

# Electrolytic Polishing

## 7.0 ELECTROLYTIC POLISHING

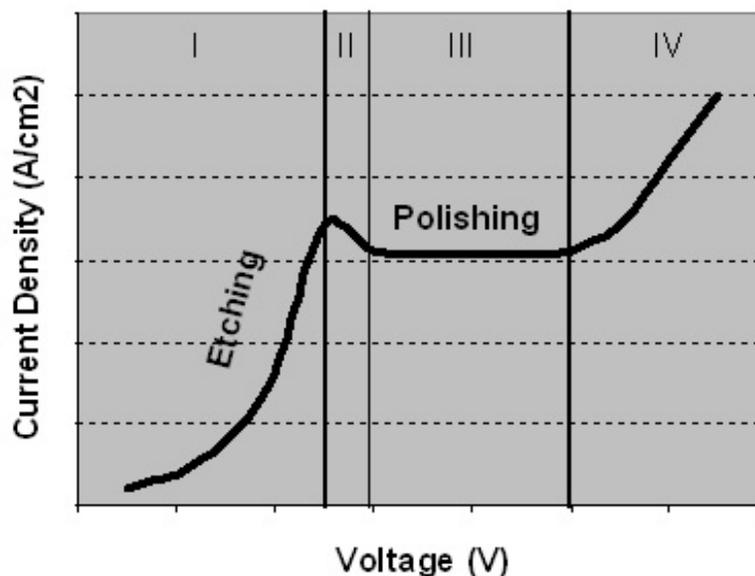
A less commonly used polishing technique is electrolytic polishing. Electrolytic polishing/etching, commonly known as anodic dissolution, is perhaps the best way to polish very soft materials which are prone to smearing and deformation. Materials that work well for electropolishing or etching include soft austenitic stainless steels, aluminum and aluminum alloys, copper and copper alloys, among others. The primary requirement for electropolishing is that the specimen be conductive.

Electrolytic polishing/etching essentially dissolves the higher surface energy sites associated with rough surfaces by smoothing the rough ridges or peaks. This is accomplished by making the specimen surface the anode in an electrolytic cell.

The voltage-current density plot shown in Figure 7-1 represents the mechanism by which electrolytic etching and polishing occurs. In Zone I, the primary mechanism is the direct dissolution of the metal. In this region, etching occurs. Zone II represents the voltage-current density conditions where the metal begins to form a passivation layer. In Zone III, the passivation layer is stable and dissolution of the metal is primarily by diffusion through the passivated layer. In this region, the higher surface area peaks dissolve preferentially to the lower surface area valleys, thus providing a polishing, or smoothing, effect to the surface. By increasing the voltage into Zone IV, the passivation layer breaks down as the oxygen evolution occurs at the surface. In this zone, the metal will begin to pit.

## 7.1 SPECIMEN PREPARATION

It is recommended that the specimen be rough polished down to a 600 or 1200 grit SiC surface finish. The specimen/mount must be conductive and in contact with the electrolyte, as well as the anode connection.



**Figure 7-1** Electrolytic etching and polishing conditions.

## 7.2 SAFETY PRECAUTIONS

Electrolytes suitable for metallographic electrolytic polishing and etching are usually mixtures of acids (such as phosphoric, sulfuric and perchloric in ionizing solutions (such as water, acetic acid or alcohol). Glycerol, butyl glycol, urea, etc. are added to increase the viscosity. Metals which form highly soluble hydroxides are prepared with alkaline solutions, while those forming highly soluble cyanides are treated in cyanides. Most of the electrolytes used are relatively harmless when handled according to known common-sense precautions. However, mixtures of perchloric acid are particularly prone to decompose violently and should, therefore, be treated with extreme care.

### 7.2.1 Perchloric Acid ( $HClO_4$ ) Electrolyte Precautions

Caution must be observed when electrolytically etching with perchloric acid electrolytes because of the possibility of explosion. The primary factors which lead to unsafe use of perchloric acid electrolytes include:

- Electrolyte temperature too high ( $>38^{\circ}C$ )
- Perchloric acid concentration too high due to evaporation or improper mixing
- Reaction with certain common mounting materials (phenolics, acrylics and cellulose based resins).

The tendency of perchloric acid mixtures to explode are related to concentration and temperature. Concentrations above 35% perchloric acid become extremely dangerous. If the operator is not careful, a dangerous condition can occur through evaporation of the water or additives to the electrolyte. Likewise, temperatures greater than  $38^{\circ}C$  make perchloric acid less stable.

