flake shaped particles are better for conductivity than spherical particles. This resin, besides exhibiting zero resistance between specimen and mount, also yields excellent edge retention. Carbon-filled phenolic resins provide a lower-cost alternative, but are not as conductive and do not provide as good edge retention. Conductive nickel flake can be added to cast resins, such as epoxy, for conductivity.



## GRINDING

Silicon carbide abrasive bonded to waterproof paper is commonly used for grinding. Silicon carbide paper is preferred over emery paper because SiC is harder, has sharper particles and cuts at a faster rate. The simplest technique, generally used only by students, employs rolled strips about 50 mm wide where a portion is unrolled and laid flat on a hard, tilted surface and held mechanically along the edges. Water is run onto the top end of the paper to wet the surface. The specimen is rubbed up and down on the paper strip. Simple devices exist to hold four or five rolls of graded paper, for example, 120, 240, 320, 400 and 600 grit sizes. Usually, grinding begins with the coarsest grit, and the specimen is rubbed until all traces from cutting are removed. Then, turn the specimen 45 - 90° and rub the specimen with the next finer grit until the first set of scratches are removed. Repeat at least once, because the depth of the deformed layer is several times the depth of the residual scratches. Then, progress to the next finer paper or cloth, turning the specimen through 45 - 90°, and again rub until the previous scratches are removed, then to the next finer paper similarly, until grade 600 silicon carbide paper is reached. Some soft metals are prone to embedding problems, that is, the finer SiC particle sizes will break off the paper and become embedded in the alloy surface. This is a particular problem with the low melting point alloys of lead, tin, bismuth and cadmium. To counter this tendency, wax can be rubbed onto the paper surface before grinding. Candle wax appears to be better for embedding prevention than bees wax.

A more suitable grinding practice is to use round SiC paper disks attached to a platen, usually made from aluminum. Copper-based alloys have been used in the past, but they are more expensive and are unsuitable when attack polishing agents are used in the polishing stage. The disks can be applied to the platen using a pressure-sensitive adhesive (psa) backing. This is an excellent practice as the disk will not move under the applied force during grinding. The other main alternative is to use plain-backed SiC paper disks. Water is placed on the platen surface. The disk is placed over the wet platen and a hold down ring is placed around the periphery of the platen. The motor-driven platen is turned on and set to 240-300 rpm, in most cases. When the specimen is forced against the SiC disk, the disk stalls for a few seconds until suction builds up and holds the disk against the platen. This method is satisfactory for manual polishing but has some disadvantages in automated polishing. With an automated specimen holder, the holder must be positioned over the platen so that its periphery does not strike the hold down ring. This restricts grinding out to the edge and prevents the user from setting up the head position so that it cannot sweep slightly over the edge of the SiC paper on the platen. This type of hold down system generally eliminates use of smaller diameter platen formats, e.g., an 8-inch (200-mm) diameter platen system cannot be effectively used as the holder must be made smaller than 4-inch (100-mm) diameter, so that grinding and polishing can be performed inside the hold down ring without crossing the center of the platen (when that happens, differential grinding and polishing results and specimens are not flat). If the holder must be <4-inch (100-mm) in diameter, it cannot hold many specimens and the specimen diameters must be quite small. Thus, the metallographer must choose a larger diameter platen system where the cost of consumables is higher.

For very hard metals, sintered carbides and ceramics diamond hones<sup>4</sup> and laps<sup>106</sup> have been used for grinding, although today different products are more common. The original metal-bonded diamond disks used a metal plate over which diamond of a specific size was spread and was held in place with electroless nickel. While these disks would provide effective cutting, they could not be used manually as the surface tension between specimen and disk was so great that

the specimen could not be hand held. These disks were largely unsuitable for metals, except the very hardest, but they worked adequately for sintered carbides and ceramics. Lapping disks became popular for a period and they work well as long as the surface remains flat. Their use requires a careful adjustment of the specimen holder so that the entire lap surface is in contact with the specimens. In the majority of cases, diamond slurries or suspensions were used. Procedures using one or two “lapping” stages were developed. It must be stated that these lapping platens were not actually lapping in the true sense of the word. Lapping implies that the abrasive is free to roll between the lap surface and the sample surface. But, with these laps, the abrasive would become embedded in the lap surface soon after being sprayed onto the platen. Hence, cutting resulted rather than true lapping (lapped surfaces appear to be “hammered” by the abrasive, that is, the surface is made flat and specular more by deformation than by cutting, and this is not desired as the true microstructure will not be observed).

In recent years, the rigid grinding disk (RGD) has been introduced. These are basically quite similar to the former laps that were popular from about 1975-1990, except that they are thinner and some extra relief has been introduced to reduce surface tension. The RGD costs less to produce and, because it is thin, usually wears out before it becomes too non-planar to use. One disk style incorporates round spots of epoxy containing fine particles of Fe and Cu with a fair amount of the disk surface not covered by the spots. This reduces the surface tension (specimens can be easily held manually using this disk) while actually providing a higher removal rate than a similar disk with greater surface coverage. Such a disk is used for rough polishing with diamond abrasive and sizes from 45- to 3- $\mu\text{m}$  have been used on specimens with a hardness of about 150 HV or higher. Although sheet metal specimens softer than this have been successfully prepared using a RGD in the practice, and their hardness is well below 150 HV, some deformation may persist when somewhat harder

solution annealed stainless steel or nickel-based superalloys are prepared. While titanium alloys can be prepared with such a disk, commercial purity titanium cannot, unless extra steps are taken to remove the damage. Consequently, a second disk was developed using a different epoxy and the filler is fine particles of tin, much softer than Fe and Cu. This disk is less aggressive than the previous disk and can prepare softer metals, but is still useful for very hard metals, sintered carbides and ceramics. The RGD can be used to replace the rough grinding step with SiC, or after the initial grinding step with SiC abrasive, or for the first and second steps. Specimens prepared using RGDs in one or more steps are noted for exceptional flatness and edge retention. However, the scratch pattern produced using diamond of a specific size with a RGD is more pronounced than when the same diamond is used on a hard, woven cloth or a chemotextile pad. The latter are less aggressive in removal rate than the RGD.

There are other alternatives to grinding with SiC papers. Alumina abrasive can be obtained on waterproof backings, such as paper or mylar. Alumina is a better abrasive for Fe-based metals than SiC, but these papers are less readily available and more expensive. Alumina is slightly softer than SiC (about 2000 vs 2200 HV, respectively), but is more than hard enough to grind any steel. Alumina is also tougher and less prone to embed in soft metals, such as Pb, Sn, Bi or Cd.

## MECHANICAL POLISHING

Mechanical polishing is often done in two stages, with coarse and fine abrasives (one or more of each may be used). The division between coarse and fine is somewhat arbitrary, but is usually at 3- $\mu$ m. The coarse polishing stage is carried out at 150 rpm, or less, and uses a napless cloth such as selected silk, nylon, polyester or a synthetic chemotextile pad. Napped cloths should not be used, except in the final step, as they promote poor edge retention, relief at constituents and problems such as pull-out or drag and smearing. Napped cloths, such as canvas, felt, synthetic suedes and others, were used with coarse and fine diamond abrasives for both rough and fine polishing, but in more recent years they have been shown to be poor for all but the final step. In coarse polishing, the cloth is charged with an abrasive, chiefly diamond (except for those metals where diamond is not very effective). The writer prefers to charge a cloth with diamond paste first. The amount added must be sufficient to obtain good cutting; many people add far too little diamond. Turn the platen on (with the cloth attached using a psa backing, not stretched, as it will be easily ripped using an automated specimen holder) to a speed of 120-150 rpm. Hold the diamond syringe against the center of the cloth and press on the applicator to squeeze diamond paste out of the tube onto the center of the cloth. Then, while pressing on the syringe, pull the tip towards the periphery of the cloth, while "laying" a concentric track of diamond paste. Turn off the platen. Take the tip of your index finger (which must be clean) and spread the diamond over the cloth surface. Then, squirt on some of the lubricant, that is compatible with the diamond carrier paste, and start polishing. This gets the cutting action started quickly. If, on the other hand, a fresh cloth is charged with a liquid diamond slurry or suspension of the same particle size, the cutting rate will be much lower until the diamond particles become embedded in the cloth and start cutting. If the polishing step is more than a minute or two, add some slurry or suspension to the cloth periodically during the cycle to keep the cutting rate high. The cloth must be kept moist during polishing. If a slurry or suspension is not added during the cycle (these have the lubricant built in), then the lubricant must be added periodically. If the cloth gets too

dry, smear, drag and pull-outs may result. If it gets too wet, the cutting rate can drop due to hydroplaning effects, but this does not damage the structure.

Fine polishing is carried out with abrasives smaller than 3- $\mu\text{m}$  in diameter and includes diamond, alumina and amorphous colloidal silica, plus some proprietary blends. MgO, formerly used to final polish Al and Mg alloys is rarely used today as it is very difficult to use. MgO is usually available only down to a 1- $\mu\text{m}$  size and getting really good quality MgO for polishing is difficult. Further, magnesium carbonates will form in the cloth after use, which ruins the cloth, unless the cloth is soaked in a dilute HCl solution, which is quite inconvenient. Iron oxides and chromium oxides have been used occasionally in metallography, but they have little overall value. Cerium oxide has been used to polish glass but has little value with metals. Polishing is conducted at a lower rotational speed (80-150 rpm) than for grinding using medium- or low-nap cloths, such as synthetic suedes bonded to a waterproof backing, or with napless polyurethane pads. The polishing agent should have a cutting action but it may produce a 'flowed' layer on the surface or both. The writer has made Laue patterns of coarse grained specimens and seen the sharpness of the diffraction spots decrease after final polishing with alumina slurries, indicating that some smearing is occurring. Because of this, it is common practice to etch the specimen after final polishing. If the final step is repeated, the re-etched structure will appear to be sharper and crisper in detail due to removal of the smeared metal. As an alternative, the specimen can be given a final polish using a vibratory polisher with the same cloth and abrasive as used for the final step. As little as 20 minutes is required with this device. Vibratory polishing is noted for producing excellent, deformation-free surfaces without sacrificing edge retention and relief control. However, if carried out too long, relief will be observed.

Some metals or coatings are readily stained or corroded in the presence of water, and for these a non-aqueous polishing mixture is preferred. Diamond abrasives suspended in oil are available and are effective, but cleaning is more difficult. Oil-based diamond is very effective as the oil is a fine lubricant. Final polishing can be performed with alumina powder suspended in alcohol, purified kerosene or mineral spirits. Again, cleaning is more difficult than with water-based products. A few proprietary abrasive suspensions are available that have a low water content and appear to work satisfactorily with magnesium alloys where water-based products are best avoided, at least in the final step. Galvanized steel and cadmium-plated steels cannot be final polished with aqueous suspensions. If they are, the coating is heavily attacked. Non-aqueous abrasives must be used in the final step, perhaps with some loss of fine scratch control. Some specimens are prone to staining around inclusions, such as sulfides. In this case, the use of distilled water, rather than tap water, helps to avoid staining. Also, water temperature may be important. Hot water is more reactive than cooler water.

Colloidal silica containing amorphous, spherical silica particles in a basic suspension (pH of 9.5 to 10, usually), has become a very popular final polishing abrasive and has replaced MgO as the final polish for aluminum and its alloys. Because the particles are nearly spherical, its action is more chemical than mechanical and measurements of its removal rate reveal very low values. However, it does often produce the best final polished surfaces. Its use is not without problems. If the cloth is allowed to dry out, the silica becomes crystalline and the cloth is ruined. So, after use, the cloth must be cleaned carefully. Also, specimen surfaces can be more difficult to clean as the colloid contains ions, such as sodium ions. A whitish smut may be seen on the surface when the specimen is not cleaned carefully. This will make etching a disaster. To counter these problems, when using an automated system, stop adding colloidal silica with about 20 s left in

the polishing step. With 10 s left, direct the water jet onto the platen surface. This will wash off the cloth and clean the specimen simultaneously. Then, the specimens can be rinsed under running water, wet with ethanol, and blow dried under warm air without retaining the surface smut. A similar approach can be used for manual work.

Metallographers may notice that etch response can be different when using colloidal silica. This can be good or bad. Color etchants used with Cu-based alloys generally show softer, more pastel-like colors after using colloidal silica and more gaudy, harsher colors after using standard alumina suspensions. Experiments with specimens such as Fe-Ni alloys reveals a change in etch nature with repeated use of colloidal silica. For example, an Fe-36% Ni specimen was prepared and etched with Marble's reagent after final polishing with colloidal silica. The specimen exhibited a grain-contrast etch appearance, that is, light and dark grain and twin areas. With repeated final polishing steps and re-etching, the grain contrast appearance changed to a flat, grain boundary/twin boundary etch. This switch has been observed with other metals. Detrimental effects of colloidal silica can be obtained using austenitic stainless steels or duplex stainless steels. After final polishing, etchants such as glyceresia or Vilella's may be used and the etch response is general rather slow. However, sometimes after final polishing with colloidal silica, etching is extremely rapid. As soon as the cotton swab touches the surface, it darkens. This effect is called "flashing" by metallographers. Examination of the surface reveals a heavily crazed scratch pattern and the scratches are far too deep to remove with the final polishing agent. Instead, the specimen must be completely reprepared. This appears to be due to surface passivation, probably by the ions in the colloidal silica adhering to the polished stainless steel surface. Flashing never occurs when electrolytic etching is performed. A properly electrolytically etched surface can then be etched with glyceresia or Kalling's No. 2 reagent, for example, and it may flash. Flashing appears to be most common in etchants that contain  $\text{Cl}^-$  ions and careful cleaning appears to reduce its occurrence. To prevent this problem, the writer uses a two-step final polishing procedure. The timer is set for 3 minutes. Polishing begins with colloidal silica. After about 90 s, direct the water jet onto the cloth and flush off most of the colloidal silica, then add alumina. I used a special 0.05- $\mu\text{m}$  alumina suspension made by the sol-gel process called Masterprep™ alumina. Unlike calcined aluminas, it is totally free of agglomerates. Polishing continues until about 10 s remain. At this point, direct the water jet onto the cloth and wash both the cloth and the specimens before the platen stops. Then, etching can be conducted without flashing and the benefits of both polishing agents are obtained.

Over the years a generic preparation practice was developed that is commonly called the "traditional method" today. It consists of the following steps and can be performed manually or with automated grinder/polisher units:

#### The "Traditional Method"

1. Grind with waterproof SiC abrasive paper starting with 120-grit (P120) paper, water cooled, 240-300 rpm, 6 lb (25 or 30 N) pressure/specimen until the cutting damage is removed and all specimens in the holder are at the same plane.
2. Grind with 220- or 240-grit (P240 or P280) SiC paper, as in step 1, for 1 minute.
3. Grind with 320-grit (P400) SiC paper, as in step 2.
4. Grind with 400-grit (P600) SiC paper, as in step 2.

5. Grind with 600-grit (P1200) SiC paper, as in step 2.
6. Rough polish with 6- $\mu\text{m}$  diamond paste on canvas, 150 rpm, 6 lb (25 or 30 N) per specimen, for 2 minutes. Use complementary motion with an automated device but contra rotation with manual work. Some people used 3- $\mu\text{m}$  diamond rather than 6, and some used nylon cloths.
7. Fine polish with 1- $\mu\text{m}$  diamond paste on felt or billiard cloth, as in step 6. This step was not used by all metallographers.
8. Fine polish with 0.3- $\mu\text{m}$  alpha-alumina aqueous slurry on a synthetic suede cloth at 150 rpm, 6 lbs (25 or 30 N) load per specimen, for 2 minutes. Head/platen directions as in step 6. This was often an optional step if 7 was used.
9. Fine polish with 0.05- $\mu\text{m}$  gamma-alumina aqueous slurry, as in step 8.

In this method, complementary means that the head and platen are both rotating in the counterclockwise direction while contra means that the head and platen rotate in opposite directions. Complementary rotation cannot be done manually. This method works reasonably well for many materials, but not all. It is slow because of the many steps. It is not adequate for edge retention and may lead to excessive relief. As a result, “contemporary” preparation methods are largely replacing the traditional method, because they are more efficient and yield better control of flatness.

The following is a generic example of a contemporary preparation practice. It requires use of a good laboratory sectioning machine with the proper wheel to minimize cutting damage.

#### The “Contemporary Preparation Method”

1. Grind with waterproof SiC paper as fine as possible, usually 180- 220- or 240- or 320-grit (P180, P240 or P280, or P400), at 240-300 rpm, 6 lbs (25 or 30 N) load per specimen, with water cooling, until the cutting damage is removed and the specimens are at the same plane.
2. Rough polish with 9- $\mu\text{m}$  polycrystalline diamond on a psa-backed selected silk cloth (e.g., an Ultra-Pol™ cloth), at 150 rpm, 6 lbs (25 or 30 N) per specimen, complementary or contra rotation, for 5 min.
3. Rough polish with 3- $\mu\text{m}$  polycrystalline diamond on a psa-backed chemotextile pad (e.g., a Texmet® 1000 pad), as in step 2, but 4 min.
4. Fine polish with 1- $\mu\text{m}$  polycrystalline diamond on a psa-backed polyester woven cloth (e.g., a Trident™ cloth), as in step 2, but 3 min. This is often an optional sstep but is used for more difficult specimens.
5. Fine polish with 0.05- $\mu\text{m}$  colloidal silica or sol-gel alumina (Masterprep™ alumina) slurries, on a synthetic suede (rayon) cloth (e.g., a Microcloth® pad) or a polyurethane pad (e.g., a Chemomet® pad), as in step 2, but for 2-3 min. Contra rotation is preferred for this step (see note in the next paragraph about head speed).

Choice of the final polishing solution in step 5 is often a matter of personal preference, although there are some materials that are not prepared properly with colloidal silica (Mg alloys tend to be etched, precious metals are not affected, even if an attack polish agent is added; pearlitic cast irons often have small etch spots; and, austenitic stainless steels and Ni-base superalloys may “flash” when etched, as discussed above). Contra rotation should not be used when the head speed is > 100 rpm, as the abrasive will be thrown off the wheel and will hit the operator and walls. If the head speed is 60 rpm or less, the abrasive stays nicely on the work surface. Contra is slightly more aggressive than complementary.

Variations can be made to the contemporary method in each step depending upon personal preferences and what is available for use. Several alternatives, mentioned above, exist for the first step using SiC. Rigid grinding disks can be substituted for either step one or two. For some materials, we can use as little as three steps with excellent results. These modifications are discussed when dealing with the individual metals and alloys.

*After polishing* by any method, the specimen must be thoroughly washed and dried. It is best to etch immediately after polishing, particularly for those metals and alloys that form a tight oxide on the surface with air exposure, for example, Al, Cr, Nb, Ni, stainless steels, Ti and precious metals. After the specimen is washed under running water, it may be necessary to scrub the surface carefully with cotton soaked in a soapy solution. A mild dish washing detergent can often be used, or a proprietary detergent such as liquidalconox. Then, wash again with clean running water, rinse with ethanol to displace the water, and dry with a blast of hot air. If the etch contains HF, it is best to rinse the surface in a neutralizing bath to remove any adherent HF that might damage the microscope optics (see ASTM E 407).

*Attack polishing* is a method of improving polishing action by the addition of a dilute etching agent to the abrasive suspension. For instance, ammonia may be used with advantage on the pad in polishing copper alloys. Hydrogen peroxide (30% conc.) is useful for refractory metals and precious metals to improve metal removal. Not only is the damaged layer at the surface removed more effectively, but also scratch control in these metals is enhanced over final polishing with the same abrasive without the added chemical attack. Table 10.3 gives reagents for use with various metals by this method. Several solutions have also been proposed for magnesium alloys.<sup>7</sup> Attack polishing is often performed using polyurethane pads or with synthetic suede cloths (the latter do not hold up as well, however).

Table 10.3 ATTACK POLISHING CONDITIONS FOR VARIOUS METALS AND ALLOYS

Material	Solution*		Time (min)	Remarks
Uranium	CrO <sub>3</sub> H <sub>2</sub> O HNO <sub>3</sub> (1.40)	50 g 100 ml 10 ml	20-30	Medium contrast . under polarized light, no pitting, good resistance to oxidation
Zirconium	HNO <sub>3</sub> (1.40) Glycerol	50 ml 150 ml	1-10	Good contrast under polarized light. Slight grain relief
Bismuth	HNO <sub>3</sub> (1.40) Glycerol	50 ml 150 ml	3-5	Good contrast under polarized light. Requires less pressure than usual
Chromium	(COOH) <sub>2</sub> H <sub>2</sub> O	15 g 150 cm	5-10	Bright polish revealing oxides, etc.

Molybdenum and tungsten	Pot. Ferricyanide	3.5 g
	Sodium hydroxide	1 g
	Water	300 ml

\* Acids are concentrated, unless otherwise indicated, eg. with specific gravity.

## ELECTROLYTIC POLISHING

Extensive reviews have been given by Jacquet,<sup>8</sup> Tegart,<sup>9</sup> Petzow<sup>1</sup> and Vander Voort<sup>152</sup> which may be consulted for individual references (see also ASTM E 1558). A comparison with mechanical methods has been made by Samuels.<sup>10</sup>

The specimen is made with the anode in a suitable solution, and conditions are adjusted so that the hills on the surface are dissolved much more rapidly than the valleys. When enough metal has been removed a smooth surface is obtained. The condition for polishing often corresponds to a nearly flat (i.e., constant current) region in the curve for cell current versus voltage. As the voltage is increased (*see* Figure 10.1), etching (AB) is replaced by film formation (BC). The voltage then increases and the current falls slightly as the film disappears and polishing conditions are established (CD). At higher voltages, gas evolution occurs with pitting. Near E gas evolution is rapid and polishing continues but the region just below D is preferred. By reducing, the voltage to below B, the specimen can be etched in the same operation. For many specimens, electropolishing leads to a great saving in time, and it reliably produces surfaces free from strain provided sufficient metal is removed in the process. It tends to exaggerate porosity and is unsuitable for highly porous specimens. Inclusions are often removed, though not invariably, and their place taken by severe pits. Many two-phase and complex alloys, however, can be successfully polished.

**Figure 10.1** *Idealized relationship between current density and voltage in electropolishing cell.*

*Apparatus.* To cover the widest range of applications a d.c. supply of 4-5 A at voltages variable up to at least 60 V is required, but some solutions require only 2 V. Accurate voltage regulation is essential, and a rectifier set fed from a variac, a tapped battery or a potentiometer circuit across a constant d.c. source is recommended. Published recommendations for particular solutions sometimes state the voltage, and sometimes the current density, required. It is preferable to work on voltage, as the current density for a given electrode condition is much affected by temperature and other variables. If both are stated, but cannot be simultaneously obtained, the solution is probably wrong; if it is not, the current density should be disregarded. Two general cell arrangements are used: with electrodes in a beaker of still or gently stirred solution and with flowing or pumped electrolyte.<sup>11-13</sup> The first arrangement is easily set up and often suffices; the second is more powerful but requires more complicated apparatus (obtainable commercially, however). The characteristics are quite different: with flowing electrolyte a good polish may be obtained with more strongly conducting solutions, and hence with higher current densities, and it is therefore frequently possible to remove more metal in polishing and to start with a more roughly prepared surface. A small area of an article may be electropolished by the use of electrolyte flowing from a vertical jet above the article, the jet itself containing a projecting wire to act as cathode.<sup>13</sup> In suitable conditions, polishing of an area already ground with SiC paper may be completed in 3-10 s. Apparatus for this method is also available commercially.



Jacquet has described a device (the ‘Ellapol’) in which an electrolyte is applied to the surface by a small swab surrounding the cathode. The device can conveniently be used to polish a small area of a large component *in situ* (see e.g., refs. 14-16).

*Solutions* for electropolishing particular metals are listed in Table 10.4 (see also refs. 1, 8, 9 and 152 and ASTM E 1558). Table 10.4 is not a complete list, but should cover most requirements. Minor differences between solutions are often a consequence of the cell used. The most widely useful solutions are methyl alcohol-nitric acid mixtures, strong solutions of phosphoric acid and mixtures of perchloric acid with alcohol, acetic acid or acetic anhydride. Mixtures of perchloric acid with acetic anhydride, although frequently the best polishing agents, can be explosive and should be avoided. Electrolytes containing perchloric acid must be kept cold in use; plastics (especially cellulose) and bismuth must be kept away from them, as they may cause explosions, and they must not be stored in the laboratory as they are liable to explode without apparent reason. The explosion of a few hundred millilitres is not likely

**Figure 10.2** Characteristics of perchloric acid/acetic anhydride/water solutions (after Jacquet<sup>8,17</sup>).

to do great physical damage, but larger quantities should not be used. The limits of the dangerous mixtures, according to Jacquet, the originator,<sup>8,17</sup> are indicated in Figure 10.2. Perchloric acid must always be added to the acetic anhydride-water mixture to avoid compositions in the detonation zone. Explosions outside the danger zone in this diagram have occurred. Consequently, the use of perchloric acid-acetic anhydride based electrolytes should be avoided (their use is forbidden by law in some locations). Safe operating practices in the metallography laboratory is a complex subject. In general, the metallography laboratory is a reasonably safe place, but problems can occur, particularly in “open” laboratories and at schools, where the personnel may not be as well versed in safe operating practices. It is impossible to list all possible safety issues in any text, as no one can envision all of the potential mis-uses that humans can create. Each laboratory must develop a comprehensive safety program based upon the materials that they use, their equipment, and their particular circumstances. The basic aspects of safe metallographic practices are given in references 152, 160, 161 and ASTM E 2014.

**Table 10.4a ELECTROLYTIC POLISHING SOLUTIONS FOR VARIOUS METALS AND ALLOYS**

Because of the considerable number of solutions published in the literature, a selection has been made on the basis of (a) wide usage, (b) simplicity of composition, and (c) least danger. Temperatures should be in the range 15-35°C (or below). Cooling should be used to avoid temperatures above 35°C unless stated otherwise.

Composition of solution			Usage	Cell Voltage	Time	Cathode
1	Ethanol	800 ml	Al alloys (not Al-Si)	30-80	15-60 s	Stainless steel
	Distilled water	14 ml	Most steels	35-65	15-60 s	Stainless steel
	Perchloric acid (1.61)	60 ml	Lead alloys	10-35	15-60 s	Stainless steel
			Zinc alloys	20-60	15-60 s	Stainless steel
			Magnesium alloys	20-40	up to 2 min	Nickel
2	Ethanol	800 ml	Al alloys	35-80	15-60 s	Stainless steel
	Perchloric acid (1.61)	200 ml	Stainless steels	35-80	15-60 s	Stainless steel
			Pb alloys	15-35	15-60 s	Stainless steel

			Zn alloys and many other metals	20-60	15-60 s	Stainless steel
3	Ethanol	940ml	Stainless steel	30-45	15-60 s	Stainless steel
	Distilled water	6 ml	Thorium	30-40	15-60 s	Stainless steel
	Perchloric acid (1.61)	54 ml				

**Table 10.4(a) ELECTROLYTIC POLISHING SOLUTIONS FOR VARIOUS METALS AND ALLOYS--continued**

<i>Composition of solution</i>	<i>Usage</i>	<i>Cell voltage</i>	<i>Time</i>	<i>Cathode</i>	
4	Ethanol 700 ml Water 120 ml 2-Butoxyethanol 100 ml Perchloric acid (1.61) 80 ml Glycerol (100ml) can replace butoxyethanol	Al alloy Steel, cast iron Ni, Sn, Ag, Be Ti, Zr, U, Pb Complex steels and nickel alloy general use	} 30-65	15-60 s	Stainless steel
5	Ethanol 760 ml Distilled water 30 ml Ether 190 ml Perchloric acid (1.61) 20 ml	Al alloys including Al-Si alloys Fe-Si alloys Sb Preferred solution for Al alloys	} 30-60	15-60 s	Stainless steel
6	Methanol 590 ml Water (distilled) 6 ml 2-Butoxyethanol 350 ml Perchloric acid 54 ml	Germanium and silicon Titanium Vanadium Zirconium	25-35 ~60 ~30 ~70	30-60 s 45 s 3-5 s* 15 s	Stainless steel Stainless steel Stainless steel Stainless steel
7	Glacial acetic acid 940 ml Perchloric acid (1.61) 60 ml	Cr, Ti, U, Zr, Fe Cast iron, all steels, V Re and many other metals	} 20-60	up to 5 min	Stainless steel
8	Glacial acetic acid 900 ml Perchloric acid (1.61) 100 ml	Ti, Zr, U steels Superalloys	10-60	up to 2 min	Stainless steel
9	Glacial acetic acid 800 ml Perchloric acid (1.61) 200 ml	U, Ti, Zr, Al steels Superalloys	40-100	up to 15 min	Stainless steel
10	Glacial acetic acid 700 ml Perchloric acid (1.61) 300 ml	Nickel, Pb, especially Pb-Sb alloys	40-100	up to 5 min	Stainless steel

11	Phosphoric acid (1.75)		Cobalt, Fe-Si alloys	1-2	up to 5 min	Stainless steel
12	Distilled water Phosphoric acid (1.75)	300 ml 700 ml	Cu, Cu alloys (not Cu-Sn) Stainless steels – rinse in 20% H <sub>3</sub> PO <sub>4</sub>	1-1.6	10-40 min	Copper
13	Distilled water Phosphoric acid	600 ml 400 ml	Brasses, Cu-Fe, Cu-Co Co, Cd	1-2	up to 15 min	Copper or stainless steel
14	Distilled water Ethanol Phosphoric acid (1.75)	200 ml 400 ml 400 ml	Al, Mg, Ag	25-30 at 40°C	4-6 min	Aluminium
15	Ethanol Glycerol Phosphoric acid (1.75)	300 ml 300 ml 300 ml	U (preferred solution)	20-30	4-6 min	Aluminium
16	Ethanol Glycerol Phosphoric acid (1.75)	500 ml 250 ml 250 ml	Mn, Mn-Cu	18	up to 10 min	Stainless steel
17	Ethanol Phosphoric acid (1.75)	625 ml 375 ml	Mg, Zn alloy	1.5-2.5	up to 30 min	Stainless steel
18	Ethanol Ethylene glycol Phosphoric acid (1.75)	445 ml 275 ml 275 ml	U alloys	18-20	up to 15 min	Stainless steel
19	Distilled water Sulphuric acid (1.75)	750 ml 250 ml	Stainless steel } iron, nickel } Molybdenum }	1.5-6.0 1.5-6.0	up to 10 min 1 min	Stainless steel Stainless steel
20	Methanol Sulphuric acid (1.84)	875 ml 125 ml	Molybdenum	6-18	1 min Keep below 27°C	Stainless steel

\* With vanadium, give several 3-5 s bursts and avoid heating.

Table 10.4(a) ELECTROLYTIC POLISHING SOLUTIONS FOR VARIOUS METALS AND ALLOYS-continued

<i>Composition of solution</i>			<i>Usage</i>	<i>Cell voltage</i>	<i>Time</i>	<i>Cathode</i>
21	Distilled water Chromium trioxide	830 ml 170 g	Zn, Al bronze Brass	1.5-12	up to 1 min	Stainless steel
22	Distilled water Phosphoric acid (1.75) Sulphuric acid (1.84)	450 ml 390 ml 160 ml	Tin Tin bronzes (high tin) (rinse in 20% H <sub>3</sub> PO <sub>4</sub> )	2	up to 15 min	Copper
23	Distilled water Phosphoric acid (1.75) Sulphuric acid (1.84)	330 ml 580 ml 90 ml	Tin Tin bronzes (low tin < 6%) (rinse in 20% H <sub>3</sub> PO <sub>4</sub> )	2	up to 15 min	Copper
24	Distilled water Chromium trioxide Phosphoric acid (1.75) Sulphuric acid (1.84)	170 ml 105 g 460 ml 390 ml	Stainless steel (use at 35-40°C)	2	up to 60 min	Stainless steel
25	Distilled water Chromium trioxide Phosphoric acid (1.75) Sulphuric acid (1.84)	240 ml 80 g 650 ml 130 ml	Stainless steel Alloy steels (use at 40-50°C)	2	up to 60 min	Stainless steel
26	Hydrofluoric acid (40%) Sulphuric acid (1.84)	100 ml 900 ml	Tantalum Niobium (use at ~ 40°C)		5-15 min	Graphite
27	Glycerol Glacial acetic acid Nitric acid (1.40) <i>(Warning: This solution will decompose vigorous if kept, especially if cathode left in it. Throw away solution as soon at finished with)</i>	750 ml 125 ml 125 ml	Bismuth	12	1-5 min	Stainless steel

28	Methanol Hydrochloric acid (1.19) Sulphuric acid (1.84) Keep cool below 2°C. Avoid water contamination.	685 ml 225 ml 90 ml	Molybdenum	19-35	30 s	Stainless steel
29	Ethanol n-Butyl alcohol Hydrated aluminium trichloride Anhydrous Zn chloride	885 ml 100 ml 109 g 250 g	Ti and most other alloys	25-50	5 min	Stainless steel
30	The above diluted with 120 ml distilled water		Zinc	20-40	up to 3 min	Stainless steel
31	Glycerol Hydrofluoric acid (40%) Nitric acid (1.40) As 27-will decompose on standing and must be thrown away as soon as possible	870 ml 43 ml 87 ml	Zirconium	9-12	up to 10 min	Stainless steel
32	Potassium cyanide Potassium carbonate Gold chloride Distilled water to 1000 ml	80 g 40 g 50 g	Gold, silver	7-5	2-4 min	Graphite
33	Sodium cyanide Potassium ferrocyanide Distilled water to 1000 ml	100 g 100 g	Silver	2-5	up to 1 min	Graphite

Table 10.4(a) ELECTROLYTIC POLISHING SOLUTIONS FOR VARIOUS METALS AND ALLOYS-continued

<i>Composition of solution</i>	<i>Usage</i>	<i>Cell voltage</i>	<i>Time</i>	<i>Cathode</i>	
34 Sodium hydroxide Distilled water to 1000 ml	100 g	Tungsten lead	6	10 min	Graphite
35 Methanol Nitric acid (1.40)  <i>Warning: Do not keep longer than necessary. May become explosive. On no account substitute ethanol for methanol</i>	600 ml 330 ml	Ni, Cu, Zn, Ni-Cu Cu-Zn, Ni-Cr Stainless steel, In, Co Very versatile	40-70	10-60 s	Stainless steel

Table 10.4(b) RECOMMENDED ELECTROPOLISHING SOLUTION FROM TABLE 10.4(a) FOR SPECIFIC METALS AND ALLOYS

Alloy	Electrolyte (No. in Table 10.4 (a))
Aluminium	1, 2, 4, 9, 14
Aluminium-silicon	5
Antimony	5
Beryllium	4
Bismuth	27
Cadmium	13
Cast iron	4, 7
Chromium	7
Cobalt	11, 13, 35
Copper and alloys	12, 13, 35
Copper-tin alloys	22, 23
Copper-zinc alloys	13, 21
Germanium	6
Gold	32
Hafnium	4
Indium	35
Iron-base alloys	4, 7, 8, 9, 19
Lead	1, 2, 4, 10, 34
Magnesium	1, 14, 17
Manganese	16
Molybdenum	19, 20, 28
Nickel and superalloys	4, 8, 9, 10, 19, 35
Niobium	26
Rhenium	7
Silver	4, 14, 32, 33

Stainless steels	1, 2, 3, 4, 7, 8, 9, 12, 19, 24, 25, 35
Steels: carbon and alloy	1, 4, 7, 8, 9, 19, 25
Tantalum	26
Thorium	3
Tin	4, 22, 23
Titanium	4, 6, 7, 8, 9, 29
Tungsten	34
Uranium	4, 7, 8, 9, 15, 17
Vanadium	6, 7
Zinc	1, 2, 17, 21, 30, 35
Zirconium	4, 6, 7, 8, 9, 31

## CHEMICAL POLISHING

Chemical polishing is usually adopted as a quick method of obtaining a passable result, rather than as a method of preparing a perfect surface. However, where it is difficult to prepare a work-free surface by other means, as with some very soft metals or where other difficulties are encountered, it may provide the best method of preliminary or final preparation. Chemical polishing of refractory metals is often performed after mechanical polishing to improve polarized light response (e.g., for Zr, Hf), or to remove minor deformation (e.g., Nb, Ta, V).

In general, a ground specimen is immersed in the polishing agent, or swabbed with the solution, until a polish is obtained, and it is then etched or washed and dried, as appropriate. Reagents are listed in Table 10.5.

**Table 10.5** REAGENTS FOR CHEMICAL POLISHING <sup>1, 2, 9, 152</sup>

<i>Metal</i>	<i>Reagent*</i>	<i>Time</i>	<i>Temperature (°C)</i>	<i>Remarks</i>
Aluminium and alloys	Sulphuric acid (1.84) 25 ml Orthophosphoric acid 70 ml Nitric acid 5 ml	30 s– 2 min	85	Very useful for studying alloys containing intermetallic compounds, e.g. Al-Cu, Al-Fe and Al-Si alloys
Beryllium	Sulphuric acid (1.84) 1 ml Orthophosphoric acid (1.75) 14 ml Chromic acid 20 g Water 100 ml	Several min	49-50	Rate of metal removal is approx 1 $\mu\text{m min}^{-1}$ . Passive film formed may be removed by immersion for 15-30 s in 10% sulphuric acid
Cadmium	Nitric acid (1.4) 75 ml Water 25 ml	5-10s	20	Cycles of dipping for a few seconds, followed immediately by washing in a rapid stream of water are used until a bright surface is obtained
Copper	Nitric acid 33 ml Orthophosphoric acid 33 ml Glacial acetic acid 33 ml	1-2 min	60-70	Finish is better when copper oxide is absent
Copper alloys	Nitric acid 30 ml Hydrochloric acid 10 ml Orthophosphoric acid 10 ml Glacial acetic acid 50 ml	1-2 min	70-80	Specimen should be agitated
Copper-zinc alloys	Nitric acid (1.40) 80 ml Water 20 ml	5 s	40	Use periods of 5 s immersion followed immediately by washing in a rapid stream of water. Slight variations in composition are needed for $\alpha$ - $\beta$ and $\beta$ - $\gamma$ brasses to prevent differential attack. With $\beta$ - $\gamma$ alloys, a dull film forms and this can be removed by immersion in a saturated solution of chromic acid in fuming nitric acid for a few seconds followed by washing
Germanium	Hydrofluoric acid 15 ml Nitric acid 25 ml Glacial acetic acid 15 ml 3-4 drops	5-10 s	20	–

Hafnium	Nitric acid Water Hydrofluoric acid	45 ml 45 ml 8-10 ml	5-10 s	20	As for zirconium
Iron	Nitric acid Hydrofluoric acid (40%) Water	3 ml 7 ml 30 ml	2-3 min	60-70	Dense brown viscous layer forms on surface; layer is soluble in solution. Low carbon steels can also be polished, but the cementite is attacked preferentially
Irons and steels	Distilled water Oxalic acid (100 g l <sup>-1</sup> ) Hydrogen peroxide (30%)	80 ml 28 ml 4 ml			The solution must be prepared freshly, before use. Careful washing is necessary before treatment. A microstructure is obtained similar to that produced by mechanical polishing, followed by etching with Nital

\* Acids are concentrated, unless otherwise indicated.

<i>Metal</i>	<i>Reagent*</i>		<i>Time</i>	<i>Temperature</i> (°C)	<i>Remarks</i>
Lead	Hydrogen peroxide (30%) Glacial acetic acid	80 ml 80 ml	Periods of 5-10 s	20	Use Russell's reagent (Table 10.11) to check that any flowed layer has been removed before final polishing in this reagent
Magnesium	Fuming nitric acid Water	75 ml 25 ml	Periods of 3 s	20	The reaction reaches almost explosive violence after about a minute, but if allowed to continue it ceases after several minutes, leaving a polished surface ready for examination. Specimen should be washed immediately after removal from solution
Nickel	Nitric acid (1.40) Sulphuric acid (1.84) Orthophosphoric acid (1.70) Glacial acetic acid	30 ml 10 ml 10 ml 50 ml	½-1 min	85-95	This solution gives a very good polish
Silicon	Nitric acid (1.40) Hydrofluoric acid (40%)	20 ml 5 ml	5-10 s	20	1:1 mixture also used
Tantalum	Sulphuric acid (1.84) Nitric acid (1.40) Hydrofluoric acid (40%)	50 ml 20 ml 20 ml	5-10 s	20	Solution is useful for preparing surfaces prior to anodizing
Titanium	Hydrofluoric acid (40%) Hydrogen peroxide (30%) Water	10 ml 60 ml 30 ml	30-60 s	–	Swab till satisfactory
	Hydrofluoric acid (40%) Nitric acid (1.40) Lactic acid (90%)	10 ml 10 ml 30 ml			Few seconds to several minutes according to alloy
Zinc	Fuming nitric acid Water	75 ml 25 ml	5-10 s	20	As for cadmium
	Chromium trioxide Sodium sulphate Nitric acid (1.40) Water to 100ml	20 g 1.5 g 5 ml	3 min – 30 min	20	Solution must be replaced frequently
Zirconium (also Hafnium)	Acid ammonium fluoride Nitric acid (1.40) Fluosilicic acid Water	10 g 40 ml 20 ml 100 ml	½-1 min	30-40	Rate of dissolution varies markedly with temperature and is about 20-60 µm min <sup>-1</sup> in the given range
	Nitric acid (1.40) Water Hydrofluoric acid	40-45 ml 40-45 ml	5-10 s repeated	–	Reaction is vigorous at air/solution interface, and specimen is therefore held near surface of liquid. Hydrogen peroxide (30%) can be used in place of

(40%)

10-15 ml

water.

\* Acids are concentrated, unless otherwise indicated.

## ETCHING

Specimens should first be examined after polishing and before etching. This reveals features that have a significant difference in reflectivity from the main structure, or differences in color and relief due to phases of large difference in hardness from the matrix. Nonmetallic inclusions, nitrides, graphite, cracks, pores, voids and various kinds of pits can be recognized clearly and should be recorded. These features can be quite difficult to see after etching.

In order to obtain the maximum resolution from the light optical microscope (LOM) with minimum reflections from stray light, the microscope must be set up using the 'Köhler' principle of illumination.<sup>25</sup> Most modern microscopes are constructed to achieve this principle and it is only necessary to adjust the two iris diaphragms. The first of these, usually called the field diaphragm, should project an image sharply in focus on the specimen and should be adjusted so that the image just lies outside the field of view. The aperture diaphragm should be sharply in focus on the rear of the objective lens. It can be viewed by removing the eyepiece and should be adjusted (through an auxiliary lens on some microscopes) so that the image is centrally located on the rear of the objective and it illuminates 90% of the lens area. If after these adjustments the image is too bright, it should be dimmed by either reducing the light intensity or interposing a filter. Reduction of the aperture reduces the resolution achieved by the lens, emphasizes differences in level and can introduce artefacts. Bright field illumination is the most commonly used illumination mode in metallographic work.

To emphasize small differences in surface topography, or to take advantage of the optical anisotropy of certain metals with non-cubic crystal structures, several techniques are available which are usually available on good light optical microscopes. These include:

### *1. Dark field illumination*<sup>2,26</sup>

By this technique a specimen is illuminated by an annulus of light which passes up the outside of the objective and is focussed as a cone by a concave reflector. Thus, the normal beam of light is not used to form the image. Instead, the light scattered by angled surfaces is focused to make the image and thus the contrast is reversed. Cracks, inclusions and defects are seen as bright features on a black background. In some cases, the color of particles may be quite different in dark field vs. bright field. Cuprous oxide in tough pitch copper is pale blue gray in bright field, as is the sulfide, but the oxide appears bright ruby red in dark field while the sulfide is invisible. Manganese sulfide, calcium sulfide and Mn,Ca sulfide all appear to be dove gray in color in bright field. However, in dark field MnS is dark, although the interface with the matrix may be visible, but the Ca-containing sulfides are bright, with pure CaS the brightest. So, dark field can be quite useful for studying calcium-treated steels. Dark field is also quite useful for the examination of polymers and many minerals.

### *2. Interference microscopy*<sup>27-30</sup>

Interference microscopes have been described by several authors but the most sensitive and useful techniques have been developed by Tolansky<sup>27</sup>. His multiple-beam interferometer can be used with conventional microscopes, at magnifications of up to about 250 times. Monochromatic

light is essential and a parallel beam normal to the surface is used. An optical flat, silvered or aluminized to give about 95% reflectivity, is placed in contact with the specimen and is slightly tilted to produce a thin wedge between the two. The light is repeatedly reflected between the specimen and the optical flat, and interference takes place to produce very thin, sharp, dark fringes. The spacing can be varied by the tilt of the plate. Where a change in the surface of the specimen occurs, e.g. a step or depression, the interference fringe is displaced one way or the other. A total fringe displacement corresponds to a change in height of half the wavelength of light used; it is possible to measure surface displacements of about 5-250 nm. To obtain sharp fringes, the reflectivity of the metallic surface should be the same as the reference plate, i.e., approximately 95%, and it may be necessary to aluminize the specimen surface for the best results, or use a lower reflectivity reference mirror.

Normarski has designed a very sensitive microscope for detecting height variations on the surface of a specimen.<sup>26, 30</sup> He used a conventional polarizing microscope, into which a double quartz prism is inserted between the objective and the analyser. If a step is present, this produces two images slightly displaced to one another and interference between these produces light and dark fringes, the spacing of which can be varied by adjusting the prism. A modification of the technique produces interference contrast in images. This is often called DIC - differential interference contrast.<sup>146</sup> DIC can be a very effective tool for viewing microstructures that have slight height differences that may be invisible in bright field but show up clearly using this method.

### *3. Polarized light*

Polarized light is an extremely powerful illumination method for studying inclusions and structures of unetched, electropolished or mechanically polished surfaces of metals and alloys with non-cubic crystal structures, for example, Be, Hf, alpha-Ti, U and Zr. In certain cases, metals with cubic crystal structures may be examined more effectively after etching using polarized light.

The equipment needed includes a strong source of illumination, a polarizer (prism or Polaroid filter) that can be rotated to change the plane of polarization, and an analyser of comparable material which can also be rotated. At least one of these, usually the polarizer, must be adjustable and the other can be fixed. When the analyser is oriented so that its plane of polarization is at 90° to that of the polarizer, an isotropic specimen will appear black if the objectives and the microscope are well adjusted and no depolarization occurs. The objectives should be strain free for the highest sensitivity. Then, if a properly prepared metal with a non-cubic crystal structure is examined, the structure will be revealed.

Bausch and Lomb developed the Foster prism,<sup>25</sup> which used a special calcite crystal that gave excellent polarized light images. However, the original source for this material has been long exhausted. This system has a fixed crossed position and cannot be adjusted to move slightly off the crossed position. It is now available again on certain microscopes.

With isotropic metals and the polarizer and analyser set in the 'crossed' position, no light reaches the eyepiece. However, with an optically anisotropic material, e.g., a hexagonal metal like beryllium, magnesium or zinc, the reflected beam becomes elliptically polarized and the intensity of the component normal to the plane of polarization of the incident light depends on



the orientation of the anisotropic structure. Thus, the intensity of light which passes through the analyser will be dependent on the orientation of the structure to the surface of the specimen and to the incident beam. The image will vary from dark to bright, according to orientation and the grain structure of an anisotropic material will be revealed. On rotating the specimen, the intensity of light passing through the analyser from any one grain will pass from minimum to maximum intensity every 45° to give four maxima per revolution at 90° to each other, with a minimum intensity at 45° to each maximum. If the analyser and polarizer are not quite crossed and differ by a few degrees, only two maxima and minima occur. The difference in contrast between the maxima and minima is much greater under these conditions and improves the sensitivity of the method, especially for weakly anisotropic or pleochroic materials.

The method can be used for studying grain structures, twins and martensites. In uranium alloys, for instance, the isotropic gamma phase can be distinguished from weakly anisotropic retained beta phase and the strongly anisotropic variants of the alpha phase. Martensite can be produced in eutectoidal aluminum bronze (Cu – 11.8% Al) when quenched from the beta field. This martensite is easily observed in as-polished specimens using polarized light. Martensites can be made in certain nonferrous shape-memory alloys and observed with polarized light after polishing. In other systems, such as aluminium, the grain structure can be revealed by anodizing with Barker's reagent and is observed with polarized light. If a sensitive tint filter (sometimes called a full-wave plate, a first-order red plate, or a  $\lambda$  plate) is added to the light path, the gray-contrast image is converted into color contrast. Some anodized alloys apparently produce an anisotropic oxide film which has orientations related to the underlying lattice orientations. But, anodizing of aluminum with Barker's reagent<sup>67</sup> does not produce such a film, as often claimed, but disproved by Perryman and Lack<sup>151</sup>. If such a film is present, color should be observed with bright field illumination due to interference effects, as with heat tinting or color etching. But, color is not observed. Instead, a roughened surface is produced that creates elliptical polarization effects. The grains are colored according to variations in crystal orientation but Barker's reagent does not reveal variations in composition within grains, even in as-cast specimens, as color tint etches do.

The other useful application is in the identification of inclusions, although this is rarely used today due to the widespread availability of energy-dispersive or wavelength-dispersive spectroscopy systems with scanning electron microscopes and electron microprobes. Glassy inclusions such as silicates display the so called 'optical cross' in polarized light. Other inclusions are optically isotropic or anisotropic, e.g., MnO and MnS can be distinguished in steels. Both look similar in bright field but under polarized light, the oxide is bright and the sulfide is dark. Other inclusions are pleochroic and display characteristic colours under crossed polars. Examples are the grey-blue Cu<sub>2</sub>O phase in tough-pitch copper which is ruby red under polarized light, and Cr<sub>2</sub>O<sub>3</sub> which changes from blue grey to a beautiful, emerald green. References 26, 41, 44 and 146 should be consulted for more detail.

The anisotropic metals include:

Antimony	Tin
Beryllium	Titanium
Cadmium	Uranium
Hafnium	Zinc
Magnesium	Zirconium

If correctly prepared, these metals will reveal their structure under crossed polarized light, although the quality of the images, and the strength of any observed colors, does vary.

The following metals can be made to respond to polarized light by anodizing to produce an anisotropic film (see the note above about Barker's reagent), or by deep etching to produce an uneven surface with etch pits.

Aluminium	Molybdenum
Chromium	Nickel
Copper	Tungsten
Iron	Vanadium
Manganese	

Any fine lamellar structure, when etched, will reveal color under polarized light because the etched fine lamellar structure produces elliptical polarization. In a similar manner, solution annealed and aged beryllium copper produces beautiful colors under polarized light when etched due to the roughness created on the etched surface due to the overlapped coherency strains associated with the strengthening precipitates.

#### 4. Color <sup>44,146, 152</sup>

Only two metals demonstrate natural color: gold and copper. A few intermetallic phases exhibit natural color, for example,  $\text{AuAl}_2$ , known as the "purple plague" in the electronics industry. Others can be rendered in color by:

(a) Optical methods of examination, such as polarized light, especially of etched structures with a sensitive tint plate inserted between polarizer and analyser. This is available on most microscopes today and converts shades of grey into shades of color. Unaffected regions that are white appear as magenta with a fixed sensitive tint filter. The color pattern can be altered if the sensitive tint filter is adjustable (available on certain microscopes). Brighter colors are obtained in etched structures. Nomarski DIC also produces colored surfaces where the colors correspond to height differences and can be adjusted by altering the Wollaston prism setting. These methods change shades of grey to color contrast because of the use of the sensitive tint filter.

(b) By producing interference films by heat tinting or by chemical processes ("tint etching"). They can color phases according to their reactivity or grains according to their crystal orientation. Most frequently, the reagents used deposit thin films of oxide, sulphide, chromate, phosphate or molybdate which cause coloration by interference of light. The color depends on the thickness of films. Films that form on the less noble phase, usually the matrix, are produced by an anodic tint etch. Films that are preferentially deposited on the more noble phase, usually the second-phase particles, are produced by cathodic tint etches. A few tint etches, complex tint etches, color both matrix and second phases. The anodic tint etches are most common. Heat tinting usually colors the matrix phase. The films grow according to the crystal orientation of the matrix phase, and growth is influenced by chemical segregation and residual deformation. A few tint etchants will color MnS inclusions in steels white. Several etchants are known to preferentially attack or color intermetallic compounds in Al and Mg alloys, but these are not tint etchants. They are usually called selective etchants. Some useful etchants are given in Tables 10.6 to 10.8. More details and examples are given in refs. 44, 152-158.

Interference films can also be produced by vapor deposition of a compound to produce a thin dielectric film with a high refractive index. This increases the minor reflectivity differences between matrix and second-phase particles rendering them visible in color contrast. Materials such as ZnTe, ZnSe, TiO<sub>2</sub>, and ZnS have been commonly used for this purpose. The method was developed by Pepperhoff (1960) and is described in great detail by Bühler and Hougardy<sup>159</sup>. Gas contrast and reactive sputtering can also produce interference films.

### 5. Physical methods

(a) *Cathodic vacuum etching (ion etching)*. The specimen is made a cathode in a high voltage gas discharge. High energy ions such as argon are accelerated at voltages of 1-10 kV and gas pressures of 10 $\mu$ m. This bombardment removes atoms at a rate dependent on orientation, presence of grain boundaries and intermetallic compounds.

(b) *Thermal etching*. On heating specimens, e.g., in vacuum or inert atmosphere, atoms are lost from regions of low binding energy, e.g. grain boundaries. Surface tension forces lead to changes in surface topography at grain boundaries, leaving a structure characteristic of the high temperature. Thermal etching is commonly used with ceramics.

### 6. Chemical and electrochemical etching

Etching is usually an oxidation process. In general, elements with electrode potentials more negative than hydrogen will pass into solution in many solutions, the rate depending on the local environment, so resulting in grain boundary attack or outlining of phases or other structures. For elements with electrode potentials more positive than hydrogen, or for elements which polarize, solutions containing oxidizing agents are needed. Making the specimen the anode in a low voltage cell has the same effect. Indeed, most electropolishing solutions will cause etching if the voltage is reduced, usually by a factor of 10.

Detailed etching procedures for individual metals are given below but, as a general principle, iron alloys are usually etched in dilute oxidizing agents, e.g., nitric acid or picric acid in ethanol. Stainless steels are usually etched in weak oxidizing reagents in alkaline solution, e. g., alkaline ferricyanides. Virtually the same result is achieved electrolytically in a 1% potassium hydroxide solution.

In the case of copper alloys, most etchants require an ammoniacal atmosphere plus an oxidizing reagent such as air (by swabbing), hydrogen peroxide or dichromates, permanganates, persulphates, etc. Electrolytic etching in an oxidizing acid, e.g., 1% chromium trioxide often suffices, the control of etching being achieved by varying the voltage.

Nearly all pure metals are notoriously difficult to etch, e.g., aluminium. If there are no natural impurities present to induce grain boundary attack, etchants should be used which can chemically deposit elements that can be reduced and diffuse into the boundaries, e.g., gallium from a gallium salt solution.

Reduction reactions can also be used and these cause staining or coloration of phases, especially intermetallic compounds.

A wide variety of etching reagents have been devised by empirical methods. Some of these are reproduced but the perceptive reader will see that these can be modified easily to cope with new compositions. Small amounts of some components are needed to control pH or potential. Some solutions are not stable and their effectiveness will change with time. Others containing mixtures of oxidizing agents and organic chemicals can become very dangerous with time and should only be retained for short times and be discarded immediately after use.