It is also recommended that specimens not be mounted in phenol-formaldehyde (phenolics), acrylic-resins or cellulose-base insulating lacquers. These materials produce very violent reactions with perchloric acid and may result in an explosion. However, polyethylene, polystyrene, epoxy resins, and polyvinyl chloride can be used as mounting materials for perchloric acid solutions without danger.

When working with perchloric acid, take precaution to avoid the explosive conditions listed above. In addition, before working with perchloric acid electrolytes they should be stirred and cooled for additional safety.

## 7.3 ELECTROLYTIC EQUIPMENT

Electrolytic polishers are composed of the following elements (Figure 7-2):

- Polishing cell
- Anode connection arm
- Cathode mask (stainless steel or platinum are most common)
- Electrolyte circulating pump
- Power controller for varying voltage and/or current



**Figure 7-2** Electropolisher cell and control unit (Photo courtesy of Remet Italy).

## 7.4 ELECTROLYTE SOLUTIONS

Table I. Electrolyte Solution Guidelines

Material	Etchant	Procedure
Aluminum Pure Al, Al-Cu, Al-Mn, Al-Mg, Al-Mg-Si alloys (1)	90 ml DI water 10 ml H <sub>3</sub> PO <sub>4</sub>	5-10 s, 1-8 V DC, Stainless steel cathode
Beryllium and alloys (2)	294 ml ethylene glycol 4 ml HCl 2 ml HNO <sub>3</sub>	6 min, 30°C (85°F), 13-20 V DC, Stainless steel cathode
Beryllium grain boundary etch. Also used to increase contrast in polarized light (2)	100 ml H <sub>3</sub> PO <sub>4</sub> 30 ml glycerol 30 ml ethanol (96 %) 2.5 ml H <sub>2</sub> SO <sub>4</sub>	1 min, cool (10°C, 50°F), 25 V DC, Stainless steel or Mo cathode
Boride ceramics, TaB <sub>2</sub> , LaB <sub>4</sub> (3)	10 ml DI water 1-2 gm NaOH	Few seconds to minutes, 10-15 V DC, Stainless steel cathode
Boron carbide (B <sub>4</sub> C) and B <sub>4</sub> C composites (4)	100 ml DI water 1 gm KOH	30-60 s, 30-60 V, 3 A/cm <sup>2</sup> , V2A steel cathode, room temperature
Boron carbide (5)	10 ml DI water 0.1 gm KOH	40 V DC, 3 A/cm <sup>2</sup> , Stainless steel cathode, Move specimen
Cadmium (Cd), In (6)	100 ml DI water 200 ml glycerol 200 ml H <sub>3</sub> PO <sub>4</sub>	5-10 min, 8-9 V DC, Cd cathode
Carbide ceramics - TiC, TaC (7)	10 ml DI water 2 gm KOH	2-30 s, 2 V DC, 30-60 mA/cm <sup>2</sup> , Pt cathode, Move specimen

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Copper-Beta brasses, German silver, Monel, Cu-Ni alloys, Bronze (8).	950 ml DI water 50 ml H <sub>2</sub> SO <sub>4</sub> 2 gm NaOH 15 gm iron (III) sulfate	Up to 15 s, 8-10 V DC, Cu cathode
Copper -All types of Cu. Cartridge brass. Tombac. Muntz metal, easily machinable brasses (8)	90 ml DI water 10 ml H <sub>3</sub> PO <sub>4</sub>	5-10 s, 1-8 V DC, Cu cathode
Copper and copper alloys (Cu), Beryllium copper and aluminum bronze (9)	1% CrO <sub>3</sub> 99% water	3-6 s, 6 V, Al cathode
Copper -Al bronzes, Cu-Be alloys (8)	Aq. solution of chromium (VI) oxide (1 %)	3-6 s, 6 V DC, Al cathode
Germanium and its alloys. Grain boundaries (10)	100 ml DI water 10 gm oxalic acid	10-20 s, 4-6 V DC, Stainless steel cathode
Fe-Ni-Cr heat resistant casting alloys (Fe). Blackens sigma phase without outlining other phases (11).	5-6 gm KOH 100 ml DI water	1 s, 1.5 V, Stainless steel cathode, Room temperature
Fe-Ni-Cr heat resistant casting alloys (Fe). Stains austenite, then sigma phase, then carbide particles (11)	38 gm Pb(C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O DI water to make 100 ml	30 s, 1.5 V, Stainless steel cathode, Room temperature