Reference is given to simple electrolytic etches. They can be used with simple direct current power supplies. This gives more control over etching than provided by simple immersion or swabbing. For further control of the etch process it is recommended that these etchants be used with a potentiostat<sup>18, 19</sup> to control the potential at a known and reproducible value. This will yield selective, reliable and consistent etching.<sup>20, 21, 22</sup>

Although most etching work is conducted to reveal the phases and constituents in metals and alloys, there are etchants that will reveal dislocations. Etching to reveal dislocations in minerals goes back to at least 1817 with a publication by Daniels. In 1927, Honess listed etchants used to reveal dislocations in minerals. However, it was not until the work of Shockley and Read in 1949 that dislocations were studied scientifically in metals. The first deliberate use of etch pitting reagents to reveal dislocations was published in 1952 by Horn and Gevers. This was the first direct proof that dislocations (the concept of dislocations was proposed in the 1930s to explain the apparent low strength of metals compared to their theoretical strength) could be revealed by etching. A wide range of etching techniques exist for revealing dislocations and many are listed in Table 10-9 (see also 152).

### *7. Washing and drying*

On completion of etching (with most etches) the specimen should at once be flooded with water, washed free from water with ethanol (avoid using ether or methanol) and dried in a blast of hot air from a hand dryer, hair dryer or equivalent. With non-aqueous etches it may be preferable to do the initial washing with alcohol or acetone rather than water.

Porous specimens are often easily stained by residual etching solution seeping out of the pores. This trouble can usually be avoided by prolonging the washing and drying stages and in severe cases by prolonged soaking of the specimen in alcohol or acetone before final drying, or by ultrasonic cleaning. When working with porous specimens, it is best to infiltrate the pores, if interconnected to the surface, with a low viscosity epoxy resin using a vacuum impregnation system. If the pores are not interconnected, place the polished surface in a vacuum impregnation chamber, face up, apply a thin layer of a low viscosity epoxy to the surface and drive the epoxy into the surface pores under vacuum, or by applying pressure (this requires a special pressurization chamber). After it hardens, carefully remove the excess epoxy on the top surface and final polish the specimen. But, very little metal can be removed or the impregnated layer will be removed. Some metallographers have used molten wax to fill surface pores, then scrapped off the hardened wax on the surface and completed polishing. As the pores and voids are filled, bleed out does not occur. Gifkins demonstrated that EDTA (ethylene-diaminetetraacetic acid) could be used to remove tarnish from the surface of polished lead specimens. He also found that cracked specimens of steel and brass could be etched stain-free by adding a few drops of EDTA to the etchant. An aqueous 2% EDTA solution can be used ultrasonically to

remove stains. This solution can etch certain metals, so the time in the ultrasonic cleaner must be minimized (see 152 for more details).

Table 10.6 COLOR ETCHES FOR STEEL

Reagent			Procedure	Comments
1	Saturated sodium thiosulfate Potassium metabisulfite	50 mL 1 g	Immerse up to 2 min.	Klemm's I for carbon and alloys steels (also colors Cu alloys) Colors ferrite, bainite and martensite, but not cementite
2	Saturated sodium thiosulphate Potassium metabisulphate	50 ml 5 g	Immersion up to 90s	Klemm's II for austenitic Mn steels (also colors Cu alloys) $\alpha$ martensite-brown, $\epsilon$ martensite-white Austenite-yellow to brown or shades of blue
3	0.6-10% HCl in water Ammonium bifluoride Potassium metabisulphite	100 ml 0-1 g 0.5-1 g	Immersion up to 60 s	Carbon, alloy and tool steels Colors ferrite, bainite and martensite Carbides unaffected
4	10-20% HCl in water Ammonium bifluoride Potassium metabisulfite	100 ml 0-2.4 g 0.5-1 g	Immerse up to 120 s	Stainless and maraging steels Use lower HCl, no $\text{NH}_4\text{FHF}$ for martensitic grades Colors martensite and austenite but not carbides or nitrides

Table 10.7 COLOR ETCHES FOR CAST IRON.

Reagent			Procedure	Comments
1	HCl (35%) Selenic acid Ethanol	2 ml 0.5 ml 100 ml	5-6 min immersion 2-3 min if pre-etched in 2% Nital	$\text{Fe}_3\text{C}$ -red/violet Ferrite-white Phosphides-blue/green
2	Sodium thiosulphate Lead acetate Citric acid Sodium nitrite Water	24 g 2.4 g 3 g 0.2 g 100 ml	Pre-etch in 2% Nital Immerse until surface blue/violet	Phosphides-yellow/brown Sulphides-white Ferrite and carbides } blue/violet
3	Sodium thiosulphate Citric acid Cadmium chloride Water	24 g 3 g 2 g 100 ml	Pre-etch in 2% Nital (a) Immerse 20-40s (b) Immerse 50-90s	(a) Ferrite-red/violet (b) Phosphides-orange/brown Carbides-blue/violet Ferrite-yellow

Table 10.8 COLOR ETCHES FOR ALUMINIUM ALLOYS

Reagent			Procedure	Comments
1	Sodium molybdate Ammonium bifluoride HCl (35%) Water	3 g 2 g 5 ml 100 ml	Immersion by trial	AlCuFeMn script-blue FeSi Al-brown/blue $\text{Ni}_3\text{Al}$ , FeNiAlg-brown $\text{CuAl}_2$ -pale blue
2	Chromic trioxide Sulphuric acid (1.84) Ammonium bifluoride Water	20 g 20 g 5 g 100 ml	Immerse 5-30 s	If alloy susceptible to intergranular corrosion, grain boundaries coloured black
3	20% sulphuric acid (1.84) Water	80 ml	Immerse 30 s at 70°C	AlCuFeMn-brown $\text{Mg}_2\text{Si}$ -brown to black Outlines other phases
4	Sodium hydroxide Water	10% 90 ml	Immerse 5 s at 70°C	$\text{CuAl}_2$ } brown $\text{Mg}_2\text{Si}$ }
5.	Potassium permanganate NaOH 100 ml water	4 g 1 g	Immerse for up to 20 s	Weck's reagent Colors alpha matrix

**Table 10.9** ETCHING REAGENTS FOR DISLOCATIONS (Taken largely from Lovell, Vogel and Wernick<sup>61</sup>)

<i>Metal or alloy</i>	<i>Reagent*</i>		<i>Remarks</i>
Aluminium (99.99%) (see ref. 62)	Hydrochloric acid	50%	–
	Nitric acid	4%	
	Hydrofluoric acid	3%	
	Hydrochloric acid	50 ml	Lacombe and Beaujard's reagent <sup>69, 70</sup>
	Nitric acid	47 ml	
	Hydrofluoric acid	3 ml	
	Hydrofluoric acid	37 ml	Make A: 49: 51 HF: H <sub>2</sub> O <sub>2</sub>
	Hydrochloric acid	18 ml	Make B: 65: 35 HCl: HNO <sub>3</sub>
	Nitric acid	9 ml	Mix in ratio A:B = 5:2, care required
	Hydrogen peroxide (29% w/v)	36 ml	Keep at 0-15°C in use (ref. 62)
Antimony	Hydrofluoric acid	3 pts	Electrolytic etch on cleaved surface. 2-3 s,
	Nitric acid	5 pts	
	Acetic acid	3 pts	
	Bromine	3 drops	
	Hydrofluoric acid	1 pt	Electrolytic etch. 1 s
	Superoxol†	1 pt	
Bismuth	1% Iodine in methyl alcohol		Cleaved surface. 15 s
Brass (65% Cu-35%Zn)	0.2% Sodium thiosulphate		Electrolytic etch. 10 A dm <sup>-2</sup> 18-20°C. Remove film with hydrochloric acid
Brass (Alpha) <sup>63</sup>	Saturated aqueous ferric chloride	50 ml	–
	Hydrochloric acid	2 drops	
Brass (Beta) <sup>63</sup>	Saturated aqueous ammonium molybdate	30 ml	Immerse the electrolytically polished surface for 30 min
	Hydrochloric acid	6-7 drops	
Columbium (Niobium)	Sulphuric acid	10 ml	Agitate specimen in solution
	Hydrofluoric acid	10 ml	
	Water	10 ml	
	Superoxol†	a few drops	
Copper (pure)	Saturated ferric chloride solution	4 pts	Rinse in ammonia solution See Ruff <sup>61</sup> for further solutions and references
	Hydrochloric acid	4 pts	
	Acetic acid	1 pt	
	Bromine	a few drops	
Germanium (also 0.2 at. % boron, 6.0 at. % silicon, 0.2 at. % tin)	Hydrofluoric acid	3 pts	3-5 s. Polish etch. 600-grit carborundum ground surface
	Nitric acid	5 pts	
	Acetic acid	3 pts	
	Bromine	3 drops	
Germanium	Potassium ferricyanide	8 g	600-grit carborundum ground surface. 2-5 min. Boiling solution
	Potassium hydroxide	12 g	
	Water	100 ml	
Iron (99.96%)	4% metanitrobenzoesulphonic acid in ethyl alcohol		Long etch. Rinse in alcohol. Result questionable
Iron	(a) 1% nitric acid in ethyl alcohol		1 min in (a) followed by rinse in methyl alcohol and 5 min in (b). Pits appear only in specimen cooled slowly from 750° to 800°C‡
	(b) 0.5% picric acid in methyl alcohol		
	Fry's reagent Table 10.1, C(f)		10 s etch of chemically polished surface

\* Acids are concentrated, unless otherwise indicated.

† Superoxol contains hydrogen peroxide (30%) 1 pt, hydrofluoric acid (40%) 1 pt, water 4 pts.

**Table 10.9** ETCHING REAGENTS FOR DISLOCATIONS—*continued*

<i>Metal or alloy</i>	<i>Reagent*</i>	<i>Remarks</i>	
Iron (99.99%)	Disa Electropol solution A-Z	Electrolytic etch. Observation by electron microscopy	
Iron	2% Nital containing 2% of saturated picral	15 min	
	Saturated picral	4 min. Anneal to decorate dislocations‡	
Iron-silicon (3.25 Si)	Acetic acid	133 ml	
	Chromium trioxide	25 g	
	Water	7 ml	
Nickel-manganese	Orthophosphoric acid	100 ml	
	Ethyl alcohol	100 ml	
Silicon	Hydrofluoric acid	1 pt	
	Nitric acid	3 pts	
	Acetic acid	12 pts	
	Hydrofluoric acid	4 pts	
	Nitric acid	2 pts	
	3% aqueous mercuric nitrate	4 pts	
	Hydrofluoric acid	3 pts	
	Nitric acid	5 pts	
	Acetic acid	3 pts	
	3% aqueous mercuric nitrate	1.5-2 pts	
Hydrofluoric acid	160 ml	600-grit carborundum ground surface	
	Nitric acid		80 ml
	Water		160 ml
	Silver nitrate		8 g
Hydrofluoric acid	50 g	Use in ratio: 2:1 by vol. for large etch pits 1:1 for medium etch pits 2:3 for small etch pits Time 15 s <sup>65</sup>	
	Chromium trioxide		per 100 g
	Water		
Tellurium	Hydrofluoric acid	3 pts	
	Nitric acid	5 pts	
	Acetic acid	6 pts	
Zinc	Chromium trioxide	160 g	
	Hydrated sodium sulphate	50g	
	Water	500 ml	
Zinc with 0.002% tin <sup>66</sup>	Saturated aqueous ammonium tungstate	35 ml	
	Saturated aqueous ammonium molybdate	5 drops	
	Hydrochloric acid	5 drops	

\* Acids are concentrated, unless otherwise indicated.

‡ Note that this heat treatment must alter the dislocation structure.

*Etching to Reveal Magnetic Domains. See under IRON AND STEEL, Microferrographic Technique, p. 10-39.*

## TAPER SECTIONING

Taper sectioning<sup>25, 26</sup> is used to give an apparent magnification of as much as 10 times by using a plane of section to cut the surface at a shallow angle, typically  $6^\circ$  (i.e.,  $\sin^{-1} 1/10$ ) so that the vertical features of the surface are given an apparent relative magnification of about 10 times. This magnification is only in the direction perpendicular to the coated surface when the taper angle is made as indicated in Figure 10.3.

Taper sectioning requires plating of the surface to be examined, followed by mounting in plastic at a suitable angle. The plating may conveniently be done with nickel or copper from conventional plating baths. Assuming that the surface is ready to be examined, it must not be altered during the plating procedure; cleaning before plating must be confined to methods such as solvent washing and cathodic alkaline degreasing, which have no appreciable effect on the particular surface under examination. The mounting procedure is evident from Figure 10.3.

This method may also be used for examining thin intermediate layers, for example in electroplating, or in the study of diffusion couples.

**Figure 10.3** *Taper sectioning (from Vickers Projection Microscope Handbook)*

### 10.3 Metallographic methods for specific metals

#### 10.3.1 Aluminium

##### PREPARATION

Aluminium and its alloys are soft and easily scratched or distorted during preparation. For cutting specimens, a laboratory abrasive cut-off saw should be used, with the correct wheel, and with light pressure and proper cooling, to avoid excessive heating and minimize deformation. Specimens are ground with waterproof SiC papers by the usual methods, but with slightly lower loads than in the contemporary method. Use 5 lbs (20N) per specimen. Fine silicon carbide papers (600-grit (P1200) and finer) may cause embedment, particularly in the softer alloys. For high-purity aluminium, it may be advisable to coat the finer paper (if used) with paraffin wax. After the first grinding step (see the contemporary method described above) polishing is carried out in three or four steps, depending upon the alloy. Rigid grinding disks specially made for softer metals, such as the BuehlerHercules S disk, or the Struers Largo disk, can be used for the second step if substantial material must be removed. If heavy stock removal is not required, cloths can be used for step 2. Natural silk (with a psa backing) will yield the best surface finish, with excellent relief control and a reasonable removal rate. For steps 3 and 4 (if step 4 is chosen), use a woven polyester cloth rather than the chemotextile pad. For final polishing, either the napless polyurethane pad or a synthetic suede (rayon), medium nap cloth, can be used. The preferred final abrasive is colloidal silica. The sol-gel alumina suspension (Masterprep alumina) works nearly as well, and certainly far better than standard calcined aluminas. MgO is rarely used today as the final abrasive due to the many problems associated with its use, as discussed previously. The contemporary preparation method, with these minor changes, yields excellent surfaces with no relief, good edge retention, and freedom for artifacts, so that the true structure



can be revealed. Many different second-phase particles, or intermetallic phases, can be encountered in aluminium and its alloys, see Table 10-10, and their polishing characteristics can vary somewhat.

Avoid using slurry or suspensions of fine diamond abrasives when polishing aluminium and its alloys as they are likely to become embedded in the surface. This is chiefly a problem with 1- $\mu\text{m}$  diamond and finer sizes. When these fine sized diamond abrasives are added as a slurry, the particles roll between the specimen and the woven cloth or pad and can become embedded in the specimen as easily as in the cloth. This problem is not observed with coarser diamond added as slurries or suspensions. Fine diamond is best added as a paste where it is embedded in the cloth even before the wheel is turned on. See the previously described practice for charging a cloth with diamond paste.

Many aluminium alloys contain the reactive compound  $\text{Mg}_2\text{Si}$ . If this constituent is suspected, non-aqueous solvents, such as mineral spirits, purified kerosene or ethanol may be substituted for water during the final polishing step to avoid loss of the reactive particles by corrosion.

It should be noted that some aluminium alloys are liable to undergo precipitation reactions at the temperatures used to cure thermosetting mounting resins; this applies particularly to aluminium-magnesium alloys, in which grain boundary precipitates may be induced. A "cold" setting resin should be used, but care must be taken with the set up to minimize the heat generated in polymerization (see previous discussion under Mounting).

*Electropolishing* is often rapid and convenient (see Tables 10.4(a) and 10.4(b) but there may be nonuniform polishing or attack of the intermetallic phases.

## ETCHING

Aluminium alloys now in use cover many complex alloying systems. A relatively large number of etching reagents have been developed; only those whose use has become more or less standard practice are given in Table 10.11. Many etches are designed to render the distinction between the many possible microconstituents easier, and the type of etching often depends on the magnification to be used. The identification of constituents, which is best accomplished by using cast specimens where possible, depends to a large extent on distinguishing between the colors of particles, so that the illumination should be as near as possible to daylight quality. It is recommended that a set of specially prepared standard specimens, containing various known metallographic constituents, be used for comparison. Because of these problems, and with the development of EDS and WDS techniques available on scanning electron microscopes and electron microprobes, the use of etchants to identify precipitates is infrequent today. However, as an aid to selecting constituents for image analysis measurements, these etchants have value as they can enhance the detectability of the desired particles.

Some etching reagents for aluminium require the use of a high temperature; in such cases the specimen should be preheated to this temperature by immersion in hot water before etching. For washing purposes, a liberal stream of running water is advisable.

**Table 10.10** MICROCONSTITUENTS WHICH MAY BE ENCOUNTERED IN ALUMINIUM ALLOYS*Microconstituent Appearance in unetched polished sections*

$\text{Al}_3\text{Mg}_2$	Faint, white. Difficult to distinguish from the matrix.
$\text{Mg}_2\text{Si}$	Slate grey to blue. Readily tarnishes on exposure to air and may show iridescent colour effects. Often brown if poorly prepared. Forms Chinese script eutectic.
$\text{CaSi}_2$	Grey. Easily tarnished
$\text{CuAl}_2$	Whitish, with pink tinge. A little in relief, usually rounded
$\text{NiAl}_3$	Light grey, with a purplish pink tinge
$\text{Co}_2\text{Al}_9$	Light grey
$\text{FeAl}_3$ <sup>(1)</sup>	Lavender to purplish grey; parallel-sided blades with longitudinal markings
$\text{MnAl}_6$	Flat grey. The other constituents of binary aluminium-manganese alloys ( $\text{MnAl}_4$ , $\text{MnAl}_3$ and 'δ') are also grey and appear progressively darker. May form hollow parallelograms
$\text{CrAl}_7$	Whitish grey; polygonal. Rarely attacked by etches
Silicon	Slate grey. Hard, and in relief. Often primary with polygonal shape-use etch to outline
$\alpha$ ( $\text{AlMnSi}$ ) <sup>(2)</sup>	Light grey, darker and more buff than $\text{MnAl}_6$
$\beta$ ( $\text{AlMnSi}$ ) <sup>(2)</sup>	Darker than $\alpha$ ( $\text{AlMnSi}$ ), with a more bluish grey tint. Usually occurs in long needles
$\text{Al}_2\text{CuMg}$	Like $\text{CuAl}_2$ but with bluish tinge
$\text{Al}_6\text{Mg}_4\text{Cu}$	Flat, faint and similar to matrix
( $\text{AlCuMn}$ ) <sup>(3)</sup>	Grey
$\alpha$ ( $\text{AlFeSi}$ ) <sup>(4)</sup>	Purplish grey. Often occurs in Chinese-script formation. Isomorphous with $\alpha$ ( $\text{AlMnSi}$ )
$\beta$ ( $\text{AlFeSi}$ ) <sup>(4)</sup>	Light grey. Usually has a needle-like formation
( $\text{AlCuFe}$ ) <sup>(5)</sup>	Grey $\alpha$ phase lighter than phase ( <i>see</i> Note 5)
( $\text{AlFeMn}$ ) <sup>(6)</sup>	Flat grey, like $\text{MnAl}_6$
( $\text{AlCuNi}$ )	Purplish grey
( $\text{AlFeSiMg}$ ) <sup>(7)</sup>	Pearly grey
$\text{FeNiAl}_9$	Very similar to and difficult to distinguish from $\text{NiAl}_3$
( $\text{AlCuFeMn}$ )	Light grey
$\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$	Purplish grey
$\text{MgZn}_2$	Faint white; no relief

In Table 10.10, constituents are designated by symbols denoting the compositions upon which they appear to be based, or by the elements, in parentheses, of which they are composed. The latter nomenclature is adopted where the composition is unknown, not fully established, or markedly variable. The superscript numbers in column 1 refer to the following notes:

- (1) On very slow cooling under some conditions,  $\text{FeAl}_3$  decomposes into  $\text{Fe}_2\text{Al}_7$  and  $\text{Fe}_2\text{Al}_5$ . The former is micrographically indistinguishable from  $\text{FeAl}_3$ . The simpler formula is retained for consistency with most of the original literature.
- (2)  $\alpha$  ( $\text{AlMnSi}$ ) is present in all slowly solidified aluminium-manganese-silicon alloys containing more than 0.3% of manganese and 0.2% of silicon, while  $\beta$  ( $\text{AlMnSi}$ ), a different ternary compound, occurs above approximately 3% of manganese for alloys containing more than approximately 1.5% of silicon.  $\alpha$  ( $\text{AlMnSi}$ ) has a variable composition in the region of 30% of manganese and 10-15% of silicon. The composition of  $\beta$  ( $\text{AlMnSi}$ ) is around 35% of manganese and 5-10% of silicon.
- (3) ( $\text{AlCuMn}$ ) is a ternary compound with a relatively large range of homogeneity based on the composition  $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$ .

- (4)  $\alpha$  (AlFeSi) may contain approximately 30% of iron and 8% of silicon, while  $\beta$  (AlFeSi) may contain approximately 27% of iron and 15% of silicon. Both constituents may occur at low percentages of iron and silicon.
- (5) The composition of this phase is uncertain. Two ternary phases exist.  $\alpha$  (AlCuFe) resembles FeAl<sub>3</sub>;  $\beta$  (AlCuFe) forms long needles.
- (6) The phase denoted as (AlFeMn) is a solid solution of iron in MnAl<sub>6</sub>.
- (7) This constituent is only likely to be observed at high silicon contents.

**Table 10.11** ETCHING REAGENTS FOR ALUMINIUM AND ITS ALLOYS

No.	Reagent		Remarks
1	Hydrofluoric acid (40%) Hydrochloric acid (1.19) Nitric acid (1.40) Water  (Keller's etch)†	0.5 ml 1.5 ml 2.5 ml 95.5 ml	15 s immersion is recommended., Particles of all common micro-constituents are outlined. Color indications: Mg <sub>2</sub> Si and CaSi: blue to brown $\alpha$ (AlFe-Si) and (AlFeMn): darkened $\beta$ (AlCuFe): light brown MgZn <sub>2</sub> , NiAl <sub>3</sub> , (AlCuFeMn), Al <sub>2</sub> Cu Mg and Al <sub>6</sub> CuMg: brown to black $\alpha$ (AlCuFe) and (AlCuMn): blackened Al <sub>3</sub> Mg <sub>2</sub> : heavily outlined and pitted  The colors of other constituents are little altered. Not good for high Si alloys
2	Hydrofluoric acid (40%) Water	0.5 ml 99.5 ml	15 s swabbing is recommended. This reagent removes surface flowed layers, and reveals small particles of constituents, which are usually fairly heavily outlined. There is little grain contrast in the matrix.

\* These are isomorphous and the color depends on the proportion of Mn and Fe.

† Sodium fluoride can be used in place of HF in mixed acid etches.

Table 10.11 ETCHING REAGENTS FOR ALUMINIUM AND ITS ALLOYS--continued

No.	Reagent		Remarks
2 (cont.)			<p>Color indications:</p> <p>Mg<sub>2</sub>Si and CaSi<sub>2</sub>: blue</p> <p>FeAl<sub>3</sub> and MnAl<sub>6</sub>: slightly darkened</p> <p>NiAl<sub>3</sub>: brown (irregular)</p> <p>α (AlFeSi): dull brown</p> <p>(AlCrFe): light brown</p> <p>Co<sub>2</sub>Al<sub>6</sub>: dark brown</p> <p>(AlFeMn): brownish tinge</p> <p>α (AlCuFe), (AlCuMg) and (AlCuMn): blackened</p> <p>α (AlMnSi), β (AlMnSi) and (AlCuFeMn) may appear light brown to black</p> <p>β (AlFeSi) is colored red brown to black</p> <p>The remaining possible constituents are little affected</p>
3	Sulphuric acid (1.84) Water	20 ml 80 ml	<p>30 s immersion at 70°C; the specimen is quenched in cold water.</p> <p>Color indications:</p> <p>Mg<sub>2</sub>Si Al<sub>3</sub>Mg<sub>2</sub> and FeAl<sub>3</sub>: violently, attacked, blackened and may be dissolved out</p> <p>CaSi<sub>2</sub>: blue</p> <p>α (AlMnSi) and β (AlMnSi): rough and attacked</p> <p>NiAl<sub>3</sub> and (AlCuNi): slightly darkened</p> <p>β (AlFeSi): slightly darkened and pitted</p> <p>α (AlFeSi), (AlCuMg) and (AlCuFeMn): outlined and blackened</p> <p>Other constituents are not markedly affected</p>
4	Nitric acid (1.40) Water	25 ml 75 ml	<p>Specimens are immersed for 40 s at 70°C and quenched in cold water.</p> <p>Most constituents (not MnAl<sub>6</sub>) are outlined. Color indications:</p> <p>β (AlCuFe) is slightly darkened</p> <p>Al<sub>3</sub>Mg<sub>2</sub> and AlMnSi: attacked and darkened slightly</p> <p>Mg<sub>2</sub>Si, CuAl<sub>2</sub>, (AlCuNi) and (AlCuMg) are colored brown to black</p>
5	Sodium hydroxide Water	1 g 99 ml	<p>Specimens are etched by swabbing for 10 s. All usual, constituents are heavily outlined, except for Al<sub>3</sub>Mg<sub>2</sub> (which may be lightly outlined) and (AlCrFe) which is both unattacked and uncolored. Color indications:</p> <p>FeAl<sub>3</sub> and NiAl<sub>3</sub>: slightly darkened</p> <p>(AlCuMg): light brown</p> <p>α (AlFeSi): dull brown*</p> <p>α (AlMnSi): rough and attacked; slightly darkened*</p> <p>MnAl<sub>6</sub> and (AlFeMn): colored brown to blue (uneven attack)</p> <p>MnAl<sub>4</sub>: tends to be darkened</p> <p>The colors of other constituents are only slightly altered</p>
6	Sodium hydroxide Water	10 g 90 ml	<p>Specimens immersed for 5 s at 70°C, and, quenched in cold water.</p> <p>Color indications:</p> <p>β (AlFeSi): slightly darkened</p> <p>Mn<sub>11</sub>Ni<sub>4</sub>Al<sub>60</sub>: light brown</p> <p>β (AlCuFe): light brown and pitted</p> <p>CuAl<sub>2</sub>: light to dark brown</p> <p>FeAl<sub>3</sub>: dark brown</p> <p>(FeAl<sub>3</sub> is more rapidly attacked in the presence of CuAl<sub>2</sub> than when alone)</p> <p>MnAl<sub>6</sub>, NiAl<sub>3</sub>, (AlFeMn), CrAl<sub>7</sub> and AlCrFe: blue to brown</p> <p>α (AlFeSi), α (AlCuFe), CaSi<sub>2</sub> and (AlCuMn): blackened</p>

\* These are isomorphous and the colour depends on the proportion of Mn and Fe.

† Sodium fluoride can be used in place of HF in mixed acid etches.

**Table 10-11** ETCHING REAGENTS FOR ALUMINIUM AND ITS ALLOYS-co\*ntinued

No.	Reagent		Remarks
7	Sodium hydroxide Sodium carbonate (in water)	3%-5% 3%-5%	Useful for sensitive etching where reproducibility is essential. In general, the effects are similar to those of Reagent 5, but the tendency towards color variations for a given constituent is diminished. Particularly useful for distinguishing FeNiAl <sub>9</sub> (dark blue) from NiAl <sub>3</sub> (brown). Potassium salts can be used.
8	Nitric acid Hydrofluoric acid Glycerol	20 ml 20 ml 60 ml	A reliable reagent for grain boundary etching, especially if the alternate polish and etch technique is adopted. The colors of particles are somewhat accentuated
9	Nitric acid, 1% to 10% by vol. in alcohol		Recommended for aluminium-magnesium alloys. Al <sub>3</sub> Mg <sub>2</sub> is colored brown. 5-20% chromium trioxide can be used
10	Picric acid Water	4 g 96 ml	Etching for 10 min darkens CuAl <sub>2</sub> , leaving other constituents unaffected. Like reagent 4
11	Orthophosphoric acid Water	9 ml 91 ml	The reagent is used cold. Recommended for aluminium-magnesium alloys in which it darkens any grain boundaries containing thin β-precipitates. Specimen is immersed for a long period (up to 30 min). Mg <sub>2</sub> Si is colored black, Al <sub>3</sub> Mg <sub>2</sub> a light grey, and the ternary (AlMnFe) phase a dark grey
12	Nitric acid		10 s immersion colors Al <sub>6</sub> CuMg <sub>4</sub> greenish brown and distinguishes it from Al <sub>2</sub> CuMg, which is slightly outlined but not otherwise affected
13	Nitric acid (density 1.2) Water Ammonium molybdate, (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>21</sub> , 4H <sub>2</sub> O	20 ml 20 ml 3 g	20 ml of reagent are mixed with 80 ml alcohol. Specimens are immersed and well washed with alcohol after etching. Brilliant and characteristic colors are developed on particles of intermetallic compounds. The effects depend on the duration of etching, and for differentiation purposes standardisation against known specimens is advised
14	Sodium hydroxide (various strengths, with 1 ml of zinc chloride per 100ml of solution)		Generally useful for revealing the grain structure of commercial aluminium alloy sheet <sup>67</sup>
15	Hydrochloric acid (37%) Hydrofluoric acid (38%) Water	15.3 ml 7.7 ml 77.0 ml	Recommended (30 s immersion at room temperature) for testing the diffusion of copper. Through claddings of aluminium, aluminium-manganese-silicon, or aluminium-manganese on aluminium-copper-magnesium sheet. Zinc contents up to 2% in the clad material do not influence the result <sup>68</sup>
16	Ammonium oxalate Ammonium hydroxide, 15% in water	1 g 100 ml	Develops grain boundaries in aluminium-magnesium-silicon alloys. Specimens are etched for 5 min at 80°C in a solution freshly prepared for each experiment

\* These are isomorphous and the colour depends on the proportion of Mn and Fe.

† Sodium fluoride can be used in place of HF in mixed acid etches.

*Electrolytic etching for aluminium alloys.* In addition to the reagents given for aluminium in Table 10.11, the following solutions have been found useful for a restricted range of aluminium rich alloys:

1. The following solution has been used for grain orientation studies:

Orthophosphoric acid (density 1.65)	53 ml
Distilled water	26 ml
Diethylene glycol monoethyl ether	20 ml
Hydrofluoric acid (48%)	1 ml

The specimen should be at room temperature and electrolysis is carried out at 40 V and less than 0.1 A dm<sup>-2</sup>. An etching time of 1.5-2 min is sufficient for producing grain contrast in polarized light after electropolishing.

2. The solution below is also used for the same purpose and is more reliable for some alloys:

Ethyl alcohol	49 ml
Water	49 ml
Hydrofluoric acid	2 ml (quantity not critical)

The specimen is anodized in this solution at 30 V for 2 min at room temperature. A glass dish must be used. Not suitable for high-copper alloys.

3. For aluminium alloys containing up to 7% of magnesium:

Nitric acid (density 1.42)	2 ml
40% hydrofluoric acid	0.1 ml
Water	98 ml

Electrolysis is carried out at a current density of 0.3 A dm<sup>-2</sup> and a potential of 2 V. The specimen is placed 7.6 cm from a carbon cathode.

4. For cast duralumin:

Citric acid	100 g
Hydrochloric acid	3 ml
Ethyl alcohol	20 ml
Water	977 ml

Electrolysis is carried out at  $0.2 \text{ A dm}^{-2}$  and a potential of 12 V.

5. For commercial aluminium:

Hydrofluoric acid (40%)	10 ml
Glycerol	55 ml
Water	35 ml

This reagent, used for 5 min at room temperature, with a current density of  $1.5 \text{ A dm}^{-2}$  and a voltage of 7-8 V, is suitable for revealing the grain structure after electropolishing.<sup>72</sup>

6. For distinguishing between the phases present in aluminium-rich, aluminium-copper-magnesium alloys, electrolytic etching in either ammonium molybdate solution or 0.880 ammonia has been recommended. In both cases,  $\text{Al}_2\text{CuMg}$  is hardly affected,  $\text{CuAl}_2$  is blackened,  $\text{Al}_6\text{Mg}_4\text{Cu}$  is colored brown, while  $\text{Mg}_2\text{Al}_3$  is thrown into relief without change of color.<sup>73</sup>

## ANODIZING

Etching to reveal the grain structure of aluminium alloys is not always easy. In cases where standard etchants do not reveal the grain structure, anodizing solutions are utilized. Of these, Barker's reagent<sup>67</sup> is the most widely used. This is an electrolytic etching method where an aluminium cathode is used; its area should be substantially greater than the polished surface to be etched. The specimen is the anode and is parallel to the cathode with about a 10-mm spacing. A dc current of 20-45 V is placed across the anode and cathode while they are immersed in the electrolyte, a 1.8% solution of fluoboric acid in water. Voltage is not too critical. Good results have been obtained with 2 minutes of etching at 20 or 30 V dc. This roughens the specimen surface and no color is observed in bright field. Contrary to many publications, Barker's reagent does not create a film at the polished face. High magnification examination of the anodized surface with the SEM reveals a fine roughening. When viewed with polarized light, the grain structure is revealed with grains in different shades from white to black. If a sensitive tint plate is inserted in the light path, then the grains exhibit colors. Anodizing does not reveal chemical segregation ("coring") within the grain structure, only grain orientation differences. There are other anodizing solutions for aluminium, and for other metals (see 152 for a complete listing). Some of these may produce an interference layer but Barker's does not.

## GRAIN COLOR ETCHING<sup>74</sup>

For many aluminium alloys containing copper, and especially for binary aluminium-copper alloys, it is found that Reagent No. 1 of Table 10.11 gives copper films on cubic faces which are subject to preferential attack and greater roughening of the surface. Subsequent etching with 1% caustic soda solution converts the copper into bronze-colored cuprous oxide, and a brilliant and contrasting representation of the underlying surfaces is obtained. The technique is of use in orientation studies in so far as the films are dark and unbroken on (100) surfaces, but shrink on drying on other surfaces. In particular (111) faces have a bright yellow color with a fine network on drying, which has no preferred orientation, while (110) faces develop lines (cracks in film) which are parallel to a cube edge.

## ETCHING TO PRODUCE ETCH PITS<sup>69</sup>

The orientation of crystal grains may be determined by developed etch pits on specimens previously electropolished (*see* Table 10.4). The following reagents develop pits with facets parallel to the (100) cube planes:

	<i>a</i>	<i>b</i>	<i>c</i>
Fuming nitric acid	15 ml	15 ml	47 ml
Pure hydrochloric acid	45 ml	46 ml	50 ml
Hydrofluoric acid	15 ml	10 ml	3 ml
Distilled water	25 ml	29 ml	—

Mixture *c* is recommended where only a few large well-formed etch figures are preferred. Etching with dry gaseous hydrochloric acid gives pits with facets parallel to (111) planes.

### 10.3.2 Antimony and bismuth

#### PREPARATION

Antimony, as usually obtained, is hard and brittle, and easily breaks up into fragments. Mounting in a press may cause fracturing. It is safer to mount specimens in a castable resin. Preparation can be conducted using either the traditional or contemporary methods. Pure antimony is not a commonly encountered metallographic subject but alloys containing Sb are. These are easier subjects than the pure metal. Sb is often present in alloys made up of the low-melting point metals, e.g., Pb, Bi or Cd. These alloys do not respond well to diamond abrasives and are better prepared with the traditional method using candle wax on the SiC papers, especially the fine papers. Embedded SiC particles can be easily removed when polishing with aqueous alumina slurries. Copper alloys may contain antimony as a minor element.

Bismuth is a soft metal, but also brittle, but not very difficult to prepare. The pure metal is encountered less than alloys containing bismuth. The preparation follows the same guidelines as for antimony and for low-melting point alloys containing Bi.

#### ETCHING

1.	(a)	Water	22 ml	Mix equal quantities of (a) and (b) immediately before use ~ 1 min	Sb and Sb-Bi alloys
		HNO <sub>3</sub> (1.40)	8 ml		
	(b)	Water	30 ml		
		Ammonium molybdate	4.5 g		
2.		Water	100 ml	~ 1 min	Grain structure of Sb and Bi alloys
		Citric acid	25 g		
		Ammonium molybdate	10 g		

### 10.3.3 Beryllium

#### PREPARATION

Due to its toxicity, preparation of Be and its alloys is usually restricted to laboratories designed to handle Be and suitable inspected and licensed. Be is not easy to prepare as it is easily deformed (mechanical twinning) by handling. Conventional methods must be modified. All operations which produce Be dust must be done in a glove box. Wet cutting and grinding are absolutely necessary to reduce damage to the specimens and to prevent dust formation. However, the sludge created must be properly disposed. All metallic dusts, regardless of the

chemical element, are dangerous if inhaled but Be dust is among the most dangerous dusts. The metal easily deforms by mechanical twinning, so light loads must be used during grinding and polishing. Some authors claim that water must be avoided, even when grinding Be, while others state that no difficulties were encountered using water as the coolant or lubricant. A four-step procedure can be used to prepare beryllium and its alloys. Start with 320-grit SiC paper (P400), at 4 lbs load (15-20 N), 240-300 rpm, with water cooling, until cutting damage has been removed. Next, use a natural silk cloth with a psa backing and 6- $\mu$ m diamond paste, 120-150 rpm, same load, for 5 minutes. Follow with 3- $\mu$ m diamond paste on a woven polyester cloth, used as in the second step, but for 4 minutes. Final polish with colloidal silica or with the sol-gel alumina suspension, using 3 lb (10-15N) per specimen, 80-120 rpm, for 2 minutes. An attack-polish agent is often added to the final polishing suspension to facilitate damage removal and enhance polarized light response. Aqueous 5% oxalic acid and 30% concentration hydrogen peroxide have been used as the attack polishing agents. Be is difficult to etch and, due to its hcp crystal structure, excellent results are obtained with as-polished surfaces viewed with cross-polarized light.

Other methods of preparation have been discussed,<sup>43, 76</sup> including *electropolishing* (see Table 10.4).

#### ETCHING

- |    |  |                |
|----|--|----------------|
| 1. | Hydrofluoric acid (40%)<br>Ethyl alcohol | 10 ml<br>90 ml |
|----|--|----------------|

On immersion for 10-30s microconstituents are in general outlined, and some colour differentiations are observed. The identifications of constituents commonly met with in commercial beryllium, both in the etched and unetched condition, are as shown in Table 10.12.

- |    |                                |                |          |   |
|----|--------------------------------|----------------|----------|---|
| 2. | Water<br>Sulphuric acid (1.84) | 95 ml<br>5 ml  | 1-15 s   | Be alloys   |
| 3. | Water<br>Oxalic acid           | 100 ml<br>10 g | 2-16 min | Outlines precipitates first then grain boundaries. Better used electrolytically |



**Table 10.12** MICROCONSTITUENTS IN COMMERCIAL BERYLLIUM

<i>Constituent</i>	<i>Appearance unetched</i>	<i>Effect of etching</i>
Carbide	Hard angular grey particles, staining in air to many colours, finally brown	No effect on color
Silicon-rich phase	Light blue grey	Not stained, but outlined
Nitride	Needle-like particles, darker grey than Carbide	Unaffected
TiBe <sub>12</sub>	Angular particles, slightly pink	Unaffected
CaBe <sub>13</sub>	Light yellow, usually angular	Unaffected
FeBe <sub>12</sub>	Almost invisible unetched	Colored reddish brown
MnBe <sub>12</sub>	Similar to iron, but slightly pink	Outlined
Boride	Reddish particles in grain boundaries	Colored blue or purple
MoBe <sub>22</sub>	Almost invisible unetched	Colored chocolate brown
UBe <sub>13</sub>	Invisible unetched	Phase revealed as a yellow or green dendritic structure
Aluminium	Bright yellow, often appearing speckled. Soft and difficult to polish	Outlined
Magnesium	Very soft, and white in appearance	Removed
ZrBe <sub>13</sub>	Barely distinguishable dendritic phase	Outlined and colored light blue

### 10-3.4 Cadmium

#### PREPARATION

The preparation of cadmium for metallographic examination should be carried out in the same manner as for zinc. Cd and its alloys are soft and easily deformed by mechanical twinning if cutting and grinding are too aggressive. When possible, use a precision saw to cut the specimens or a good quality laboratory abrasive cut-off saw. Pure Cd and high-Cd alloys do not respond well to diamond abrasive and it is better to use the “traditional” method of preparation (see Mechanical Polishing), but substitute aqueous alumina slurries for diamond. Grinding with SiC can be continued to grit sizes finer than 600 (P1200) and then polish with 3- and 1- $\mu$ m aqueous alumina slurries, before finishing polishing with colloidal silica (works very well with cadmium). Cd plated steels and other metals can be challenging to prepare as water must be avoided, at least in the final polishing step. Consequently, colloidal silica cannot be used. Final polishing is usually performed with alumina powders mixed in mineral spirits, purified kerosene or ethanol. These are less satisfactory but there is no attack of the coating, as with an aqueous suspension.

*Electrolytic polishing* is satisfactory<sup>25, 34</sup> for pure Cd (see Table 10.4).

#### ETCHING

	<i>Reagent</i>		<i>Conditions</i>	<i>Remarks</i>
1.	Ethanol Nitric acid (1.40)	2 ml 98 ml	Few seconds to a minute	Most alloys Thallium also
2.	Water Hydrochloric acid (1.19) Ferric chloride	100 ml 25 ml 8 g	Up to a minute	Eutectics of Cd
3.	Water	40 ml		

Hydrofluoric acid (40%)	10 ml	5-10 s	Most Cd alloys also thallium and indium
Hydrogen peroxide (30%)	10 ml		

### 10.3.5 Chromium

#### PREPARATION

Pure Cr is soft but brittle; however, plated Cr is hard and brittle and is characterized by an internal crack pattern. Chromium and its alloys are not too difficult to prepare but they are very difficult to etch. Mechanical polishing using the contemporary approach can be followed by a brief electrolytic polish or an attack polish can be used in the last step (*see* Tables 10.3 and 10.4). Hard or decorative chromium plate may be mounted in the thermosetting epoxy resin to enhance edge retention and prepared using the contemporary method. Water is not a problem.

#### ETCHING

**Table 10.13** ETCHING REAGENTS FOR CHROMIUM

No.	Reagent*	Remarks	
1	Dilute hydrofluoric acid	After electropolishing with the reagent listed in Table 10.4, the specimen is agitated for a few seconds in dilute hydrofluoric acid	
2	Hydrochloric acid (concentrated)	Shows striations in electrodeposits	
3	Nitric acid Hydrochloric acid Glycerol	10 ml 20 ml 30 ml	Suitable for alloys. Also used electrolytically; specimen is made anode at 4 V, 45 s. Proportions 1:3:2 also used. This decomposes on standing, especially in contact with stainless steel. <i>Beware!</i>
4	Sulphuric acid (10%)	Used hot with swabbing	

\* Acids are concentrated, unless otherwise indicated.

### 10.3.6 Cobalt

#### PREPARATION

Cobalt and its alloys are more difficult to prepare than stainless steels or nickel-based superalloys and much more difficult to etch. Cobalt is a tough metal with an hcp crystal structure. However, it does not respond well under polarized light. While it is sensitive to deformation by mechanical twinning, this is not as big a problem as with Be or Mg. Preparation of cobalt and its alloys can be done by the contemporary method. Always cut specimens with a high quality laboratory abrasive cutter using a softly bonded wheel, such as used to section Ti. Co cuts slowly, like refractory metals, and can be damaged by aggressive cutting. Two steps of SiC may be needed, but start with as fine a grit as possible, 220- or 240-grit or 320-grit SiC (P240-P400). Three diamond steps are advised with 9-, 3- and 1- $\mu$ m diamond. Final polishing is best conducted using an attack polishing agent added to colloidal silica for up to 3 minutes. An etch-repolish-etch cycle may be needed to remove the last bit of disturbed metal. Some metallographers follow mechanical polishing with a brief chemical polish.

#### ETCHING

Cobalt may be etched with some of the reagents used for nickel and iron alloys, but some alloys are strongly resistant to attack. *See* Table 10.14.

**Table 10.14** ETCHING REAGENTS FOR COBALT AND ITS ALLOYS

No.	Reagent*	Remarks
1	Hydrochloric acid	60 ml
	Nitric acid	15 ml
	Acetic acid	15 ml
	Water	15 ml
The solution should be aged for 1 hour. Grain boundaries and the general structure of alloys are revealed. May also be used electrolytically. Of wide application, including hard metals		
2	Nitric acid	10 ml
	Hydrochloric acid	20 ml
	Glycerol	30 ml
Reveals general structure. May be used electrolytically ( <i>see</i> Table 10.13, Reagent 3. Same precautions		
3	Potassium ferricyanide	10 g
	Potassium hydroxide	10 g
	Water	100 ml
For hard cobalt-chromium alloys containing carbon. Used at approx. 70°C, 10-20 s. Can be replaced by electrolytic 3% KOH. Suitable for carbides		
4	Chromium trioxide	2-10 g
	Sulphuric acid	10 ml
	Water	90ml
Used electrolytically, the specimen being made the anode at 6 V		

\* Acids are concentrated, unless otherwise indicated.

### 10.3.7 Copper

#### PREPARATION

Pure copper is low in hardness, extremely ductile and highly malleable. There are a number of relatively pure Cu grades made with minor differences in deoxidation for electrical applications. Preparation of these grades can be rather challenging, particularly for scratch removal and obtaining a high degree of grain boundary delineation. Cu-Zn alloys (brass) are also difficult to prepare scratch-free and difficult to bring out all the grain boundaries. This is a common problem with all face-centered cubic metals that exhibit annealing twins. Sectioning is a critical step as damage from sectioning can be extensive. The least damaging cutting methods are needed. Damage from band sawing can extend to nearly a mm in depth. Always cut Cu and its alloys with a high quality abrasive cut-off saw with the proper wheel, good coolant and low pressure. Use the contemporary preparation method describe above, and in 154. After careful sectioning, start grinding with the finest possible SiC grit, e.g., 240- or 320-grit, to remove the cutting damage. Do not grind with worn paper. With an automated machine using six specimens at a time, a sheet of SiC paper is worn out (i.e., its removal rate is reduced to a very low value) in about 60 s. For good scratch control, use of the psa-backed selected silk cloth (an Ultra-Pol™ cloth, specifically) in step 2 is critical. Final polishing can be effectively performed using a medium nap synthetic suede cloth (e.g., a Microcloth® pad) without need for an attack polish. Attack polishing agents have been used, and can be helpful, but they are unnecessary if sectioning is done with minimal damage and the contemporary practice is used. To study inclusions, examine the specimens before etching. Tough-pitch copper (Cu – 0.4% O) contains numerous Cu<sub>2</sub>O particles but can also contain copper sulfides. Both types of particles look similar in bright field illumination. Under dark field illumination, the cuprous oxide particles are bright ruby red while the sulfides are invisible. There are several alloys, cast and wrought, with lead additions. These can be easily observed with bright field and are well retained using the contemporary method.

#### ETCHING

Cast copper alloys are easy to etch due to their chemical inhomogeneity, although grain boundaries may be difficult to reveal. Dendrites are usually easily revealed, particularly using color tint etches<sup>152-158</sup>. Most homogeneous copper alloys have much the same etching

characteristics as copper, and the same etching reagents as are used for copper may be tried. Reagents 1 and 2, and several other variations, are widely used to reveal the structure of most coppers and copper alloys. Alloys containing more than one phase usually etch easily, but careful attention must be paid to the time of etching. Most etchants reveal one phase, but not the other. Etchants can be used to selectively color or darken specific phases in metals and alloys<sup>162</sup>, and Cu alloys are no exception. For example, when alpha-beta alloys are etched, such as naval brass, there are a few etchants that will color or darken the alpha phase only, many that will darken only the beta phase, and a few that will color both alpha and beta. For example, equal parts of NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> (3% conc.) will darken the alpha phase; Klemm's I (see Table 10-6) will color beta phase; and, Beraha's selenic acid reagent for copper (similar to etch 1 in Table 10-7, but 300 ml ethanol) will color both phases. There are a number of excellent color "tint" etchants for copper and its alloys<sup>152,154</sup> and these are very useful for Cu alloys.

**Table 10.15** ETCHING REAGENTS FOR COPPER AND ITS ALLOYS

<i>Principal use</i>	<i>No.</i>	<i>Reagent</i>	<i>Remarks</i>
Copper, copper alloys in general. Brass, bronze and nickel-silver	1	Ammonium hydroxide 50 ml Water 50 ml Hydrogen peroxide (30 vol.) 20 ml	Used for copper, and many copper-rich alloys. Gives a grain boundary etch, and also tends to darken the $\alpha$ solid solution, leaving the $\beta$ solid solution lighter. The hydrogen peroxide content may be varied. Less is required the lower the copper content (see Reagent 2)
	2	Ammonium hydroxide 50 ml Water 50 ml Hydrogen peroxide (30 vol.) 10 ml	Used for bronze, 70:30 and 60:40 brasses; this etch may with advantage be followed by a ferric chloride etch (Reagent 6) to darken the $\beta$ areas in duplex alloys
	3	Ammonium hydroxide 10 ml Water 10 ml Ammonium persulphate, 2 1/2 % solution 10 ml	Recommended for polish attack on copper and copper alloys
	4	Ammonium persulphate 10 g Water 100 ml	Used cold or boiling for copper, brass, bronze, nickel-silver and aluminium-bronze. Tends to produce relief effects. Good for aluminium bronzes followed by Reagent 23 to darken $\beta$ martensite (retained $\beta$ is pink) and then Reagent 24 to etch $\gamma_2(\delta)$ brown
	5	Dilute ammonium hydroxide solution (10-50%)	May be used for polish or swab attack on brass and bronze. The oxidising action of atmospheric oxygen is necessary for the process
	6	Ferric chloride, various strengths and compositions. To 100 parts of water are added: Hydrochloric acid (1.19) Ferric chloride (g) 20 1 10 5 50 5 25 8 6 19 25 25 1 10† 10 3‡	Used as a general reagent for copper, brass, bronze, nickel-silver, aluminium-bronze and other copper-rich alloys. It darkens the constituent in brasses and gives grain contrast following ammoniacal or chromic acid etches. The most suitable composition should be found by trial and error in specific cases. This reagent generally emphasizes scratches in imperfectly prepared specimens, and tends to roughen the surface. For sensitive work it is frequently a great advantage to replace the water in the reagent by a 50:50 water-alcohol mixture or by pure alcohol

† Usually used with 1 part of chromic acid CrO<sub>3</sub>

‡ Used with 1 part of cupric chloride and 0.05 parts of stannous chloride.

**Table 10-15** ETCHING REAGENTS FOR COPPER AND ITS ALLOYS-continued

<i>Principal use</i>	<i>No.</i>	<i>Reagent</i>	<i>Remarks</i>
Copper, copper alloys in general. Brass, bronze and nickel-silver	7	Ethyl alcohol (commercial) 96 ml Ferric chloride (anhydrous) 59 g	Dilute 5:1 with alcohol. Wash with alcohol or acetone. More delicate and controllable than aqueous solutions

(continued)

	Hydrochloric acid	2 ml	
8	Chromic acid CrO <sub>3</sub> saturated in water		Used for copper, brass, bronze and nickel-silver. The etching time is 1 to 1 ½ min. Grain boundaries are attacked and β constituents are coloured pale yellow, while the primary solid solution is coloured dark yellow
9	Chromic acid, 100-150 g l <sup>-1</sup> of water, 1-2 drops of hydrochloric acid are added immediately before use to a 50 ml portion		Used for copper, brass, bronze, nickel-silver, and recommended for revealing the silicides of Ni, Co, Cr and Fe in certain alloys. Alternate polishing and etching is recommended when a grain contrast is obtained. The primary solid solution is not attacked. The β copper-zinc phase is coloured light yellow while the δ copper-tin phase is coloured brown to black. The reagent may be followed by a ferric chloride etch
10	Chromic acid Nitric acid (1.40) Water	25 g 40 ml 35 ml	This reagent is useful for distinguishing the general constituents of many copper alloys. The γ and δ phases are particularly well shown up as shining blue crystals
11	Sulphuric acid (1.84) Potassium dichromate saturated in water	5 ml 100 ml	Etching time ½ to 1 min. Suitable for copper, but attacks oxide inclusions strongly
12	Nitric acid, various strengths		Used for any purpose requiring deep etching and the removal of a thick layer of surface material. The times of etching are short and difficult to control
13	Sulphuric acid (1.84) Hydrogen peroxide (10 vol.)	5 ml 100 ml	Etching time is to 1-1 ½ min. Used for pure copper, but attacks oxide
14	Silver nitrate, 100 g l <sup>-1</sup> of water, following exposure to hydrogen sulphide		This technique has been used for 70:30 and 60:40 brasses, and produces satisfactory contrast
15	Silver nitrate, 20 g l <sup>-1</sup> of water		Immerse for 30 s, and wash off silver stain under water. Useful in certain cases for pure copper
16	Ammonium hydroxide Ammonium oxalate saturated in water	10 ml 30 ml	Used for high-zinc brasses
17	Ammonium hydroxide Potassium arsenate saturated in water	10 ml 30 ml	Used for high-zinc brasses
18	Copper ammonium chloride. 100 g l <sup>-1</sup> of water, plus ammonium hydroxide to slight alkalinity		Copper, brass and nickel-silver. Specially recommended for darkening large β areas in duplex brasses
19	Ammonia Potassium permanganate (0.4%) in water	20 ml 30 ml	Used for pure copper. Etching time 2 to 3 min. Liable to produce staining
20	Bromine water, saturated		Etching time 30 to 60 s. May be used, satisfactorily with pure copper if the coating which forms is removed by washing in strong ammonia

Table 10.15 ETCHING REAGENTS FOR COPPER AND ITS ALLOYS--continued

Principal use	No.	Reagent	Remarks
Aluminium-bronze	4	See above	As for Reagent 4
	6	See above	As for Reagent 6. Darkens
	10	See above	As for Reagent 10. Also generally useful for aluminium-bronzes
	21	Chromic acid 20 g Nitric acid (1.40) 50 ml Water 30 ml	Recommended for aluminium-bronze after pretreatment with 10% hydrofluoric acid solution in order to remove surface oxide films
	22	Chromic acid 20 g Nitric acid (1.40) 5 ml Water 75 ml	As for Reagent 21
	23	Nitric acid (1.40) 0.5 ml Hydrogen peroxide (100 Vol.) 99 ml	Darkens martensite
	24	Sod. hydroxide 10 g Water 100 ml	$\gamma_2$ ( $\delta$ ) etched brown
Aluminium-bronze	25	Ferric nitrate 20 g Ammonium nitrate, 20 g Nitric acid 2 ml Water 500ml	Good for complex aluminium bronzes
	26	Ammonium hydroxide 25 ml Water 25 ml Hydrogen peroxide 3% solution 20 ml	Age 1 week in loosely stoppered bottle before use. To distinguish eutectoid ( $\alpha + \gamma_2$ ) from acicular $\beta$ - $\gamma_2$ attacked
Copper alloys with beryllium, silicon, manganese and chromium	8	—	As for Reagent 8. Is also useful for manganese bronze
	27	Potassium dichromate 2 g Water 100 ml Sodium chloride (saturated) 4 ml Sulphuric acid (s.g. 1.84) 8 ml	Used for copper, and copper alloys with beryllium, manganese and silicon. Also suitable for nickel-silver, bronzes and chromium-copper alloys. This reagent should be followed by a ferric chloride etch to give added contrast
High-nickel alloys	28	Nitric acid (s.g. 1.42) 50 ml Glacial acetic acid 25 ml Water 25 ml	Recommended for high-nickel alloys which might prove resistant to attack by the more usual reagents, and for bright copper electro-deposits. 1:1 nitric acid : acetic acid is also used
Copper-nickel-aluminium	29	Acetic acid, 75% 30 ml Nitric acid 20 ml Acetone 30 ml	Recommended for copper-rich copper-nickel-aluminium alloys. NiAl shows as dove-grey rectangular needles; Ni <sub>3</sub> Al is globular and darker grey. The $\gamma_2$ phase of the aluminium-copper system is a pale grey; see also Reagent 24
Copper-silicon alloys	30	Hydrogen peroxide (30 vol.) 20 ml Water 25 ml Potassium hydroxide (20%) 5 ml Ammonium hydroxide (s.g. 0.90) 50 ml	Used specifically to distinguish the $\kappa$ phase in copper-silicon alloys, and in ternary and more complex alloys based on this system.
Leaded copper and bearing metals of this material	31	Nitric acid 20 ml Glacial acetic acid 20 ml Glycerol 80 ml	General reagent for leaded copper, bronzes, etc. See below for further notes on leaded coppers. Darkens lead
	32	Trichloroacetic acid 20 g Water 20 ml Ammonium hydroxide to make 100 ml	As for Reagent 31. Etches and outlines lead constituent, bringing it into prominence. Monochloroacetic acid may be substituted

Table 10.15 ETCHING REAGENTS FOR COPPER, AND ITS ALLOYS--continued:

Principal use	No.	Reagent	Remarks
Macro-etching	33	Heat tinting	This technique occasionally gives useful results. Phosphor bronzes react the most favourably
	34	No-etching	Several constituents which may be present may be observed in unetched sections. Thus the selenide and telluride, appear blue grey, while the oxide appears blue. Metallic bismuth appears a very pale blue grey. Cuprous oxide, unless the particles are very small, appears ruby-red in polarised light or with dark-field illumination; selenide and telluride remain dark. Zinc oxide (in brass) appears transparent and anisotropic in polarised light, blue-grey with ordinary illumination

## LEADED COPPER ALLOYS

Difficulties can arise in the preparation and examination of leaded alloys, owing to the different hardnesses of the constituents, and also because specimens are particularly susceptible to smearing of the lead over the copper matrix. The contemporary method of preparation, as described above and in the section on Mechanical Polishing, works well on leaded brasses and bronzes. It may be helpful, if there is any flowed metal after polishing, to lightly etch the specimen, then repeat the final polishing step before examination. Colloidal silica is quite good for minimizing smeared surface metal and works well with leaded bronzes. If it is necessary to etch, Reagents 31 and 32 of Table 10.15 may be used to etch the lead, or ferric chloride or chromic acid reagents to attack the copper-rich matrix.

The dithizone process described under *Iron and steel* (p. 10-XX, 10-XX) is also applicable to brasses. (See also *Electrolytic etching*, below.)

## ELECTROLYTIC ETCHING OF COPPER ALLOYS

Copper alloys are particularly suitable for electrolytic etching, and this technique frequently gives good results with alloys (e.g., high-nickel alloys) which are otherwise difficult to etch. Solutions which have been found effective are given in Table 10.16; potential differences and current densities must be adjusted to suit specific materials. Reagents listed for electrolytic polishing of copper (Table 10.4) may also be tried (at about one-tenth the voltage).

A very sensitive etching of homogeneous copper alloys may be obtained by electrolytically polishing in phosphoric acid solution ( $1000\text{g l}^{-1}$ ), and short-circuiting the electrodes when polishing is complete. The polarisation current set up gives anodic action at the crystal boundaries only.

Table 10.16 ELECTROLYTIC ETCHING OF COPPER ALLOYS

Principal use	No.	Reagent	Remarks	
General	1	Ferrous sulphate	30 g	May be used to develop contrast after the use of ammoniacal hydrogen peroxide reagents. $\beta$ in brasses is darkened. A current density of $0.1\text{ A dm}^{-2}$ at 8-10 V is suitable
		Sodium hydroxide	4 g	
		Sulphuric acid (1.84)	100 ml	
		Water	1900 ml	
Cupro-nickel and Nickel-silvers	2	Citric acid	100 g/l	Also useful for brasses
	3	Ammonium molybdate in excess of ammonia		Also useful for brasses

Brasses	4	Glacial acetic acid Nitric acid (1.40) Water	5 ml 10 ml 85 ml	This reagent tends to minimize the effect on the microstructure of the coring which usually occurs with these alloys
	5	Ammonium acetate 100 g l <sup>-1</sup> of water		Current density 0.3 A dm <sup>-2</sup>
	6	Ammonium sulphate 10 g l <sup>-1</sup> of water		Current density 0.3 A dm <sup>-2</sup>
	7	0.10 M ammonium acetate 0.50 M sodium thiosulphate 14 M ammonium hydroxide Distilled water	10 ml 30 ml 30 ml 30 ml	Carried out at 31 A dm <sup>-2</sup> . The etching time is approximately inversely proportional to the copper content of the material

**Table 10.16** ELECTROLYTIC ETCHING OF COPPER ALLOYS -continued

<i>Principal use</i>	<i>No.</i>	<i>Reagent</i>		<i>Remarks</i>
	8	Chromic acid CrO <sub>3</sub> 170 g l <sup>-1</sup> of water		Useful for distinguishing the $\gamma$ and $\epsilon$ phases of the copper-zinc system. At current densities above 23A dm <sup>-2</sup> the $\gamma$ phase is attacked, but not the $\epsilon$ phase. At low current densities the order of the attack is reversed. The zinc-rich solid solution is attacked under both conditions.
Aluminium-bronze and copper-beryllium alloys	9	Chromic acid Water	10 g 900 ml	This reagent is satisfactory for all stages of heat treatment, and is useful for following the stages of precipitation in the age-hardening of copper-beryllium alloys. Distilled water must be used as tap water leads to staining. A potential of 6 V, with an aluminium cathode, is satisfactory
Leaded copper and brass	10	Dilute sulphuric acid (up to 10% by vol.)		Electrolytic etching at 6 V, with a carbon cathode, has been recommended for lead-bearing copper and brass, in order to avoid misinterpretation of the structure due to surface flow

## 10.3.8 Gold

### PREPARATION

Gold and its alloys, as well as the other precious metals, are very soft, easily deformed (they are exceptionally malleable), and are quite difficult to prepare for metallographic examination. Control of deformation, smeared metal and scratch removal is a challenge. As one might expect, they are among the most difficult metals to etch due to their great corrosion resistance. Embedding of abrasive can be a problem with precious metals. Nevertheless, they can be prepared using a variation of the contemporary practice.

Sectioning must be done with a good metallographic laboratory cut-off saw, with a precision saw, or a low-speed saw, with the proper blade and low pressure to minimize the depth of damage. Gold and its alloys can be mounted in a thermosetting resin or in cast epoxy. Start by grinding with 220-, 240- or 320-grit SiC (P240 to P400) waterproof paper, 3 lbs (10-15 N) load per specimen, 150-250 rpm, with water cooling, until the cutting damage has been removed. Polishing is done only with diamond paste using the chemotextile pads (known variously as Texmet® 1000, Pellon or Pan W), with only a minor amount of water as the lubricant. The waxiness of the carrier in the paste will be the main lubricant. Loads in all steps are low, as in the SiC step, at 3 lbs per specimen. The rotational speed is in the range 150-250 rpm. Use three



diamond steps in this way with 9-, 3- and 1- $\mu\text{m}$  diamond paste for 5, 3 and 2 minutes, respectively.

Final polishing is conducted using a polyurethane pad, such as a Chemomet® pad with the 0.05- $\mu\text{m}$ , sol-gel alumina suspension (Masterprep alumina) at 2 lbs (10 N) per specimen, 100-150 rpm, for 2 minutes. Colloidal silica is useless with precious metals. Its amorphous silica particles are spherical in shape and produce little, if any cutting action, while its pH of 9.5 – 10 is inadequate to yield a chemical attack-polish action. Ordinary calcined alumina abrasives do not yield as good a surface finish as the sol-gel alumina. For high Au content specimens, such as 18-karat gold and higher ( $\geq 75\%$  Au), it is necessary to add an attack polish agent to the suspension for scratch removal. Several attack polishing agents can be used.  $\text{CrO}_3$  in water is excellent and has been used in several concentrations from 5 to 20 g per 100 ml of water. This solution does contain undesirable  $\text{Cr}^{+6}$  ions which may pose a problem with its disposal (consult your local regulations on how to properly dispose of the residue). Hydrogen peroxide (30% conc.) presents few environmental disposal problems and also works well. Generally, the attack polishing agent is added to the sol-gel alumina slurry in a 1:5 ratio by volume. If the slurry thickens too much, add some distilled water. When an attack polishing agent is used, the operator must avoid any physical contact with the abrasive and must properly clean up the equipment after use so that residues of it do not affect the next user of the equipment. It is advisable to wear proper personal protective equipment. When the attack polishing agent must be used, due to the higher purity of the alloy, polishing may be conducted for 3-6 minutes.

## ETCHING

Etching of gold and its alloys, and all precious metals, is challenging due to their great corrosion resistance. Etch 1 works well with gold, but its use is unusual. The two solutions must not be pre-mixed. One person holds the specimen with tongs and a tuft of cotton with a second pair of tongs. Another person takes two eyedroppers and fills each with one of the solutions. That person then drips equal amounts of the two etchants onto the specimen surface while the first person swabs the surface. Dripping and swabbing is continued until the correct degree of etching has been obtained. This must be done over something that will collect anything that drips from the specimen, so it requires careful pre-planning and execution.  $\text{NaCN}$  can be used in place of  $\text{KCN}$  and hydrogen peroxide (30% conc.) can be substituted for the ammonium persulfate solution with equivalent results. But, this etch becomes less effective for gold contents above 18 karat.

## ETCHING

The five solutions given in Table 10.17 are of general suitability.

**Table 10.17** ETCHING REAGENTS FOR GOLD AND ITS ALLOYS

No.	Reagent		Remarks
1	Potassium cyanide, 10% in water	10 ml	Used for gold and its alloys. A fresh solution, warmed if necessary, must be used for each experiment. The etching time varies from ½ to 3 min. The attack may be speeded up by the addition of 2% of potassium iodide, but this is liable to give staining effects
	Ammonium persulfate, 10% in water	10 ml	
2	Tincture of iodine, 50% solution in aqueous potassium iodide		Used for gold alloys. With silver-gold alloys a silver iodide film may form. This may be removed by immersion in potassium cyanide solution

Table 10.17 ETCHING REAGENTS FOR GOLD AND ITS ALLOYS-Continued

No.	Reagent	Remarks
3	Aqua regia (20 ml conc. nitric acid + 80 ml conc. hydrochloric acid)	The hot solution is used. If much silver is present a silver chloride film may form; this may be removed by ammonium hydroxide or potassium cyanide solutions. Use fresh only; liable to decompose with evolution of chlorine and NO <sub>2</sub>
4	Potassium sulphide solution	Solution used hot; particularly useful for gold-nickel alloys
5	Chromic acid (chromium trioxide) Hydrochloric acid (1.19)	3 g Gold-rich alloys (up to 1 min)

## ELECTROLYTIC ETCHING OF GOLD

The microstructure of gold may be developed by anodic treatment in concentrated hydrochloric acid to which a little ferric chloride has been added. Dilute solutions of hydrochloric acid, potassium cyanide or potassium cyanide plus potassium iodide may also be used.

### 10.3.9 Indium

#### PREPARATION

The pure metal and many of its alloys are very soft and should be prepared by the methods recommended for lead or cadmium. It is frequently sufficient to cut suitable specimens with a sharp razor blade; however, the damage introduced must be removed. Pure In and its alloys can be more difficult to prepare than lead and its alloys, although some In-based intermetallic compounds are relatively easy to prepare. See the discussions on preparing Cd or Pb.

#### ETCHING

Etching reagents containing hydrofluoric acid, nitric acid, or mixtures of the two acids, are in general satisfactory, and the following are recommended for indium-rich alloys:<sup>77, 78</sup> Vilella's reagent for steels, etch 2 (below) has been used successfully.

1.	Potassium dichromate	1.3 g	
	Sulphuric acid conc. (1.84)	4.5 ml	
	Saturated sodium chloride solution	2.7 ml	
	Hydrofluoric acid (40%)	17.7 ml	
	Nitric acid conc. (1.40)	8.8 ml	
	Water	66.3 ml	Use up to 1 min
2.	Hydrochloric acid (1.19)	20 ml	
	Picric acid	4 g	
	Ethyl alcohol	400 ml	

For alloys containing bismuth it is necessary to increase the proportions of alcohol and hydrochloric acid.

### 10.3.10 Iron and steel

#### PREPARATION

Iron and low-carbon steels are more susceptible to surface deformation during preparation than higher alloyed steels and tool steels so sectioning and grinding must be carefully performed. The development of excessive heat at the surface must be avoided. Pure iron, and sheet steels, are soft and ductile. Removing all deformation and scratches is difficult because the structure is mainly ferrite. Higher hardness steels are easier to deal with and are more forgiving. However, some of the highly alloyed stainless steels can be rather challenging. It is not uncommon to see deformation-induced martensite in an austenitic stainless steel due to overly aggressive preparation. Preparing tool steels is usually easy, but there are situations where they can be quite difficult; for example, preparing as-quenched specimens or over-austenitized specimens. An as-quenched tool steel frequently exhibits hardnesses in the 60-70 HRC range. Sectioning must be done with the greatest care, low pressure and a very softly bonded wheel, to avoid introducing heat, or worse yet, burning. Some metallographers prefer to break the specimen in three-point bending to avoid the heat introduced during cutting an as-quenched tool steel. Over-austenitized tool steels generally contain excessive amounts of retained austenite because more carbon than desired was put into solution, which depresses the martensite start and finish temperatures. Excessive heat generated in section and grinding, and even polishing, can alter the retained austenite content. Austenitic stainless steels must be cut with low applied pressure as they can be work hardened dramatically. Hadfield manganese steels, also austenitic, have an even greater ability to be work hardened. Austenitic Fe-Ni magnetic alloys can be very difficult to prepare scratch free. Graphite retention is a problem with certain cast iron grades (gray iron, compacted graphite iron, ductile iron, malleable iron). Metallographers used to advocate grinding specimens with SiC paper up to 600-grit with water as the coolant, and then repeat the 600-grit step without water, claiming this enhanced graphite retention. That approach is unnecessary. A four or five step contemporary practice (see Mechanical Polishing), gives perfect surfaces with excellent graphite retention. White cast iron is easier to prepare but one must avoid any procedure that would create relief, that is, height differences between different phases. The use of the hard, woven napless cloths or synthetic napless pads in polishing ensure that relief is absent, when the correct load is used.

Galvanized steel (Zn coated) is a frequent metallographic subject. Final polishing steps must be performed without water, or the Zn coating will be heavily attacked. A similar technique may be employed for tin-plate, although Sn-coated layers are thinner and more difficult to study by light microscopy, and for Cd-coated steels (see section on cadmium).

The contemporary preparation practice works very well for irons and steels (see Mechanical Polishing). This practice can be altered depending upon needs and materials being prepared. Rigid grinding disks can be used for steps 1 or 2. For example, high hardness tool steels and alloy steels can be prepared perfectly in as little as three steps. Step 1 uses SiC paper for grinding to remove the cutting damage. Grits from 120-320 (P120-P400) can be used. Step 2 uses the BuehlerHercules H disk, or equivalent, with a 3- $\mu\text{m}$  polycrystalline diamond suspension at 120-150 rpm, 6 lbs (25-30N) load per specimen, for 5 minutes. Step 3 uses either a 0.05- $\mu\text{m}$  sol-gel alumina suspension (e.g., Masterprep alumina), or 0.05- $\mu\text{m}$  colloidal silica at 120-150 rpm, same load, for 5 minutes on either a medium nap synthetic suede cloth (e.g., a Microcloth pad), or a polyurethane pad. If the specimens are mounted in the thermosetting epoxy resin, with a modern mounting press that cools the specimen under pressure after polymerization so that there are no shrinkage gaps, then edge retention will be superb despite the 5 minute time, even if the medium napped cloth is used.

## MICROGRAPHIC CONSTITUENTS OBSERVED

The metallography of iron and steel is complex, and the various constituents likely to be observed may be very briefly summarized as follows:

1. *Ingot iron and wrought iron.* These consist mainly of *ferrite* ( $\alpha$ -iron; body centered cubic crystal structure), the etching characteristics of which may be affected by phosphorus, manganese or silicon in solid solution, or by the presence of slag inclusions (wrought iron is no longer made commercially). Carbon is usually present in low amounts, and is revealed as *cementite* (iron carbide,  $\text{Fe}_3\text{C}$ ). Sulfur may be present as *iron sulfide* if Mn is not present, but otherwise as *manganese sulfide*. Several other forms of relatively pure iron are made, such as: *electrical iron*, *interstitial-free steel*, and sheets steels of various compositions. These are all essentially ferritic in content with minor amounts of nonmetallic inclusions and cementite. Dual-phase sheet steels have a more complicated structure, as they contain small grains consisting of martensite and retained austenite.

2. *Normalized and annealed carbon steels.\** The microconstituents present vary according to the carbon content. Below 0.8% of carbon, specimens consist of *ferrite* and a interlamellar eutectoidal mixture of *ferrite* and *cementite* which is known as *pearlite*. At 0.8% of carbon, specimens are entirely *pearlitic*. Above 0.8% carbon, the constituents are a network of massive *cementite* surrounding *pearlitic* areas. Normalized and annealed steels (<0.8% C) differ in the character and extent of the pearlitic areas, which are usually coarser in the latter case. Very rapid cooling gives very fine, unresolvable (by LOM) pearlite. Very slow cooling gives a coarse, easily resolved interlamellar spacing in the pearlite. Special annealing cycles can “spheroidize” the cementite leading to the formation of *globular cementite*, producing a softer, more ductile condition than offered by fine pearlite. Prolonged heating of high carbon steels at 600-800°C decomposes cementite into *ferrite* and free *graphite*, which must be considered as a possible constituent.

3. *Hardened and tempered carbon and alloy steels.* At a high temperature (above that at which the transformation of  $\alpha$ - into  $\gamma$ -iron takes place), carbon steels consist of *austenite*, a solid solution of carbon in  $\gamma$ -iron. Some austenite can be retained in highly alloyed steels, such as tool steels, depending upon the austenizing temperature used in heat treatment. In most steels a variety of decomposition products may arise depending on the severity of quenching locally, the alloy content (“hardenability”), and the section size. The structures obtained are:

- (a) Martensite, which requires rapid quenching (the rate required is a function of the steels hardenability and the section size). In high-carbon steels, particularly when too much carbon is put in solution, this structure appears as an intersecting system of parallel or lenticular “needles” (often called, erroneously, “acicular” martensite). In high-carbon steels, particularly when over-austenitized, some residual austenite may be retained in between the “needles”. The three-dimensional shape, however, is not acicular but looks like two dinner plates facing each other, hence, the more correct name, “plate” martensite. Electron microscopy is needed for a detailed study of martensite. Plate martensite exhibits a mid-rib and is highly dislocated. In low-carbon alloy steels and maraging steels, *lath martensite* is formed that has a parallel-banded structure containing high densities of dislocation. Medium-carbon steels have mixtures of lath and plate martensite. When the prior-austenite grain size is fine, as it should be, the structure of martensite is difficult to reveal with the light microscope.
- (b) Bainite is formed at lower rates of quenching. It is a non-lamellar aggregate of ferrite and cementite.

*Upper bainite* comprises bundles of parallel laths of ferrite between which carbide precipitates. It can form by continuous cooling, or during isothermal decomposition of austenite at 400-500°C (it is usually easier to discern bainite types that are formed isothermally). It etches up more darkly, the lower the temperature at which it forms, but the structure is only seen in clear detail by electron microscopy.

\* By ‘normalizing’ is meant the reheating of a steel to a temperature at which it consists of a solid solution of carbon in  $\gamma$ -iron, followed by free cooling in air. By ‘annealing’ is meant the reheating of a steel to a similar temperature for an appreciable time, followed by slow cooling, usually in a furnace.

*Lower bainite* is more usually found in alloy steels with high Cr, Ni and/or Mo contents that were quenched too slowly to form fully martensitic structures or were isothermal transformed to deliberately form lower bainite. Like upper bainite, it is diffusion controlled but forms at lower temperatures, usually below 350°C. It is difficult to distinguish from a tempered martensite by optical examination and needs electron microscopy for full identification. It is acicular or plate-like with subsidiary plates or needles nucleated from existing plates (unlike upper bainite, which is nucleated from austenitic boundaries). Lower bainite comprises ferrite plates or needles with carbides precipitated internally on one orientation. (In tempered martensite, two or more orientations of carbides are found.) Lower bainite is also free from twins.

- (c) Pearlite. This is a lamellar eutectoid of iron and cementite, the spacing of which is dependent on the temperature at which it forms. It nucleates as nodules which grow from prior-austenitic grain boundaries or in low-carbon steels from ferrite/austenite interfaces.
- (d) In alloy steels, manganese sulfides are present, not iron sulfide, which would melt at ordinary hot working temperatures and cause "hot shortness".
- (e) In cast irons, similar structures are found, but the higher carbon content results in either primary cementite or flakes of graphite depending on alloy content and/or cooling rate. Graphite can also be present as a eutectic or as nodules. By careful preparation, the internal structure of graphite can be revealed by polarized light. Phosphorus introduces a characteristic eutectic of ferrite and  $\text{Fe}_3\text{P}$  or a ternary eutectic with  $\text{Fe}_3\text{C}$  called Steadite.

## ETCHING OF IRON, STEEL AND CAST IRONS

Etching reagents are used for many purposes, such as:

1. To reveal the general structure of the steel for which a few reagents can be used for most steels.
2. To differentiate between various carbides or to differentiate carbides from nitrides (remain unetched). For these an enormous variety of quite complex reagents has been developed. It may be difficult to reproduce the effects claimed by those skilled in the use of these reagents, particularly the colors produced. Some of these reagents are used hot. In general, most reagents are based on an alkaline solution containing a mild, oxidizing reagent and a chemical likely to cause selective staining of the minor phases. Phenolic mounts do not hold up well in boiling reagents, but the thermosetting epoxy resins, such as Epomet resin, are not degraded. In Table 10.18 a few tried and reliable etches are given which should be used before considering the more complex etches in the literature.
3. To reveal the prior-austenite grain boundaries in heat treated steels. The most successful etch is water saturated with picric acid plus a wetting agent. Sodium dodecylbenzene sulfonate is very effective. A small teaspoon full is added to about 200 ml of the solution. The tridecyl version is also very effective as the wetting agent, but is harder to obtain. If the steel contains some Cr, it may be necessary to add a few drops of HCl per 100 ml of the etch. This etch works only when there is P in the steel, usually  $>0.005\%$  is needed. The phosphorus segregates to the austenite grain boundaries during austenitization. Good results are obtained with as-quenched steels and with steels tempered up to about  $550\text{ }^\circ\text{C}$ . Tempering in the range of about  $350\text{-}550\text{ }^\circ\text{C}$  will also drive P to the prior-austenite grain boundaries, with the maximum rate at about  $454\text{-}482\text{ }^\circ\text{C}$ . This etch is less effective or ineffective for steels with less than about  $0.2\%$  C. Reference 152 describes the use of etchants for revealing prior-austenite grain boundaries in great detail and lists many etchants for this purpose.
4. To reveal a phase selectively or to reveal segregation or dendrites in castings. These are specialized tasks that can often be done effectively with color etchants. In stainless steels, one might want to preferentially color or darken delta ferrite so that it can be

measured. Other such phases include sigma and chi. In quality studies, a longitudinal section might be prepared to evaluate the degree of chemical segregation. In carbon and alloy steels, segregation might promote a banded, or layered pattern of alternating ferrite and pearlite, and in the pearlitic band other constituents, such as bainite and martensite, might be observed. In heat treated steels, the structure may be fully martensitic, nevertheless, chemical variations can be detected. In austenitic stainless steels, chemical variations can be detected in fully austenitic structures. To achieve these goals, color tint etches are used. Dendritic structures in cast steels and cast irons are well revealed using color etchants.

- To reveal austenite grain boundaries in austenitic stainless steels, Fe-Ni magnetic alloys or austenitic Hadfield manganese steels. This requires special etchants. When annealing twins are present, it would facilitate grain size measurement if the twins were not revealed while bring up the grain boundaries. This is possible in basic austenitic stainless steels using 60% HNO<sub>3</sub> in water, 20 °C, 1.4 V dc, Pt cathode, 60-120 s. Other less noble materials work for the cathode, but voltage control may be different. If the voltage increases, twins will be revealed. This etch also has the advantage of revealing virtually all of the grain boundaries, while “standard” stainless steel etchants used by immersion or swabbing, do not reveal a high percentage of the grain boundaries, and also bring up twin boundaries (this makes grain size measurements more difficult).

## LEAD IN STEELS

Lead particles in free-cutting steels can be revealed by three reagents:

- |    |   |  |
|----|---|--|
| 1. | 10% ammonium acetate in water,  | Brown stains on lead particles after 30 s immersion.   |
| 2. | 30 g potass. dichromate<br>225 ml water (hot to aid solution)<br>30 ml acetic acid added to cold solution | 10-20 s etch reveals lead as yellow to gold particles under cross-polars with polarized light. (Steel not etched)  |
| 3. | 1 g potassium cyanide<br>100 ml water, mixed with<br>0.25 g diphenyl diacarbazon<br>in 10ml chloroform    | Etch first in picrate. Rinse and dry. Then swab with this solution. Lead colored red, especially under polarized light. Note: this is a very dangerous etch and some of the ingredients may be illegal to use. |

The general distribution of lead can be displayed by the following:

- Etched ground surface in nitric acid, wash and dry.
- Cover for 5 min with absorbent paper soaked in mixture of 50% glacial acetic acid and 50% of 10% chromium trioxide in water.
- Strip paper and wash with 10% acetic acid leaving yellow lead chromatic coloration. Wash with water.
- Develop paper in either the third etchant above or in 1% potassium cyanide in 100 ml water plus 10 ml of 0.1% solution of dithizone in chloroform. After washing and drying, the distribution of lead is indicated by red spots. (This is generally applicable to distribution of lead in metals, e.g. in brasses.)

Today, most metallographers examine leaded steels with the SEM using a backscattered electron image, as the strong atomic number contrast produces excellent images.

## INCLUSIONS AND PRECIPITATES IN STEEL

Many of these can be recognized by shape and color without etching and can be identified positively by EDAX analysis on scanning electron microscopes. The following notes are a useful guide to a quick optical assessment.

Iron phosphide	Brilliant white, especially in cast irons. Distinguished from cementite ( $\text{Fe}_3\text{C}$ ) by alkaline potassium ferricyanide (Murakami's reagent) which darkens phosphide before cementite or by alkaline sodium picrate which darkens cementite.
Iron nitride	Bluish grey. Not attacked by alkaline potassium ferricyanide. Colored yellow in 4% picric acid in ethanol.
Iron sulfide	Brownish yellow (only present in steels made before the 20 <sup>th</sup> C)
Manganese sulfide	Dove grey. Ferrous sulfide is attacked by 1% oxalic acid in water; manganese sulphide is attacked by 10% chromic acid in water. Both deformed by hot rolling.
Chromium oxide	Dark bluish grey; brilliant green under polarized light (crossed polars)
Silicates	Iron silicate dark grey; manganese silicate somewhat lighter, greenish tint. Often glassy as spheres (as-cast condition) which show 'optical cross' under polarized light.
Titanium nitride	Sections of golden yellow cubes. If large amounts, dendritic growth from corners of cube but this is rare
Zirconium nitride	As TiN but more lemon yellow
Alumina	Angular particles in groups not elongated by rolling, usually bluish gray.
Silica	Dark angular particles, often not elongated by rolling (only sand entrapped in a casting will contain silica.

## FERROMAGNETIC ANALYSIS

To distinguish between magnetic and non-magnetic phases, e.g. ferrite from austenite in iron-chromium-nickel alloys, a thin film of a colloidal suspension of magnetic particles is applied to the surface of a specimen subject to a magnetic field. The particles concentrate on the magnetic constituent, usually in a characteristic banded or mosaic pattern. The following suspension has been recommended.<sup>80</sup>

A coarse flaky precipitate of magnetite is prepared by dissolving 2 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 5.4 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 300 ml of hot water, and adding, with constant stirring, 5 g of caustic soda in 50 ml of water. The precipitate is filtered, washed with water and with 0.1 N hydrochloric acid. On transferring the precipitate to 1 l of 0.5% soap solution and boiling, a colloidal suspension is obtained, which should be filtered from the unsuspended residue. The suspension may now be applied to the surface of the specimen, which is placed in the field of an electric magnet. The magnetic properties of the particles gradually deteriorate owing to oxidation. The addition of small amounts of photographic reducing agents has been found an advantage in this connection.<sup>80</sup> Commercially prepared ferromagnetic solutions ("Ferrofluid") can be obtained.

Table 10.18 ETCHING OF IRON STEEL AND CAST IRONS  
(See also refs. 1 and 2 for extended list of etchants)

<i>No.</i>	<i>Etchant</i>	<i>Conditions</i>	<i>Remarks</i>
1	Nitric acid (1.40) Ethanol (Nital)	1.5-5 ml to 100 ml	5-30 s depending on steel Ferrite g.b.'s in low carbon steels. Darkens pearlite and gives contrast with ferrite or cementite network. Etches martensite and its decomposition products in many steels. Better than Picral for ferritic grain boundaries



**Table 10.18** ETCHING OF IRON STEEL AND CAST IRONS--continued (See also ref. 1 and 2 for extended list of etchants)

No.	Etchant			
2	Picric acid Ethanol (Picral)	4 g 100 ml	5-30s depending on steel	Similar to Reagent 1 but gives more uniform etch of pearlite. Better for detail of pearlite, and bainite. Reveals undissolved carbides in martensite and gives better distinction of carbides in spheroidized steels. Differentiates pearlite and bainite. Does not etch ferrite grain boundaries or as-quenched martensite
3	50/50 mixture of Reagents 1 and 2		5-30s depending on steel	Used for low alloy steels. Gives lower contrast but more even etching than Reagent 1
4	HCl (1.19) Picric acid Ethanol (5 ml HCl and 1 g picric acid usually referred to as Vilella's reagent)	1-5 ml 1-4 g to 100 ml	5-10 s	May attack prior-austenite boundaries; increased contrast between grains. (Attack of boundaries in martensite alloys increased if tempered for 30 min at 310°C). Good for tool steels and martensitic stainless steels.
5	Chromium trioxide Water Sodium hydroxide (add carefully)	16 g 145 ml 80 g	10-30 min in boiling solution	Reveals intergranular oxidation of medium carbon alloy (nickel) steels as a white layer
6	Sodium metabisulfite Water	1-20 g to 100 ml	5-60 s	Increases contrast in martensitic steels; distinguishes pearlite, bainite and martensite in high carbon alloy steels
7	Picric acid Sod. hydroxide Water	2 g 25 g to 100 ml	Either 10 s to 2 m. boiling soln. or electrolytically cold at 0.5-2 Aft <sup>-2</sup> for 2 min (stainless steel cathode)	Blackens cementite (in alloy with 10% Cr). No effect on M <sub>7</sub> C <sub>3</sub> , M <sub>23</sub> C <sub>6</sub> , M <sub>6</sub> C or MC
8	Potassium ferricyanide Potassium or sodium hydroxide (Murakami's reagent)	10 g 10 g to 100 ml	2-20min at 20-50°C (or electrolytically as Reagent 7)	Cementite in alloys > 10% Cr stained black. M <sub>7</sub> C <sub>3</sub> , M <sub>23</sub> C <sub>6</sub> and iron phosphide stained. In cast irons, immerse 10 s at 80°C to darken iron phosphide, then 30 s, at 80°C to darken cementite unaffected by 10 s immersion. In stainless steels, carbides darken, sigma phase blue, ferrite yellow
9	Nitric acid (1.40). Hydrochloric acid (1.19) Glycerol (also known as Vilella's reagent but do not confuse with Reagent 4; also called glyceresia)	10 ml 20 ml 30 ml	Immerse up to 30 s or use electrolytically with stainless steel cathode <i>Do not keep, discard when yellow; gives off chlorine and NO<sub>x</sub>. Do not leave in contact with stainless steel</i>	Etches high chromium cast irons, stainless steel and high chromium steels
10	Sodium hydroxide Water	45 g to 100 ml	5-60 s Electrolytic with 1-3 V d.c. stainless steel or Pt cathode	In stainless steels, sigma and chi phases yellow to reddish brown (chi etches before sigma), ferrite blue grey, carbides outlined after longer etch
11	Potassium permanganate Sodium hydroxide Water	10 g 4 g to 100 ml	1-10 min in boiling soln. Electrolytic for 5-30 s as Reagent 10	In tool steels, blackens M <sub>7</sub> C <sub>3</sub> and M <sub>23</sub> C <sub>6</sub> , outlines MC (VC)
12	Ferric chloride Hydrochloric acid (1.19) Water (Kalling's reagent)	2 g 5 ml 30 ml	Immerse 1-5 min	In tool steels attacks ferrite and martensite, outlines carbides, leaves austenite unattacked

**Table 10.19** ELECTROLYTE ETCHING OF STEELS  
Some etches in Table 10.18 can be used electrolytically.  
The following are used exclusively electrolytically

No.	Etchant		Conditions	Remarks
1	Lead acetate Water	10 g to 100 ml	2 V d.c. Stainless steel cathode 5-20s	In Fe-Cr-Ni cast alloys Sigma phase blue red Ferrite Dark blue Austenite Pale blue Carbides Yellow
2	Ammonium hydroxide (0.88)		2-6 V d.c. Pt cathode 30-60 s	Stainless and high alloy steels. Etches carbides; sigma phase unattacked
3	Chromium trioxide Water	10 g to 100 ml	3-6 V d.c. Pt cathode 5-60 s	Stainless steels. Carbides outlined and at tacked Austenite, ferrite, phosphide attacked in that order
4	Oxalic acid Water	10 g to 100 ml	6 V d.c. Stainless steel cathode 5-60 s	Outlines carbides first then grains in stainless steels
5	Potass, or sod. hydro- xide Water	1 g to 100 ml	1-6 V d.c. Stainless steel cathode 5-30 s	By control of voltage, can be made to etch various phases sequentially. High voltages out- line carbides and grains Low voltages selec- tively stain phases in sequence. Establish be- haviour on a given composition (which applies to most electrolytic etches)

### 10.3.11 Lead

#### PREPARATION

The preparation of lead and its alloys for micrographical examination is difficult, owing to the softness of the metal. Lead preparation is similar in many aspects to preparing the other soft, low-melting point metals and alloys, such as Bi, Sn, In and Cd. All require careful sectioning with a metallography laboratory abrasive cut-off saw or a low-speed or precision saw. In past practices, cutting with a hack saw was recommended but this produces substantial deformation and a rough surface. Old preparation methods never removed the deformed metal and created new deformation so that the etchants used were more akin to deep etches or chemical polishes that removed a great deal of matrix. Examination by light microscopy revealed a black matrix with white second phase particles, but the etch depth was so extensive that only low magnifications could be used. Those practices should be avoided. Lead and its alloys can be prepared properly. Because diamond abrasives are largely ineffective with lead and its alloys, it is better to use the traditional method, perhaps employing SiC grits finer than 600 (P1200), followed by aqueous alumina slurries on a medium napped synthetic suede cloth, such as a Microcloth pad. After proper cutting, to minimize surface deformation and roughness, the specimen can be mounted (cast resins may be preferred if the press temperature can cause phase changes, recrystallization, grain growth, or even melting; but use a molding practice and resin that gives the lowest possible heat of polymerization).

Start grinding with the finest possible SiC paper, e.g., 320- or 400-grit (P400 or P600) with low loads (4 lbs or 20N per specimen), 150-250 rpm, for about 30 s per sheet of paper (when doing 6 specimens at the same time). The SiC paper loads up faster when grinding these soft metals and alloys and has a shorter effective life. For grits of 600 and finer (P1200 and finer), embedding is a problem. There are several things that can be done. First, waterproof alumina paper, if

available, embeds less as the alumina is tougher. Second, one can coat the surface with candle wax which helps reduce embedding. It has been scientifically shown that candle wax is much more effective than natural bees wax. If embedding occurs, whether or not you coat the paper, it can be removed by polishing with aqueous alumina slurries on the medium napped synthetic suede cloth. Diamond polishing will not remove embedded SiC particles. Grinding with 400-, 600- and 800-grit (P600, P1200 and P1500) SiC paper, with water cooling, low loads, 150-250 rpm, for 30 s each, is adequate.

For rough polishing, one or two steps of aqueous calcined deagglomerated alumina slurries, using 3- and 1- or only a 1- $\mu\text{m}$  particle size, on the synthetic suede medium napped cloth, at 5 lbs (20-25N) per specimen, 120-150 rpm, for 4-5 minutes is adequate. If you grind only to a 600-grit SiC paper, use both steps. Final polishing can be performed with the same type cloth using either the 0.05- $\mu\text{m}$  sol-gel alumina slurry (Masterprep alumina), or colloidal silica, at 4 lbs (15-20N) per specimen, 80-150 rpm, for 4 minutes. If the automated polishing head speed is <100 rpm, use contra rotation. Examine the specimen and then etch with a mild etchant, such as Pollack's reagent (100 ml water, 10 g citric acid and 10 g ammonium molybdate). Remove the etch by repeating the final polish, then re-etch. Even better results can be obtained by following this procedure with a brief vibratory polish using colloidal silica on the synthetic suede medium napped cloth. Perfect surfaces can be obtained and fine detail of the structure, revealed using Pollack's reagent, can be examined at 1000X.

## ETCHING

Rapid tarnishing (oxidation) of polished and etched samples may be avoided by the use of EDTA in the etchant, or as a rinse after etching with a 2% solution (see: washing and drying under Etching). Table 10.20 lists many etchants that have been used for lead and its alloys. Bear in mind that nearly all were developed for use on specimens that were poorly prepared and the etch was designed for heavy attack. This makes examination of the matrix phase almost impossible and permits examination of second phases only at low magnification. Pollack's reagent (100 ml water, 10 g citric acid, 10 g ammonium molybdate) is a leaner version of etch 15 and produces superb results. 2% nital is also acceptable.

**Table 10.20 ETCHING REAGENTS FOR LEAD AND ITS ALLOYS**

No.	Etchant*	Remarks	
1	Nitric acid	Recommended for pure lead. Specimen is alternately etched and washed until the desired result is obtained. Macro etch mainly	
2	Acetic acid 5% in alcohol	Slow-acting grain contrast etch for lead	
3	Acetic acid Hydrogen peroxide (30 vol.)	30 ml 10 ml	This is recommended as a general-purpose reagent for lead, and its alloys with tin, antimony, calcium, sulfur, selenium and tellurium, as well as many other metals. The proportions may have to be adjusted slightly to suit individual cases. The reagent may be made somewhat less vigorous by dissolving a little lead in it before use. The usual etching time is 3-5 s. The action is exothermic and may give rise to recrystallization and grain growth if continued for too long a time. The reagent should not be kept for more than 1 h. It is recommended that the surface of the specimen be cleaned after etching with nitric acid. ( <i>See also</i> Table 10.5)
4	Acetic acid Nitric acid Water	30 ml 40 ml 160 ml	Used at 40-42°C for lead, and lead-tin alloys rich in lead
5	Acetic acid Nitric acid Glycerol	10 ml 10 ml 40 ml	This reagent is recommended when the alternate etching and polishing technique is employed. Used for lead, lead-calcium alloys and lead-antimony and lead-cadmium alloys. Also used for ternary lead-cadmium-antimony. The lead-rich matrix is grey, the compound SbCd blue, the antimony-rich solid solution whitish yellow, and the cadmium-rich solid solution brownish yellow. This reagent may be used hot (up to 80°C). (Beware of recrystallization!)
6	Hydrochloric acid Nitric acid Alcohol	10 ml 5 ml 85 ml	Used for eutectic, lead-tin alloys
7	Hydrochloric acid Ferric chloride Water	30 ml 10 g to 150 ml	Used mostly for lead-antimony alloys
8	Hydrochloric acid, (1.19)	General reagent for grain boundary etching. Usually good for alloys containing antimony	
9	Hydrochloric acid, 1-5% in alcohol	Used for lead-tin alloys. For higher tin contents the 5% reagent is preferable	
10	Nitric acid, 5% in alcohol	Produces grain contrast in lead-rich alloys	
11	Nitric acid, 10% in water	Used for lead-rich alloys. May be improved by the addition of a little chromic acid	
12	Sodium hydroxide saturated in water	Used for lead-tin alloys	
13	Silver nitrate, 5-10% in water	Swab etch used for lead-tin and lead-antimony alloys. Useful for anti-friction alloys in general	
14	Molybdic acid Ammonium hydroxide Water Filter solution and add to nitric acid	100 g 140 ml 240 ml 60 ml	This reagent, applied by the alternate swab and wash technique, gives a rapid etching which is very effective for removing thick layers of cold worked metal. It may be followed by Reagent 5 An alternative is Russell's reagent ( <i>see</i> Table 10.1)
15	Citric acid Ammonium molybdate Water	25 g 10 g 100 ml	A useful grain boundary etch for lead and dilute lead alloys. Often used after chemical polish

\* Acids are concentrated, unless otherwise indicated.

### 10.3.12 Magnesium

#### PREPARATION

Magnesium and its alloys are among the most difficult metals to prepare that are routinely encountered by metallographers. Magnesium and its alloys are low in hardness, although precipitates can be present that are substantially harder and relief control can be difficult. Mg is an hcp metal and deformation twinning occurs readily during handling, even in compression mounting. Sectioning must be done with a proper laboratory cut-off saw, or with a low speed or precision saw, using the correct wheel and ample coolant to minimize damage. There is considerable debate in the literature over avoiding or not avoiding water during preparation. Some say that water must be avoided in the last step, others say water must be avoided in all steps, still others say water need not be avoided. Pure Mg is attacked rather slowly by water, while Mg alloys exhibit a greater attack rate. Our experiments showed that careful, restricted use of water in cleaning after the final step (and all preceding steps), was not harmful. Some metallographers use a 3:1 mixture of glycerol to ethanol as the coolant in all steps, including grinding. Always use a coolant when grinding as all metal dusts, including Mg dust, is harmful if inhaled.

The contemporary preparation practice can be used, but with certain modifications. After obtaining a proper cut, mount the specimen. If precipitation reactions are possible, use a castable resin and a practice that minimizes the heat of polymerization (see Mounting). Grind the specimens with water cooled SiC paper starting with the finest grit size possible, 220-320 grit (P240-P400), 5 lbs (20N) per specimen, 250 rpm, until the cutting damage is removed and the samples in the holder are on the same plane. Oil-based diamond slurries can be used in place of aqueous slurries, for example. Oil is a better lubricant, so the surface finish is better after each step, with less drag, but cleaning is more difficult than with water-based diamond suspensions. Use three steps of oil-based diamond slurries with 9-, 3- and 1- $\mu\text{m}$  particle sizes, 120-150 rpm, contra rotation (if the head speed is  $< 100$  rpm) if possible, for 6, 5 and 4 minutes, respectively, on the synthetic chemotextile pad (know variously as Texmet 1000, Pan W or Pellon). Cleaning after each step was done by holding the specimen holder under running tap water (use lukewarm water) for about a second, just enough to remove much of the residue. Then, scrub the samples and the holder with ethanol using cotton, rinse with ethanol and blow dry under warm air.

The final step can be performed with several abrasives. Colloidal silica, although aqueous, works fine with pure Mg, but it etches the alloys. The sol-gel alumina suspension, Masterprep alumina, is an aqueous suspension, but does not seem to attack constituents in Mg alloys. A proprietary suspension called Masterpolish® suspension, which is nearly water free, has also been used and the results were excellent. All were utilizing 0.05- $\mu\text{m}$  particle size abrasives. They were used on a polyurethane synthetic pad with light load, 3 lbs (10-15N) per specimen, 120-150 rpm (slower speeds are fine), for 90-180 s. The same washing procedure was used, brief rinse with lukewarm tap water, scrubbing with ethanol, rinse with fresh ethanol, and blow dry with hot air. Examine the specimen as-polished to see if the surface scratch control and relief control were adequate. Etch with one of the common reagents. If the structure is not crisp enough, repeat the last polishing step and re-etch. It is best to use surgical grade cotton as imperfections in cosmetic cotton puffs have been known to scratch polished Mg surfaces. Pure Mg, with its hcp crystal structure, will respond to polarized light. The response may be improved by using a polish-etch-polish cycle, or by using the vibratory polisher.

## ETCHING

The general grain structure of alpha-Mg is revealed by examination under crossed polarized light. This will also reveal mechanical twins formed before or during preparation. A selection of etching reagents suitable for magnesium and its alloys is given in Table 10.21. Of these, 4 and 1 are the most generally useful reagents for cast alloys, while 16 is a useful macro-etchant and, followed by 4, is invaluable for showing up the grain structure in wrought alloys. The acetic-picric solutions are quite useful.

*The appearance of constituents after etching.* The micrographic appearances of the commonly occurring microconstituents in cast alloys are as given in Table 10.22.

**Table 10.21** ETCHING REAGENTS FOR MAGNESIUM AND ITS ALLOYS

No.	Etchant	Remarks	
1	Nitric acid Diethylene glycol Distilled water	1 ml 75 ml 24 ml	This reagent is recommended for general use, particularly with cast, die-cast and aged alloys. Specimens are immersed for 10-15 s, and washed with hot distilled water. The appearance of common constituents following this treatment is outlined in Table 10.22. Mg-RE (rare earth) alloys also
2	Nitric acid Glacial acetic acid Water Diethylene glycol	1 ml 20 ml 19 ml 60 ml	Recommended for solution-heat-treated castings, and wrought alloys. Grain boundaries are revealed. The proportions are somewhat critical. Use 1-10 s
3	Citric Acid Water	5 g 95 ml	This reagent reveals grain boundaries, and should be applied by swabbing. Polarized light is an alternative
4	Nitric acid, 2% in alcohol		A generally useful reagent
5	Nitric acid, 8% in alcohol		Etching time 4-6 s. Recommended for cast, extruded and rolled magnesium-manganese alloys
6	Nitric acid, 4% in alcohol		Used for magnesium-rich alloys containing other phases, which are coloured light to dark brown
7	Nitric acid, 5% in water		Etching time 1-3 s. Recommended for cast and forged alloys containing approximately 9% of aluminium
8	Oxalic acid 20 g l <sup>-1</sup> in water		Etching time 6-10 s. Used also for extruded magnesium-manganese alloys
9	Acetic acid, 10% in water		Etching time 3-4 s. Used for magnesium-aluminium, alloys with 3% of aluminium

**Table 10.21** ETCHING REAGENTS FOR MAGNESIUM AND ITS ALLOYS – continued

No.	Etchant	Remarks	
10	Tartaric acid 20 g l <sup>-1</sup> of water	Etching time 6 s } These reagents are recommended for magnesium alloys with 3 to 6% of aluminium	
11	Orthophosphoric acid, 13% in glycerol		Etching time 12 s }
12	Tartaric acid 100 g l <sup>-1</sup> of water	Used for wrought alloys. Mg <sub>2</sub> Si is roughened and pitted. 10 s to 2 min for Mg-Mn-Al-Zn	
13	Citric acid and nitric acid in glycerol	Used for magnesium-zirconium alloys The magnesium-rich matrix is darkened and other phases left white	
14	Orthophosphoric acid Picric acid Ethyl alcohol	0.7 ml 4 g 100 ml	Recommended for solution-heat-treated-castings. The specimen is lightly swabbed, or immersed with agitation for 10-20 s. The magnesium-rich matrix is darkened, and other phases (except Mg <sub>2</sub> Sn) are little affected. The maximum contrast between the matrix and Mg <sub>17</sub> Al <sub>12</sub> is developed. The darkening of the matrix is due to the development of a film, which must not be harmed by careless drying
15	Picric acid satu-	A grain boundary etching reagent; especially for Dow metal (Al 3%	

	rated in 95% alcohol Glacial acetic acid	10 ml 1 ml	Zn 1%, Mn 0.3%). Reveals cold work and twins
16	Picric acid, 5% in ethyl alcohol Glacial acetic acid Distilled water	50 ml 20 ml 20 ml	Useful for magnesium-aluminium-zinc alloys. On etching for 15 s an amorphous film is produced on the polished surface. When dry, the film cracks parallel to the trace of the basal plane in each grain. The reagent may be used to reveal changes of composition within grains, and other special purposes
17	Picric acid, 5% in ethyl alcohol Glacial acetic acid Distilled water	50 ml 16 ml 20 ml	As for reagent 16, but suitable for a more restricted range of alloy composition <sup>86</sup>
18	Picric acid, 5% in ethyl alcohol Glacial acetic acid Nitric, acid (1.40)	100 ml 5 ml 3 ml	General reagent <sup>86</sup>
19	Picric acid, 5% in ethyl alcohol Distilled water	10 ml 10 ml	Mg <sub>2</sub> Si is colored dark blue and manganese-bearing constituents are left unaffected <sup>86</sup>
20	Hydrofluoric acid (40%) Distilled water	10 ml 90 ml	Useful for magnesium-aluminium-zinc alloys. Mg <sub>17</sub> Al <sub>12</sub> is darkened, and Mg <sub>3</sub> Al <sub>2</sub> Zn <sub>3</sub> is left unetched. If the specimen is now immersed in dilute picric acid solution (1 vol. of 5% picric acid in alcohol and 9 vol. of water) the matrix turns yellow, and the ternary compound remains white <sup>86</sup>
21	Picric acid, 5% in ethyl alcohol Distilled water Glacial acetic acid	100 ml 10 ml 5 ml	Reveals grain-boundaries in both cast and wrought alloys. This reagent is useful for differentiating between grains of different orientations, and for revealing internally stressed regions <sup>86</sup>
22	Nitric acid conc.		Recommended for pure metal only. Specimen is immersed in the cold acid. After 1 min a copious evolution of NO <sub>2</sub> occurs, and then almost ceases. At the end of the violent stage, the specimen is removed, washed and dried. Surfaces of very high reflectivity result, and grain boundaries are revealed

## ELECTROLYTIC ETCHING OF MAGNESIUM ALLOYS

This has been recommended for forged alloys. The specimen is anodically treated in 10% aqueous sodium hydroxide containing 0.06 g l<sup>-1</sup> of copper. A copper cathode is used and a current density of 0.53 A dm<sup>-2</sup> is applied at 4 V. After etching, the specimen is successively washed with 5% sodium hydroxide, distilled water and alcohol, and is finally dried.

## NONMETALLIC INCLUSIONS IN MAGNESIUM-BASED ALLOYS<sup>87, 88</sup>

The detection and identification of accidental flux and other inclusions in magnesium alloys involves the exposure of a prepared surface to controlled conditions of humidity, when corrosion occurs at the site of certain inclusions, others being comparatively unaffected. The corrosion product or the inclusion may then be examined by microchemical techniques.

**Table 10.22** THE MICROGRAPHIC APPEARANCE OF CONSTITUENTS OF MAGNESIUM ALLOYS

<i>Microconstituent</i>	<i>Appearance in polished sections, etched with Reagent 1 (zirconium-free alloys)</i>
Mg <sub>17</sub> Al <sub>12</sub> <sup>(1)</sup>	White, sharply outlined and brought into definite relief
MgZn <sub>2</sub> <sup>(2)</sup>	Appearance very similar to that of Mg <sub>17</sub> Al <sub>12</sub>
MgAl <sub>2</sub> Zn <sub>3</sub> <sup>(3)</sup>	Appearance similar to those of Mg <sub>17</sub> Al <sub>12</sub> and MgZn <sub>2</sub>

Mg <sub>2</sub> Si <sup>(4)</sup>	Watery blue green; the phase usually has a characteristic Chinese-script formation, but may appear in massive particles. Relief less than for manganese
Mg <sub>2</sub> Sn <sup>(4)</sup>	Tan to brown or dark blue, depending on duration of etching. Individual particles may differ in colour
Manganese <sup>(5)</sup>	Grey particles, usually rounded and in relief. Little affected by etching
(MgMnAl) <sup>(5)</sup>	Grey particles, angular in shape and in relief. Little affected by etching
<i>Microconstituent</i>	<i>Appearance in polished sections etched with Reagent 4 (zirconium-bearing alloys)</i>
Primary Zr (undissolved in molten alloy)	Hard, coarse, pinkish grey rounded particles, readily visible before etching
Zinc-rich particles <sup>(6)</sup>	Fine, dark particles, loosely clustered and comparatively inconspicuous before etching
Mg <sub>9</sub> Ce	Compound or divorced eutectic in grain boundaries. Appearance hardly changed by few percent of zinc or silver
Mg <sub>5</sub> Th	Compound or divorced eutectic in grain boundaries (bluish). Appearance hardly changed by few percent of zinc if Zn exceeds Th
(?) Mg-Th-Zn	Brown acicular phase. Appears in Mg-Th-Zn-Zr alloys when Th ≥ Zn
MgZn <sub>2</sub>	Compound or divorced eutectic in grain boundaries. Absent from alloys containing RE or Th

The superscript numbers in column 1 refer to the following notes:

- (1) This is the  $\gamma$ -phase of the magnesium-aluminium system, it is also frequently called Mg<sub>4</sub>Al<sub>3</sub> or Mg<sub>3</sub>Al<sub>2</sub>.
- (2) Although the phase MgZn may be observed in equilibrium conditions, MgZn<sub>2</sub> is frequently encountered in cast alloys.
- (3) This ternary compound occurs in alloys based on the ternary system magnesium-aluminium-zinc, and may be associated with Mg<sub>17</sub>Al<sub>12</sub>.
- (4) Blue when unetched.
- (5) These constituents are best observed in the unetched condition.
- (6) Alloys of zirconium with interfering elements such as Fe, Al, Si, N and H, separating as a Zr-rich precipitate in the liquid alloy. Co-precipitation of various impurities makes the particles of indefinite composition.

*Note:* The microstructure of all zirconium-bearing cast alloys with satisfactory dissolved zirconium content is characterised by Zr-rich coring in the center of most grains. In wrought alloys, zirconium is precipitated from the cored areas during preheating or working resulting in longitudinal striations of fine precipitate which become visible on etching.

For descriptions of the metallography of magnesium alloys, refs. 83-85 should be consulted.



The surface to be examined should be carefully ground and polished as described above. Alcohol or other solvents capable of dissolving the flux must be avoided. As soon as possible the prepared specimens are placed in a humidity chamber, having been protected in transit by wrapping in paper. A suitable degree of humidity is provided by the air above a saturated solution of sodium thiosulphate. The presence of corrosive inclusions is indicated by the development of corrosion spots. At this stage the corroded area may be lightly ground away to expose the underlying structure for microexamination so that the micrographic features which are holding the flux become visible. With other specimens, or with the same specimens re-exposed to the humid conditions, identification of the inclusions may be proceeded with, as follows:

#### *1. Detection of chloride*

The corrosion product is scraped off, and dissolved on a microscope slip in 5% aqueous nitric acid. A 1% silver nitrate solution is then added, and a turbidity of silver chloride indicates the presence of the chloride ion. The solution of the corrosion product should preferably be heated before adding the silver nitrate to remove any sulphide ion, which also gives rise to turbidity. Alternatively, a 10% solution of chromium trioxide may be added directly to the corrosion spot, when chloride is indicated by an evolution of gas bubbles from the metal surface, and the development of a brown stain. This method is less specific than the silver nitrate method, and may give positive reactions in the presence of relatively large amounts of sulphates and nitrates.

#### *2. Detection of calcium*

Scrapings of corrosion product are dissolved in a small watch glass on a hot plate in 2 ml water and one drop of glacial acetic acid. To the hot solution a few drops of saturated ammonium oxalate solution are added. The presence of calcium is indicated by turbidity or precipitation. Spectroscopic identification of calcium in the solution is also possible.

#### *3. Detection of boric acid in inclusions*

Scrapings of corrosion product and metal are placed in a test tube with 1 ml of water. The inclusion dissolves, and complete solution of the sample is effected by adding a small portion of sulphuric acid (density 1.84) from 9 ml carefully measured and contained in a graduated cylinder. When solution is complete, the remainder of the acid is added and the mixture is well shaken; 0.5 ml of a 0.1% solution of quinalizarin in 93% (by wt.) of sulphuric acid is now added, mixed in, and allowed to stand for 5 min. A blue colour indicates the presence of boric acid. The colour in the absence of boric acid varies from bluish violet to red according to the dilution of the acid, which must thus be carefully controlled as described.

#### *4. Detection of nitride*

A drop of Nessler's solution applied directly to the metal surface in the presence of nitride, gives an orange brown precipitate, which may take about 1 min to develop. This test should be made on freshly prepared surfaces on which no water has been used, since decomposition of nitride to oxide occurs in damp air.

#### *5. Detection of sulphide*

The corrosion product is added to a few drops of water slightly acidified with nitric acid. A drop of the solution placed on a silver surface gives rise to a dark stain if sulphide was present in the corrosion product. Sulphur printing may also be applied.

#### 6. *Detection of iron*

The corrosion product is dissolved in hydrochloric acid. A drop of nitric acid is added with several drops of distilled water. In the presence of iron, the addition of a crystal of ammonium thiocyanate develops a blood-red coloration.

In all the above tests, a simultaneous *blank* test should be carried out.

Iron-printing, analogous to sulphur-printing, can be applied using cleaned photographic paper impregnated with a freshly prepared solution of potassium ferricyanide and potassium ferrocyanide acidified with nitric or hydrochloric acid.

### 10.3.13 Molybdenum

#### PREPARATION

Refractory metals and alloys are difficult to prepare as they exhibit low grinding and polishing rates and are easily deformed or smeared during preparation. Regardless of their actual indentation hardness, which is not high, cutting of refractory metals, such as Mo and its alloys, is slow and tedious. Avoid production cutting devices, such as power hack saws. Use a good laboratory abrasive cut-off saw with a very softly bonded wheel, designed for cutting refractory metals (such as Ti, Zr, Hf, etc.). Mo and its alloys can be tough or brittle, depending upon composition. They are susceptible to damage production during cutting and grinding. The contemporary method (see Mechanical Polishing) can be used, but requires modification. After sectioning, start with the finest possible grit size SiC paper, e.g., 320-grit SiC. Use moderate loads, 6 lbs (25-30N) per specimen, 150-250 rpm, and grind until the cutting damage is removed and all surfaces are at the same plane. Next, use 9- $\mu$ m diamond on a psa-backed selected silk cloth, such as an Ultra-Pol cloth, at the same load, 150-200 rpm, for 10 minutes. Charge the cloth with diamond paste and add the proper lubricant. During the 10 minute cycle, periodically add the same size diamond in slurry or suspension form. Keep the cloth properly lubricated during diamond polishing to minimize flowed metal. Next, use 3- $\mu$ m diamond, in like manner, with a woven polyester pad, such as a Trident cloth, with the same load, 150-200 rpm, for 8 minutes. If the sample holder's head speed is <100 rpm, run these steps in contra mode. A 1- $\mu$ m diamond step, similar to the 3- $\mu$ m step, can be used for the more difficult grades. Final polishing uses either the medium-nap, synthetic suede cloth, or a polyurethane pad, with colloidal silica at the same load, 120-150 rpm, for 5 minutes. For best results, an attack polish agent must be added to the colloidal silica. Many solutions have been recommended<sup>152</sup>. A 1:5 mixture of hydrogen peroxide (30% conc.) to colloidal silica is effective. A similar mix of 5-20% CrO<sub>3</sub> in water to colloidal silica also works well (see comments regarding this attack polish reagent under preparation of gold). Diluted Murakami's reagent has also been used.

#### ETCHING

Molybdenum is not easy to etch, but there are good etchants available. An excellent etchant for Mo consists of water, hydrogen peroxide (30% conc.) and sulfuric acid in a 7:2:1 ratio. If the specimen is immersed for 2 minutes, the grain structure is revealed in color. If the etch is used by swabbing, a grain boundary etch results. Listed below are two additional useful etchants.

<i>Etchant</i>	<i>Conditions</i>	<i>Remarks</i>	
1. (a) Potassium hydroxide Water (b) Potassium Ferricyanide Water	10 g to 100 ml 10 g to 100 ml	Mix equal amounts of (a) and (b) as needed	Grain boundary etch
2. Ammonia (0.88) Hydrogen peroxide (3%) Water	50 ml 50 ml 50 ml	Boil for up to 10 min	General etch

### 10.3.14 Nickel

#### PREPARATION

Nickel is a face-centered cubic metal and shares many of the preparation problems of other fcc metals. Damage is easily introduced during cutting and grinding. Pure Ni is more difficult to prepare than its alloys. Ni-Fe and Ni-Cu alloys can be rather challenging subjects while the Ni-based superalloys are simpler. The latter are prepared much like austenitic stainless steels and share common etchants. The contemporary method works well for Ni and its alloys (see Mechanical Polishing), although it must be modified somewhat. For pure Ni, Ni-Cu and Ni-Fe alloys, start with the best possible cut surface, i.e., least amount of induced deformation and smoothest surface. Always cut with a laboratory abrasive cut-off saw using the correct wheel, low pressure and ample coolant. Grind with 220-, 240- or 320-grit (P240-P400) SiC paper, or alternative surfaces with similar abrasive sizes. Use 5 lbs (20-25N) load per specimen, 200-300 rpm, until the cutting damage is removed and all the specimens are on the same plane.

Polish with three steps of diamond abrasive, 9-, 3-, and 1- $\mu$ m diamond. Charge the cloth with diamond paste (see Mechanical Polishing) and add the recommended lubricant. Add the same diamond size as a slurry or suspension during the cycle. Use napless, woven cloths that yield the best possible surface finish, e.g., psa-backed selected silk (e.g., an Ultra-Pol cloth) with the 9- $\mu$ m diamond and a psa-backed polyester cloth (e.g., a Trident cloth) with both 3- and 1- $\mu$ m diamond sizes. Use 6lbs. (25-30N) load per specimen, 100-150 rpm, and 5, 3, and 2 minutes for the 9-, 3-, and 1- $\mu$ m steps, respectively. Final polishing is conducted with 0.05- $\mu$ m colloidal silica or sol-gel alumina (Masterprep alumina) suspensions using the medium napped, synthetic suede cloth (e.g., a Microcloth pad) or a polyurethane cloth (e.g., a Chemomet pad), both psa-backed, at the same load, 80-150 rpm, for up to 2 minutes. Contra rotation is preferred if the head speed is <100 rpm. Examine the specimen, then etch it. If the surface quality is inadequate, remove the etch by repeating the last step, and re-etch. Alternatively, particularly with these alloys, remove the etch with the last step, then place the specimens on the vibratory polisher using a psa-backed synthetic suede cloth and colloidal silica for 20-30 minutes. This will facilitate removal of the last remnants of damage. The Ni-based superalloys are prepared in a similar manner, although the 1- $\mu$ m step can usually be dropped, especially for solution annealed and aged specimens. If the 1- $\mu$ m step is dropped, increase the 3- $\mu$ m step time to 5 minutes.

## ETCHING

Since nickel is generally resistant to corrosive media, etching involves the use of rather aggressive reagents, which tend to form etch pits and may attack inclusions. The difficulty of etching increases with the purity of the metal. Some etchants for pure Ni, such as No. 10, are rather dangerous to use. They must be used under a properly working chemical fume hood by personnel well-versed in their potential danger. In general, etching reagents (Table 10.23) either reveal the grain boundaries (“flat etch”) or produce grain contrast (less common). Low-nickel copper-nickel alloys may be etched by the reagents recommended for the purpose under *Copper*. Heat-resisting nickel-base alloys are etched with the solutions used for stainless steels (Table 10.18).

Table 10.23 ETCHING REAGENTS FOR NICKEL AND ITS ALLOYS

No.	Etchant		Remarks
1	Nitric acid (1.40) Hydrochloric acid(1.19) Glycerol	10 ml 20 ml 30 ml	Pure nickel, and nickel-chromium alloys. Grain boundaries etched
2	Nitric acid (1.40) Acetic acid Acetone	10 ml 10 ml 10 ml	Used for pure nickel, cupro-nickel, Monel metal and nickel-silver
3	Nitric acid (1.40) Glacial acetic acid Water	50 ml 25 ml 25 ml	Useful for nickel and most nickel-rich alloys
4	Nitric acid, 2% in alcohol, mixed in various proportions with hydrochloric acid, 2% in alcohol		Used for pure nickel
5	Hydrochloric acid Ferric chloride Water	30 ml 10 g 120 ml	Pure nickel
6	Hydrochloric acid (1.19) Ferric chloride Water	20 ml 10 g 30 ml	Pure nickel

Table 10.23 ETCHING REAGENTS FOR NICKEL AND ITS ALLOYS -continued

No.	Etchant		Remarks
7	Sulfuric acid (1.84) Hydrogen peroxide (10%)	1 ml 10 ml	Pure nickel
8	Sulfuric acid (1.84) Potassium dichromate (saturated in water)	10 ml 50 ml	Pure nickel
9	Ammonium persulphate 100 g l <sup>-1</sup> of water		Cast nickel
10	Ammonium persulphate, 10% in water Potassium cyanide, 10% in water	10 ml 10 ml	Pure nickel. Also recommended for cross-sections of nickel plated steels. The steel is not affected but may be etched by Reagent 2 for <i>Iron and steel</i>
11	Ammonium hydroxide		Used as a polish attack for nickel plate
12	Ammonium hydroxide Hydrogen peroxide 30%	85 ml 15 ml	Used for nickel-silvers

## ELECTROLYTIC ETCHING OF NICKEL AND ITS ALLOYS

This technique frequently gives better results than ordinary immersion or swab etching. Suitable solutions are summarized in Table 10.24.

**Table 10.24** ELECTROLYTIC ETCHING OF NICKEL ALLOYS

<i>No.</i>	<i>Etchant</i>	<i>Conditions</i>		<i>Remarks</i>
1	Sulfuric acid(1.84) Hydrogen peroxide (30%) Water	22 ml 12 ml to 100 ml	6 V d.c. Pt cathode 5-30s	General etch
2	Sulfuric acid (1.84) Water	5 ml to 100 ml	6 V d.c. Pt cathode 5-15 s	All Ni-base alloys, especially Ni-Cu and Ni-Cr. Delineates carbides
3	Ammon. persulphate Water	10 g to 100 ml	6 V d.c. Nickel cathode	Most alloys, especially Ni-Fe Ni-Cr cast alloys
4	Chromium trioxide Water	6 g to 100 ml	As etchant 3	As etchant 3
5	Nitric acid (1.40) Glacial acetic acid Water	10 ml 5 ml 85 ml	1.5 V d.c. Pt cathode 20-60s <i>(do not keep)</i>	Grain contrast for all nickel alloys
6	Oxalic acid Water	10 g 100 ml	6 V d.c. Stainless steel cathode 10-15s	Superalloys, Ni-Au, Ni-Cr, Ni-Mo alloys
7	Phosphoric acid (1.71) Water (if necessary, sulphuric acid (1.84))	70 ml 30 ml 15 ml	2-10 V d.c. Ni cathode 5-60s	Superalloys (Nimonic), Ni-Cr, Ni-Fe
8	Phosphoric acid (1.71) Sulphuric acid (1.84) Chromium trioxide	85 ml 5 ml 8 g	10 V d.c. Pt cathode 5-30 s	Ni-base superalloys. Gamma prime paper. Ti and Nb segregation

### 10.3.15 Niobium

#### PREPARATION

Niobium is soft and tough while its alloys are harder and simpler to prepare. Use the method described for molybdenum. Final polishing is performed using an attack-polishing agent, such as 30% conc. hydrogen peroxide. The following attack polishing solution can be added to aqueous alumina slurries:

Hydrofluoric acid	2 ml
Nitric acid	5 ml
Lactic acid	30 ml

Attack polishing using manual methods is quite tedious and increases the risk that the metallographer will have physical contact with the chemicals, even when using the correct personal protective equipment. An automated polisher should be used to reduce the risk of accidents.

Chemical polishing solutions are often used after mechanical polishing refractory metals and alloys to further improve the surface quality. A good solution consists of 30 ml water, 30 ml nitric acid, 30 ml HCl and 15 ml HF. Use at room temperature by swabbing or by immersion. Another solution contains 120 ml water, 6 g ferric chloride, 30 ml HCl and 16 ml HF. Immerse the specimen 2 minutes. This chemical polish is also recommended for V (immerse 1 minute) and for Ta (immerse for 3 minutes).

**Table 10.25** ETCHING REAGENTS FOR NIOBIUM ALLOYS

<i>No.</i>	<i>Etchant</i>		<i>Conditions</i>	<i>Remarks</i>
1	Hydrochloric acid (1.19)	15 ml	Immerse 10-60 s	The only general-purpose etch free from HF
	Sulphuric acid (1.14)	15 ml		
	Nitric acid (1.40)	8 ml		
	Water	62 ml		
2	Hydrofluoric acid (40%)	10 ml	Immerse 15-20 s	General etch
	Nitric acid (1.40)	10 ml		
	Lactic acid	30 ml		
3	Hydrofluoric acid (40%)	10 ml	Immerse up to 3 min <i>or</i> Use electrolytically 12-30 V d.c. Pt cathode up to 1 min	Grain boundary etch, especially at low voltages, electrolytically
	Nitric acid (1.40)	20 ml		
	Water	70 ml		

### 10.3.16 Platinum group metals

#### PREPARATION

The preparation of these metals is similar to that of gold (see section on Gold). The method described to prepare gold and high gold alloys works well for the other precious metals and will produce surfaces free of damage.

#### ETCHING

The reagents given in Table 10.25 will produce satisfactory microstructures if the preparation and polishing have been done carefully. These reagents are very strong and great care must be exercised in their use. They should only be used by people well trained in the use of dangerous chemicals.

**Table 10.26** ETCHING REAGENTS FOR PLATINUM GROUP

<i>No.</i>	<i>Etchant</i>		<i>Condition</i>	<i>Remarks</i>
1	Aqua Regia		Up to 1 min. May need to be warmed	Pt, Pd, Rh alloys
	Nitric acid (1.4)	34 ml		
	Hydrochloric acid (1.19)	66 ml		
2	Potass. ferricyanide	3.5 g	Several minutes	Most alloys, including Os alloys.
	Sod. hydroxide	1 g		
	Water	150 ml		
3	Hydrochloric acid (1.19)	20 ml	Several minutes	Ru alloys.
	Hydrogen peroxide (3%)	1 ml		
	Water	80 ml		
4	Potass. cyanide	5 g	Electrolytic 1-5 V a.c.	Pt. alloys.
	Water	100 ml		

			Pt cathode 1-2 min	
5	Hydrochloric acid (1.19) Sod. chloride Water	20 ml 25 g 65 ml	Electrolytic with Pt or graphite electrode. 25 s 10 V a.c. 1 min 1.5 V a.c. 1-2 min 20 V a.c. 1 min 6 V a.c. 1 min 5-20 V a.c.	Rh alloys Pt-Rh alloys Ir alloys Pt alloys Ru-base alloys
6	Hydrochloric acid (1.19) Ethanol	10 ml 90 ml	Electrolytic 30s, 10 V a.c. Graphite cathode	Os, Pd, Pt, Ir.
7	Hydrochloric acid (1.19)		1-2 min electrolytic 5 V a.c. Pt or graphite electrode	Rh, Pt. Grain contrast

### 10.3.17 Silicon

#### PREPARATION

Silicon, which is very hard and brittle, is not often prepared for metallographic examination except in the area of electronic devices. Grinding Si with coarse grit SiC paper produces extensive damage to both the leading and trailing edges and should be avoided. Cut the specimen as close as possible to the desired plane-of-polish. Mounting in cast epoxy is preferred due to the brittleness of silicon. Si can be prepared in three steps, assuming that it has been sectioned using a low-speed saw or a precision saw. The first step uses a type A diamond lapping film, e.g., an Ultra-Prep type A film) with 15- $\mu$ m diamond abrasive and water cooling, with firm pressure, 100-150 rpm, until the cutting damage is removed, the surface is flat and has reached the desired location. Step 2 uses the synthetic chemotextile pad, such as Texmet 1000, Pan W or Pellon, with 3- $\mu$ m diamond paste, 7 lbs (30N) load, 240-300 rpm, for 2 minutes. A unique aspect of this step is the use of the 0.05- $\mu$ m sol-gel alumina suspension (Masterprep alumina) as the lubricant with the diamond, rather than the traditional lubricant. This produces a dual polishing action that is very beneficial. The third, and final, step is with colloidal silica on a synthetic polyurethane pad, 5 lbs (20-25N) load per specimen, 100-150 rpm, for 90 s. Silicon responds well to colloidal silica. Specific details about preparing integrated circuits and other devices containing Si can be found in ref. 161.

#### ETCHING

Polished surfaces of silicon may be etched with 5% aqueous hydrofluoric acid, to which various amounts of concentrated nitric acid may be added. Microstructures developed in this way show angular grains, with twin markings, together with the particles of other constituents due to the presence of impurities (e.g., iron, aluminium and calcium).

Commercial silicon may contain inclusions of slag and unreduced quartz. Silicate inclusions may be detected by etching a polished section for 3 h in a stream of chlorine. The specimen is then immersed in concentrated hydrofluoric acid for 10 min in order to etch and attack the quartz inclusions (*see also* Table 10.91 p. 10-21). This is a very dangerous etching procedure that requires properly designed equipment, correct ventilation, and well trained personnel.

### 10.3.18 Silver

## PREPARATION

Silver is very soft and ductile, and is prepared in the same manner as gold and its alloys. The method is described in the section for Gold. Embedding of abrasives can be a problem, as for gold.

Table 10.27 ETCHING REAGENTS FOR SILVER AND ITS ALLOYS

No.	Etchant	Remarks
1	Ammonium hydroxide and hydrogen peroxide-various proportions	The silver-rich matrix is in general unaffected. Other phases (e.g., the $\beta$ silver-antimony phase) are often colored blue to brown
2	Ammonium hydroxide 50 ml Hydrogen peroxide 10-30 ml (3%)	Recommended for silver, silver-nickel and silver-palladium alloys. Also useful for the examination of silver-soldered joints
3	Sulfuric acid (10% in water) to which a few crystals of chromic acid $\text{CrO}_3$ have been added (2 g)	This reagent reveals the grain structure of silver and silver-rich alloys
4	Solution containing 7.6 g $\text{l}^{-1}$ of chromic acid $\text{CrO}_3$ and 8 g $\text{l}^{-1}$ of sulfuric acid	Useful general etching reagent. Used as a sensitive etching reagent for silver-copper alloys
5	Ferric chloride 20 g $\text{l}^{-1}$ of water	Recommended for silver solders
6	Potassium cyanide, 10% in water 10 ml Ammonium persulphate, 10% in water 10 ml	Etch for pure silver and dilute alloys. Duration 1-2 min
7	Solution A: 50:50 nitric acid in water 100 ml Potassium dichromate 2 g Solution B: Chromic acid $\text{CrO}_3$ 20 g Sodium sulphate 1.5 g Water 100 ml	Used for silver alloys in general. Solution A is diluted to 20 vol. and an equal amount of solution B added. The reagent is applied by gentle swabbing or with a camel hair brush. A loose film of silver chromate should form if the reagent is working correctly. If the film is adherent, more of solution A should be added. If no film forms, more of solution B is required
8	Chromic acid, $\text{CrO}_3$ , 0.2% and sulphuric acid, 0.2% in water	Used (1 min immersion) for silver and silver-rich alloys
9	Potassium dichromate saturated in water 100 ml Sodium chloride saturated in water 2 ml Sulfuric acid 10 ml	Silver and silver-rich alloys Silver solders
10.	Chromic acid and hydrogen peroxide in water. Various proportions	General reagent. Composition adjustments must be made to suit specific cases
11	Sodium hydroxide (10%) 10 ml Potass. ferricyanide (30%) 10 ml	5-15 s (dilute with equal vol. of water if too fast) Ag alloys with W, Mo and WC

Pure silver and dilute silver alloys are difficult to etch, but several solutions will give good results on duplex or more complex alloys. The strengths of the reagents, unless otherwise noted in Table 10.27, should be adjusted to the specific alloys to be examined.

## ELECTROLYTIC ETCHING OF SILVER

In many cases excellent grain boundary and grain contrast etching is obtained by electrolysis (specimen as anode) in one of the following solutions:

Table 10.28 ELECTROLYTIC ETCHING OF SILVER ALLOYS

No.	Etchant	Remarks
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1	Citric acid 100 g l <sup>-1</sup> of water	15 s to 1 min. 6 V d.c. Ag cathode. Most alloys
2	Ammoniacal ammonium molybdate	Molybdic acid is dissolved in an excess of strong ammonia. The composition is not critical provided ammonia is in excess. The optimum potential and current density should be experimentally established for each case
3	Potassium cyanide 50 g l <sup>-1</sup> of water	This reagent is used particularly for silver when it is in contact with other metals, as in plated articles. Optimum conditions should again be established experimentally
4	Hydrofluoric acid + a little stannous chloride	Used for silver-tin alloys containing more than 73% of silver

*See also* reagents listed for electrolytic polishing of silver, Table 10.4b. The silver cyanide-potassium cyanide-potassium carbonate reagent in Table 10.4b is particularly convenient, since, on reduction of the polishing potential from 1.5 to 0.5 V for 90 s, etching occurs.

### 10.3.19 Tantalum

#### PREPARATION

The preparation of tantalum (pure and commercial) follows the same procedures as described for Mo and Nb (see these sections). Attack polishing agents are often used. The following mixture has been used as the polishing medium:

Alumina, carefully levigated	35g
Hydrofluoric acid (60%)	20 ml
Ammonium fluoride	20 g
Distilled water	1000 ml

Chemical polishing is often used after mechanical polishing to further improve the surface quality. Kelly recommends the following mixture: 25 ml lactic acid, 15 ml nitric acid and 5 ml HF. Swab vigorously for 2 minutes.

#### ETCHING

The reagents given in Table 10.29 have been found useful.

**Table 10.29** ETCHING REAGENTS FOR TANTALUM

No.	Etchant	Remarks
1	Ammonium fluoride, 20% in water Hydrofluoric acid, (43%) 60% in water	Used at 50-60°C (ineffective when cold). Immersion for 1 min etches up the structure of tantalum without colouring inclusions of tantalum sulphide, Ta <sub>2</sub> S <sub>5</sub>
2	Ammonium fluoride, 20% in water Sulphuric acid (1.84)	Used at 60°C for 1-2 min. Etching effects are similar to those for Reagent 1
3	Ammonium fluoride, 20% in water Nitric acid	Used at 60°C; the matrix is usually not adequately etched but Ta <sub>2</sub> S <sub>5</sub> is blackened. This reagent may be used after Reagent 1 or 2 to identify Ta <sub>2</sub> S <sub>5</sub>
4	Ammonium fluoride, 20% in water	Used for 5-6 min at 80°C. The grain structure of the matrix is developed, and Ta <sub>2</sub> S <sub>5</sub> is not affected
5	Ammonium fluoride,	This reagent is used boiling, and colours Ta <sub>2</sub> S <sub>5</sub> brown. The matrix is

	20% in water	20 ml	not affected
	Hydrogen peroxide	10 ml	
6	Sulphuric acid	25 ml	For general structure <sup>89</sup>
	Nitric acid	10 ml	
	Hydrofluoric acid	10 ml	

### 10.3.20 Tin

#### PREPARATION

Tin is allotropic with a body-centered tetragonal crystal structure at room temperature. It will respond to polarized light when properly polished. Because of its relative softness, the same precautions should be observed as for lead and its alloys. The method described for lead works well for tin.

For further details of methods for tin and tin alloys, refs. 1, 2, 91, 92 and 163 may be consulted.

#### ETCHING

Tin is anisotropic and the grain structure can be revealed under crossed polarized light. The reagents of Table 10.30 have been recommended for tin-rich alloys. In general, etching times are not critical and the progress of the treatment should be judged visually.

**Table 10.30** ETCHING REAGENTS FOR TIN AND ITS ALLOYS

No.	Etchant*	Remarks
1	Nitric acid, 2% in alcohol	This reagent is a general one for tin-rich alloys, and particularly for tin-cadmium, tin-antimony and tin-iron alloys. The tin-rich matrix is darkened, and the intermetallic compounds usually little affected
2	Nitric acid, 5% in alcohol	Tin, tin-cadmium and tin-iron alloys
3	Nitric acid           10 ml Acetic acid           30 ml Glycerol               50 ml	Mainly used as a reagent for tin. Used at 38-40°C
4	Nitric acid           10 ml Acetic acid           10 ml Glycerol               80 ml	Used, at 38-40°C, for tin-lead alloys, especially tin-rich alloys. Pb is blackened.
5	Picric acid and nitric acid in alcohol-proportions variable	Useful for tin-iron alloys in contact with steel.
6	Hydrochloric acid, 1-5% in alcohol	Useful for tin-lead, tin-cadmium, tin-iron, tin-antimony-copper alloys.
7	Hydrochloric acid   2 ml Ferric chloride       10 g Water                   95 ml	Useful for tin-rich alloys in general and for Babbitt metal. It is often an advantage to add alcohol to this reagent. Any cadmium-rich solid solution present is stained black, while the $\beta$ -phase of the tin-cadmium system turns brown
8	Hydrochloric acid   5 ml Ferric chloride       2 g Water                   30 ml Alcohol                 60 ml	Reveals general structure of tin and alloys without lead. Tin-iron and tin-copper compounds unattacked
9	Stannous chloride in acid solution	Tin-rich alloys in general. The composition may be varied to suit individual alloy systems
10	Potassium dichromate, in dilute acidified aqueous solution (composition variable)	Recommended for tin-cadmium alloys
11	Potassium ferricyanide in caustic soda (composition variable)	Used for tin-cadmium-antimony alloys. It distinguishes SbSn (with tin and cadmium in solid solution), which is not affected, from CdSb in tin-cadmium-antimony alloys

12	Ammonium persulphate Water	5-10 g 100 ml	Used particularly for tinplate. The tin is heavily darkened, leaving the basis metal unattacked. Most intermetallic compounds of tin are also unattacked. More dilute solution gives grain boundary etch with tin and alloys
13	Nitric acid and hydrofluoric acid in glycerol		Various strengths are recommended for tinplate. The contrast between plating and steel may be improved by the use of Reagent 2 (Table 10.17)
14	Sodium sulphide 20% in water, with a few drops of hydrochloric acid		Useful for tin-rich tin-antimony-copper alloys. The phase SbSn is not affected, but the phase Cu <sub>6</sub> Sn <sub>5</sub> is coloured brown <sup>93</sup>
15	Silver nitrate Water	5 g 100 ml	Darkens primary and eutectic lead in lead-rich lead-tin alloys <sup>91</sup>

\* Acids are concentrated, unless otherwise indicated.

## ELECTROLYTIC ETCHING OF TIN ALLOYS

A 10% aqueous solution of hydrochloric acid or 20% sulphuric acid may be used at a very low current density; this is especially useful for tin-iron alloys. Satisfactory results are also obtained from:

Glacial acetic acid	130 ml
Perchloric acid	50 ml

used at a current density of 3-6 A dm<sup>-2</sup>. (use with care; see Section 10.2, p. 10-X, *Electrolytic polishing*).

### 10.3.21 Titanium

#### PREPARATION

Pure titanium is soft and ductile. Because of its hcp crystal structure it deforms by mechanical twinning, and this can be caused by rough handling. If improperly sectioned, the depth of damage can be extensive. Sectioning, as for all refractory metals, is very difficult, as cutting rates are low. While their indentation hardness values are low compared to tool steels and high speed steels, Ti and its alloys are much more difficult to cut and require a more softly bonded abrasive wheel than the hardest steels. Grinding and polishing rates are also lower than for steels, or most other metals. Some authors have stated that Ti and its alloys should not be mounted in phenolic resins as hydrogen can be absorbed from the resin to form TiH; or, if hydrides are present (as in a specimen in a H-rich service environment), the heat from compression molding may dissolve some, or all, of the hydride. The writer has never observed hydrides in specimens mounted with different thermosetting resins. However, in a field failure of commercial purity (CP) titanium that contained vast amounts of titanium hydrides, the mount temperature was observed to dissolve some of the hydrides. A mount made using a low-viscosity, slow curing epoxy resin revealed the greatest amount of TiH. Mounts made with a fast curing epoxy (cures in about 45 min.), which generates a high heat of polymerization, had a reduced amount of TiH, similar to the amount obtained using a thermosetting resin. So, in failure analysis work, if hydrides may be present, it is best to use a slow curing epoxy resin with a conductive mounting approach (see the section on Mounting), to minimize the exotherm produced during polymerization and the chance of dissolving any TiH.

To prepare Ti and its alloys, a three step contemporary procedure is used that has been shown to be capable of producing perfect images of CP Ti in crossed polarized light, and a vast range of alpha, alpha-beta and beta alloys. Of course, we must start with a properly sectioned piece, and this is extremely important with Ti. Use only a laboratory abrasive cut-off saw, or a precision saw, with the proper wheel (extremely critical), with low pressure and copious cooling. Mount the specimens as discussed above. Step 1 uses psa-backed 320-grit (P400) SiC paper, water cooled, with 6 lbs. (25-30N) load per specimen, 240-300 rpm, until the cutting damage is removed and the specimens are at the same plane. This may require more than one sheet of paper.

Step 2 employs a psa-backed selected silk cloth, such as an Ultra Pol cloth, with 9- $\mu$ m diamond, 6 lbs. load per specimen, 120-150 rpm, for 10 minutes. The cloth is critical to the success of this method. Selected silk yields a good removal rate and a better surface finish than any other cloth while minimizing relief, and maximizing edge retention. If other cloths or rigid grinding disks are used, the results will be inadequate for CP Ti examination by polarized light (unless an additional step is added). If the polishing head rotates at <100 rpm, use contra mode. Start by charging the cloth with paste, then add the appropriate lubricant. During the 10-minute cycle, periodically add the same size diamond in slurry or suspension format to keep the cutting rate high.

Step 3 uses 0.05- $\mu$ m colloidal silica on a medium napped synthetic suede cloth, same load, 120-150 rpm, for 10 minutes. This method works much better if contra rotation can be used. This requires a polisher with a low head speed, ideally 30-60 rpm. If the head speed exceeds 100 rpm, the abrasive will be thrown off the polishing cloth onto the operator and the walls. This is especially bad, as the colloidal silica must be mixed in a 5:1 ratio with hydrogen peroxide (30% conc.). If the addition of hydrogen peroxide causes the colloidal silica to stiffen, add distilled water. With 20 s left in the third step, stop adding any abrasive. With 10 s left in the cycle, turn the water jet onto the polishing cloth surface and wash off both the abrasive from the cloth and from the specimen. Then, rinse the specimen and holder with water, scrub with cotton soaked in ethanol or in a soap solution, as desired, rinse in water, displace the water with ethanol, and blow dry under a stream of hot air. CP Ti specimens will yield excellent grain structure images under crossed polarized light. The image quality can be further enhance by a brief (20-30 minutes) vibratory polish using colloidal silica on the medium napped synthetic suede cloth.

## ETCHING

The presence of surface oxide films on titanium and its alloys necessitates the use of strongly acidic etchants, usually containing HF. Those given in Table 10.31 are useful. HF is a very dangerous acid and skin contact must be avoided as it produces very nasty burns to the bone. Reagents should be kept in polyethylene beakers, as glass is attacked by HF.

*Table 10-31* ETCHING REAGENTS FOR TITANIUM AND ITS ALLOYS'

No.	Etchant		Conditions	Remarks
1	Hydrofluoric acid (40%)	1-3 ml	5-30 s	Mainly unalloyed titanium; reveals hydrides
	Nitric acid (1.40)	10 ml		
	Lactic acid	30 ml		
2	Hydrofluoric acid (40%)	1 ml	5-30 s	As Etchant 1

	Nitric acid (1.40)	30 ml		
	Lactic acid	30 ml		
3	Hydrofluoric acid (40%)	1-3 ml	3-10 s	Most useful general etch
	Nitric acid (1.40)	2-6 ml		
	Water (Kroll's reagent)	to 100 ml		
4	Hydrofluoric acid (40%)	10 ml	5-30 s	Chemical polish and g.b. etch
	Nitric acid (1.40)	10 ml		
	Lactic acid	30 ml		
5	Potassium hydroxide (40%)	10 ml	3-20 s	Useful for $\alpha$ / $\beta$ alloys. alpha is attacked or stained. $\beta$ unattacked
	Hydrogen peroxide (30%)	5 ml		
	Water (can be varied to suit alloy)	20 ml		
6	Hydrofluoric acid (40%)	20 ml	5-15 s	General purpose, TiAlSn alloys
	Nitric acid	20 ml		
	Glycerol	40 ml		
7	Hydrofluoric acid	1 ml	3-20 s	TiAlSn alloys
	Nitric acid (1.40)	25 ml		
	Glycerol	45 ml		
	Water	20 ml		

### 10.3.22 Tungsten

#### PREPARATION

Tungsten, compared to the other refractory metals, is one of the easier to prepare. The methods described for Mo and Nb are adequate for W. See these sections. The use of an attack-polish agent is helpful when preparing tungsten.<sup>97</sup>

#### ETCHING

The etching of tungsten is not difficult as Murakami's reagent is quite satisfactory. Inclusions (e.g., thorium, uranium or calcium oxides) may be seen in the polished, unetched surface, while the general structure of filaments which have been heated *in vacuo* or in a reducing atmosphere may often be observed owing to evaporation effects. A selection of suitable etching reagents is given in Table 10.32.

#### ELECTROLYTIC ETCHING OF TUNGSTEN

This may be carried out in a mixture of 25 ml of normal aqueous sodium hydroxide and 20 ml of hydrogen peroxide. The current density and potential are somewhat critical, and should be carefully controlled after investigation to find the optimum conditions for specific cases. A sodium hydroxide solution of 0.025 normal strength has also been used, at a current density of 5 A dm<sup>-2</sup>.

**Table 10.32** ETCHING REAGENTS FOR TUNGSTEN

No.	Etchant		Remarks
1	Sodium hydroxide, 10% in water	10 ml	This reagent is used cold and, on immersion of the specimen for approximately 10 s, develops grain boundaries (Murakami's reagent)
	Potassium ferricyanide, 10% in water	10 ml	

2	Hydrogen peroxide, 3% in water		This reagent develops grain boundaries, but only after some 30-90 s in the boiling reagent
3	Potassium ferricyanide Caustic soda Water	305 g 44.5 g 1000 ml	Recommended for deep etching of single crystal bars and wires in order to produce etch-pits for the investigation of orientation
4	Hydrofluoric acid Nitric acid (1.40) Lactic acid	5 ml 10 ml 30 ml	Swab 10-20 s, rinse and dry. Follow with Murakami's reagent (Etchant 1)

### 10.3.23 Uranium

#### PREPARATION

Conventional methods are used but as the metal is toxic, pyrophoric when finely divided, and an  $\alpha$ -particle emitter, it is essential to keep the metal wet during cutting and to carry out the operation behind a screen so that particles cannot be ingested. Preparation of any radioactive metal can only be done in specially designed facilities that have been licensed to work with such metals, and requires personnel properly trained to deal with the hazards involved.

Methods utilizing attack-polish solutions are preferred and give structures which can be examined under polarized light with crossed polars, which is the most useful method of examination.<sup>43</sup>

Recommended attack-polish solutions are:

1. Dilute hydrofluoric acid and nitric acid (1 ml + 5 ml respectively in 100 ml water).
2. 50 g chromium trioxide, 10 ml nitric acid, 100 ml water is less aggressive but, like the other, needs careful handling to avoid contact with the skin. This gives the best results for polarized light examination.

#### ETCHING

Polarized light is the most useful technique.

$\alpha$ -uranium — high grain contrast under crossed polars about  $1^\circ$  off the extinction position. The various transformation products, granular  $\alpha$ , martensites, etc., can be distinguished.

$\beta$ -uranium — weakly anisotropic when retained but clearly distinguishable from  $\alpha$  and  $\gamma$ .

$\gamma$ -uranium — optically isotropic and therefore distinguished from  $\alpha$  and  $\beta$ . In uranium alloys with molybdenum, niobium and rhenium,  $\gamma_0$  is tetragonal with  $c/a = 0.5$ , is optically active, and the grain structure is visible under crossed polars.

On ageing, these alloys develop  $\gamma_0$  with  $c/a < 0.5$  and this is readily detected by polarized light metallography.

Note that chemical etching may give quite different structures, e.g., in U-Ti alloys. Chemical etching is responsive to the manner of decomposition of  $\gamma$  uranium and will reveal the sequence of decomposition, e.g., distribution of  $U_2Ti$ ,  $UZr_2$ , etc., whereas polarized light reveals the final and true grain structure which may be quite different from the etched structure.<sup>45</sup>

Table 10.33 ETCHING REAGENTS FOR URANIUM ALLOYS

No.	Etchant	Conditions	Remarks	
1	Nitric acid (1.40) Glacial acetic acid Glycerol	30 ml 30 ml 30 ml	5-60 s	Most U alloys; distinguishes precipitated phases, e.g. $U_2Ti$ $U_2Mo$ , $UZr_2$ , eutectoid nucleation at grain boundaries (like pearlite in steel)
2	Orthophosphoric acid Diethylene glycol Ethanol	30 ml 30 ml 40 ml	Electrolytic 20 V stainless steel cathode 5-30 s	Will electropolish at high voltages (30-40V) stains phases differentially at 10-20 V
3	Hydrofluoric acid (40%) Nitric acid (1.40) Glycerol	10 ml 40 ml 40 ml	5-10s	U-Mo, U-Nb, U-Zr alloys (gamma phase)
4	Hydrofluoric acid (40%) Nitric acid (1.40) Lactic acid (or distilled water)	1 ml 30 ml 30 ml	5-30 s	U-Be, U-Nb, U-Zr, U-Md. Also U-Al alloys. $UAl_2$ $UAl_3$ , $UAl_4$ Stained differentially according to time

### 10.3.24 Zinc

#### PREPARATION

Though somewhat harder than lead and tin, zinc and its alloys must be carefully prepared, as improper cutting and grinding produces mechanical twinning in a comparatively thick surface layer. The depth of damage can approach at least 2 mm on a saw cut or filed surface. If such a surface layer experiences preparation-induced heating, it is likely to cause recrystallization of the deformed surface layer.

Zinc, as with Pb, Sn, Sb, Bi and Cd, is not abraded well with diamond abrasives. It is better to use the traditional method with several stages of SiC paper. Follow the approach described for lead. Embedding can be a problem with Zn, although it is less of a problem than with Pb. Polish using aqueous alumina slurries, as described for Pb.

Table 10.34 ETCHING REAGENTS FOR ZINC AND ITS ALLOYS

No.	Etchant	Remarks	
1	Hydrochloric acid, 1% in alcohol	These reagents are of general applicability to zinc and many zinc-rich alloys. Etchant 3 is suitable for examination of microconstituents a high magnifications	
2	Sodium hydroxide 100 g l <sup>-1</sup> of water		
3	Nitric acid, 1-2% in alcohol	Rinse in 20% chromic acid in water to avoid stains. Good for Zn-Fe layers in galvanized samples	
4	Nitric acid Chromic acid	94 ml } 6 ml } Stock solution	A few drops of this stock solution are added to 100 ml of water immediately before use. The resulting solution is generally useful particularly for the recognition of small amounts of other microconstituents in zinc

5	Chromic acid, CrO <sub>3</sub> Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> Water	200 g 15 g 1000 ml	Palmeton reagent for commercial zinc and zinc alloys. If a film of stain results, this may be removed by immersion in a 20% solution of chromic acid in water.
6	Chromic acid, CrO <sub>3</sub> Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> Water	50 g 4 g 1000 ml	As for Etchant 5. This composition is recommended for die-castings Modified Palmerton reagent.
7	Chromic acid, CrO <sub>3</sub> Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> Water	200 g 7.5 ml 1000 ml	Recommended for zinc-rich alloys containing copper. Subsequent immersion in 20% chromic acid solution is again helpful
8	Chromic acid, CrO <sub>3</sub> Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> Sodium fluoride Water	200 g 7 g 2 g 1000 ml	Recommended for die-casting alloys containing aluminium, as the aluminium-rich microconstituent is satisfactorily etched with this reagent. In the presence of copper, staining may result; to prevent this, immerse after etching, without washing, in a solution of 50 g chromic acid and 4 g sodium sulphate in 1000 ml, water ( <i>see</i> Etchant 5).
9	Solution prepared thus: mix 51 ml of concentrated potassium hydroxide solution with 50 ml of water and 20 ml of concentrated copper nitrate solution. Stir in 25 g of powdered potassium cyanide. Filter, and add 2.5 ml of concentrated citric acid solution before use		Etch by immersion for 10-20 s. The zinc-rich phase is coloured dark brown to black. The iron-phase in commercial alloys usually appears as white rods, and the lead-phase as round white spots

## ETCHING

The reagents listed in Table 10.34 may be used for zinc and its alloys.

### ELECTROLYTIC ETCHING OF ZINC ALLOYS

Comparatively little work has been done on electrolytic etching of zinc alloys, because the microstructures are relatively simple and adequately brought out by the above listed reagents. For alloys containing copper, however, a 20% aqueous chromic acid solution has been recommended, the specimen being the anode.

Ternary alloys containing aluminium and copper may be conveniently etched electrolytically in a solution made by adding 20 drops of hydrochloric acid to 50 ml alcohol.

### DEVELOPMENT OF MICROSTRUCTURES WITHOUT ETCHING

Zinc and many zinc-rich alloys develop satisfactory microstructures if the polished surface is allowed to remain exposed to the air for 1-3 days. Similar results may be obtained, by heating at 100°C for a shorter time, but care must be taken to ensure that the use of the high temperature does not lead to any structural modification.

#### 10.3.25 Zirconium (and Hafnium)

##### PREPARATION

Pure zirconium, and hafnium (which is quite similar to Zr), are soft, ductile hcp metals that can easily be deformed by mechanical twinning.<sup>104</sup> As with Ti, they must be sectioned with a



laboratory abrasive cut-off machine using a very softly bonded wheel to minimize damage. As with all refractory metals, the grinding and polishing rates are low and scratch elimination can be difficult using standard methods. The contemporary preparation method is suitable for the alloys, but for the pure metals, a procedure similar to used with lead, with attack polishing additions followed by chemical polishing, works better. After proper cutting, the specimen is mounted and ground with 320-grit (P400) SiC paper with water cooling, 5 lbs. (20-25N) load, 200-250 rpm, until the surface damage is removed and the specimens are all ground to a common plane.

Step 2 uses 9- $\mu\text{m}$  diamond on a psa-backed selected silk cloth (such as an Ultra-Pol cloth), same load, 150-200 rpm, for 5 minutes. Step 3 uses 3- $\mu\text{m}$  diamond on a woven polyester cloth (such as a Trident cloth), with the same load, same rpm, for 3 minutes. Step 4 uses 0.05- $\mu\text{m}$  colloidal silica, with an attack polish agent, on a medium napped, synthetic suede cloth (such as a Microcloth pad), at 6 lbs. (25-30N) load, 120-150 rpm, for 7 minutes. In these three polishing steps, contra rotation should be used, if the head speed is  $<100$  rpm. See comments about this under Ti. A number of attack-polish agents<sup>152</sup> have been used, and those described for Ti are fine with Zr and Hf. Cain has developed several chemical polishing solutions that are used after polishing to improve polarized light response. Kelly's chemical polish solution also works quite well: 25 ml lactic acid, 15 ml nitric acid and 5 ml HF (swab vigorously for 2 minutes). For high-purity Zr or Hf, use the method for lead (coating the SiC with wax is not necessary) and add a 5- or 3- $\mu\text{m}$  aqueous alumina step. Use an attack polish agent with each alumina step and follow with a chemical polish using Ann Kelly's solution. Vibratory polishing with colloidal silica on a medium napped synthetic suede cloth (e.g., a Microcloth pad) for 20-30 minutes also improves the polarized light response of Zr, Hf and their alloys.

## ETCHING

When properly prepared, these metals and alloys can be examined in crossed polarized light. Hence, etching is often unnecessary. Etching reagents for zirconium, hafnium and their alloys are summarized in Table 10.35.

**Table 10.35** ETCHING REAGENTS FOR ZIRCONIUM AND HAFNIUM

No.	Etchant		Remarks
1	Nitric acid (1.40)	20 ml	The reaction rate may be increased, by heating the sample in a stream of hot water before immersion in the reagent. Conversely the reaction rate is decreased by chilling the specimen
	Hydrofluoric acid (1.19)	20 ml	
	Glycerol	60 ml	
2	Glycerol	60 ml	On etching for 3-5 s, microconstituents are outlined and differentiated, and carbides unattacked. In the presence of moisture the reagent tends to stain the specimen
	Hydrofluoric acid (1.19)	20 ml	
	Nitric acid	10 ml	
3	Glycerol	16 ml	Etching times of 1-2 s are used. The reagent is useful for alloys which are not satisfactorily etched by Etchant 2
	Hydrofluoric acid (1.19)	2 ml	
	Nitric acid (1.40)	1 ml	
	Water	2-4 ml	
4	Hydrofluoric acid (1.19)	20 ml	Short etching times are necessary (1-2 s). The reagent is similar to Etchant 3 but is more drastic
	Water	80 ml	
	Nitric acid (1.40)	1 ml	

## ELECTROLYTIC ETCHING

Solutions for electrolytic etching are given in Table 10.36.

Table 10-36 ELECTROLYTIC ETCHING OF ZIRCONIUM

No.	Etchant		Remarks
1	Ethyl alcohol Perchloric acid (density 1.2) 2-Butoxy-ethanol	70 ml 20 ml 10 ml	Suitable for cast zirconium
2	Acetic acid Perchloric acid (density 1.59)	1000 ml 50 ml	Suitable for worked and annealed material
3	Ethyl alcohol Hydrochloric acid conc.	30 ml 10 ml	Etching time 10-20 s at 1 A dm <sup>-2</sup>
4	Ethyl alcohol Distilled water Perchloric acid	450 ml 70 ml 25 ml	As for Etchant 3

### 10.3.26 Bearing metals (lead-tin-antimony), low-melting point solders, and type metals

#### PREPARATION

Bearing metals consist of hard particles of intermetallic compounds set in a matrix of soft lead-rich or tin-rich material. In general, bearing metals are easier to prepare than Pb, Sn, Bi, Cd, Zn. Many times, the metallographer encounters these as layers on metals, usually steels. These specimens must be mounted for edge retention and can be prepared with the contemporary method for steel. Printing metals and solders are easier to prepare than the pure metals, but the method described for lead should be used.

#### ETCHING

All the reagents listed for lead and tin alloys may be tried for revealing the structure of bearing metals, the choice depending on whether the alloy is lead-rich or tin-rich. Of the reagents used for lead, the most useful for the present purpose are: Nos. 4, 6, 8, 11 and 12; of the reagents for tin, Nos. 1, 6 and 7 are suitable.

Further reagents are summarized in Table 10.37.

Table 10.37 ETCHING REAGENTS FOR BEARING METALS

No.	Etchant	Remarks
1	Iodine in potassium iodide solution	Type metals containing small amounts of zinc
2	Iodine 10% in alcohol	Type metals containing large amounts of zinc
3	Silver nitrate (2-5%) in water	Useful for bearing metals in general

## ELECTROLYTIC ETCHING

Bearing metals may be polished electrolytically in a solution containing 60% perchloric acid and acetic anhydride in the ratio of 1 part to 4 parts by volume (see the safety comments under Electrolytic Polishing and the discussion of Figure 10.2 as this mixture can be explosive). If the voltage is reversed after polishing, sensitive etches of most bearing metal materials may be obtained.

### 10.3.27 Cemented carbides and other hard alloys

#### PREPARATION

Cemented carbides are hard, usually  $>1200$  HV. This alters the preparation procedure. Sectioning is usually performed with a low-speed saw or a higher speed, precision saw, some of which are called linear precision saws because the sample is fed into the blade at a controlled rate rather than being gravity-feed. These saws use a non-consumable diamond blade and yield excellent cuts with little damage and superb surface smoothness. Because of the high hardness of sintered carbides, SiC grinding paper (and alumina grinding paper), is not useful. Instead, diamond must be used for all steps. A wide variety of products can be employed. After sectioning, the specimens are embedded in a polymer and the thermosetting epoxy containing a silica filler (such as Epomet resin) is ideal.

Step 1 uses either a metal-bonded diamond disk (there are several types available, for example, an Ultra-Prep disk) with a coarse diamond, e.g., 45- $\mu\text{m}$  size, which is water cooled, as with SiC paper, with a load of 6 lbs. (25-30N) per specimen, 240-300 rpm, for 5 minutes. Or, a rigid grinding disk, such as the BuehlerHercules H disk, or equivalent products, can be used. In this case, the diamond abrasive is added in suspension or slurry form. A particle size of 30- to 45- $\mu\text{m}$  is used. The other parameters are the same. If the head speed is  $<100$  rpm, use contra rotation.

Step 2 can also use the same two working surface options, but with a finer diamond size. For example, a 9- $\mu\text{m}$  metal-bonded diamond disk can be used, with the same settings as for step 1, except for 4 minutes. Alternatives include another rigid grinding disk, or a psa-backed selected silk or nylon cloth. These are used with 9- $\mu\text{m}$  diamond and the same settings. Step 3 uses 3- $\mu\text{m}$  diamond on either of several cloths - selected silk, nylon, polyester or the chemotextile pad (all with psa backings). As elsewhere, charge the cloth with paste, press the paste into the cloth surface with a finger tip, add some lubricant and begin polishing. During the cycle, add diamond of the same size in slurry or suspension form. For step 3, use the same load, 120-150 rpm, for 3 minutes. Again, use contra rotation if the head speed is  $<100$  rpm. At this point the surfaces are more than adequate quality for routine examination.

If the sintered carbide is coated, and particularly when multiple CVD layers are applied, the resolution of these coatings will be enhanced if additional steps are used. A 1- $\mu\text{m}$  diamond step, in the same manner as the 3- $\mu\text{m}$  step can be added. That can be followed by final polishing with colloidal silica on a synthetic suede cloth or with the polyurethane pad, same load, 120-150 rpm, for 2 minutes. Again, use contra rotation if possible. Another option is to use a brief vibratory polish with colloidal silica, 20-30 minutes is adequate. These polishing steps enable complex coatings to be resolved clearly and give maximum detail of the cobalt binder phase.

These features must be studied at the limits of the light microscope for resolution and magnification, so SEM examination is also widely used, particularly backscattered images as the different carbides and the binder phase can be revealed nicely in the range of 2000-5000X where the backscatter electron image still has good resolution.

## ETCHING

Graphite and eta phase are observed best before etching. A number of etching reagents have been developed for these materials, and a selection is given in Table 10.38.

### ELECTROLYTIC ETCHING OF TUNGSTEN CARBIDE-COBALT AND TUNGSTEN CARBIDE-TITANIUM CARBIDE-COBALT ALLOYS

Two solutions have been recommended:

1. For tungsten carbide in a matrix of cobalt:

Sodium hydroxide	10%	} in water
Potassium ferricyanide	10%	

On electrolysis at 2 V, the carbide particles are attacked, and the cobalt binder phase is almost unaffected.

2. For tungsten and titanium carbides in a matrix of cobalt:

Nitric acid conc.	10 ml
Hydrofluoric acid	10 ml

Titanium carbide is attacked, while tungsten carbide is not attacked. The cobalt-rich matrix is attacked and dissolved.

Table 10.38 ETCHING REAGENTS FOR CEMENTED CARBIDES, ETC.

No.	Etchant	Remarks
1	Potassium hydroxide, 20% in water Potassium ferricyanide, 20% in water Equal volumes are mixed	The cold solution is used as a general reagent (Murakami's reagent) NaOH can be substituted for KOH
2	Potassium hydroxide 10 g Potassium Ferricyanide 10 g Water 10 ml	The boiling solution is used as a general reagent (Mod. Murakami's reagent) NaOH can be substituted for KOH
3	Aqua regia (20 ml nitric acid + 80 ml hydrochloric acid)	General reagent
4	Hydrofluoric acid 70 ml Nitric acid conc. 30 ml	Rapidly attacks eutectic material in iron-tungsten carbide alloys and iron-molybdenum carbide alloys
5	Picric acid, 2% in alcohol	Develops the eutectic structure in iron-tungsten carbide alloys and iron-molybdenum carbide alloys. The carbides are differentiated
6	Nitric acid, 3% in alcohol	The crystal boundaries in iron-tungsten carbide and iron-molybdenum carbide alloys are developed
7	Mixture of 5 and 6	Generally effective for this class of material
8	Phosphoric acid 10 ml Hydrogen peroxide 10 ml	Used after successive treatments in Etchants 4 and 1 for molybdenum carbide-titanium carbide-cobalt materials. The titanium carbide with tungsten in solution and the cobalt are darkened; the tungsten carbide with titanium in solution is relatively unaffected <sup>105</sup>

9	Dilute ammonium sulphide	Used after successive treatments in Etchants 4, 1 and 8 for similar materials as recommended for Etchant 8. The carbides are unaffected, but the cobalt-rich matrix is darkened and differentiated from titanium carbide <sup>105</sup>
10	Potassium permanganate Potassium hydroxide Water	WC grey, TiC, pink, TaC gold $\beta$ phase rapidly attacked 10 g 5 g to 100 ml

## ELECTROLYTIC ETCHING OF IRON-TUNGSTEN-CARBON AND IRON-MOLYBDENUM-CARBON ALLOYS

The use of a 5% solution of potassium ferrocyanide in 5% sodium hydroxide has been suggested. The metallographic effects are very similar to those of Etchant 5 in Table 10.38.

### 10.3.28 Powdered and sintered metals

#### PREPARATION

The preparation of powders, pressed compacts, and sintered metals is a specialized process, and requires special methods.

To examine powders, mix a reasonable amount of powder into a small amount (10-15 ml, for example) of cast epoxy that has been mixed in the correct ratio. Pour this into a mold cup of the desired diameter. Then, fill up the mold cup with clear epoxy, add an identification label, and allow it to cure. The powder particles are only in the bottom several mm of the mount. Grinding, polishing and etching are then carried out as for the metal involved, as described above. Coarse powder particles have been mixed with thermosetting resins and placed into the mounting press, and cured. Generally, the use of cast epoxy is preferred as epoxy is the only resin that physically adheres to the specimens.

In compacted, sintered, and even in hot isostatically pressed specimens, voids will be present. Vacuum impregnation can be used to draw cast, low-viscosity epoxy into the voids. Voids can pick up grinding and polishing materials, and absorb etching reagents and other fluids, creating preparation problems in all stages of the preparation and examination process. Of course, some voids are not interconnected, and are not filled with epoxy. In this case, one can interrupt the preparation process after the 3- or 1- $\mu$ m step, place the specimen back in the vacuum evaporation chamber, pour a small amount of mixed epoxy over the partially prepared surface (laying horizontal), and then draw the epoxy into the surface holes by alternating vacuum and atmospheric pressure steps. After the epoxy dries, carefully remove the excess epoxy on the surface by repeating the last step (it may help to switch to a polisher with individual specimen loading to do this efficiently). Then, perform the final polishing step. Some metallographers pour melted wax over the specimen surface. When the wax hardens, they take a plastic card, like a credit card, and scrap off the excess wax, then complete the preparation procedure.