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Cobalt base alloys (Co) Cobalt wrought alloys (13)	95 ml HCl (conc.) 5 ml H <sub>2</sub> O <sub>2</sub>	3 V, 10 s
Cobalt base alloys (Co) Heat resistant high temperature (superalloys) (Co-Cr-X type) (13)	25 ml HCl (conc.) 5-50 ml 10 % solution of chromic acid	6 V, 10 s, amount of CrO <sub>3</sub> determines activity
Co-Cr (40 %)-Ni-Fe alloys (Co) Co-Cr (40 %) - Ni-Fe alloys (13)	92 ml DI water 8 gm oxalic acid	6 V, 25-35°C (77-95°F), 200 mA/cm <sup>2</sup> , 5-15 s
Copper and copper alloys (Cu) (14)	5 - 14 % H <sub>3</sub> PO <sub>4</sub> remainder water	10 s, 1-4 V
Copper and copper alloys (Cu) Coppers, brasses, bronzes, nickel silver.; color by electrolytic etching or with FeCl <sub>3</sub> etchants (15)	50 ml CrO <sub>3</sub> (10-15 %) 1-2 drops HCl	Immersion (add HCl at time of use).
Copper and copper alloys (Cu) Copper and alpha brass (16)	500 ml ortophosphoric acid (conc.) 500 ml DI water	A few seconds to 1 min., 0.8 V, 0.05 A/cm <sup>2</sup> (polishing 1.8 V, 0.12 A/cm <sup>2</sup> ), Cu cathode
Copper and copper alloys (Cu) Cartridge brass, free- cutting brass, admiralty, gilding metal (14)	5 - 14 % H <sub>3</sub> PO <sub>4</sub> remainder water	5-7 s, 1-8 V

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Niobium, molybdenum (17)	65 ml DI water 17 ml HNO <sub>3</sub> 17 ml HF (40%)	Few seconds to minutes, 12-30 V DC, Pt cathode, Toxic
NiO ceramic (17)	60-70 ml DI water 25 ml HF (40 %) 25 ml glacial acetic acid	30-45 s, 2-4 mA/cm <sup>2</sup> , 6-12 V DC, Stainless steel cathode, Toxic
Nickel and Ni base superalloys; gamma precipitates; Ti and Nb microsegregations (18)	85 ml H <sub>3</sub> PO <sub>4</sub> 5 ml H <sub>2</sub> SO <sub>4</sub> 8 gm chromium (VI) oxide	5-30 s, 10 V dc, Pt cathode, Toxic
Wrought Fe-Ni-Cr heat resisting alloys, Inconel X-750 (AISI 688), general structure, no pitting (12)	5 ml HNO <sub>3</sub> 95 ml methanol Use colorless acid and absolute methanol	15-20 s, 5-10 V, Stainless steel cathode, Room temperature
Nickel-Grain contrast in Ni, Ni-Ag, Ni-Al, Ni-Cr, Ni-Cu, Ni-Fe, and Ni-Ti alloys (18)	85 ml DI water 10 ml HNO <sub>3</sub> 5 ml glacial acetic acid	20-60 s, 1.5 V DC, Pt cathode, Do not store, Toxic
Nickel, Ni-Al alloys (18)	85 ml DI water 10 ml glycerol 5 ml HF	2-10 s, 2-3 V DC, Ni cathode, Toxic
Nickel and Ni base alloys, Ni-Cr, Ni-Fe alloys; Superalloys of the Nimonic type (19)	30 ml DI water 70 ml H <sub>3</sub> PO <sub>4</sub> 15 ml H <sub>2</sub> SO <sub>4</sub>	5-60 s, 2-10 V dc, Ni cathode
Nickel -Ni and Ni base alloys; Ni-Cr and Ni-Cr alloys; carbide inclusions (19)	100 ml DI water 2-50 ml H <sub>2</sub> SO <sub>4</sub>	5-15 s, 6 V DC, Pt cathode

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Nickel -Carbides in Ni-Cr alloys (19)	100 ml DI water 10 gm KCN	Approx. 3 min, 6 V DC, Pt cathode, Toxic
Nickel superalloy 718, Inconel 718 alloy (20)	50 ml HCl 40 ml HF 10 ml HNO <sub>3</sub> 30 ml H <sub>2</sub> O	3-5 s, 5 V DC, Stainless steel cathode
Nickel superalloy 718, Inconel 718 alloy (20)	10 ml HNO <sub>3</sub> 90 ml ethanol (10 % Nital)	3-5 s, 5 V DC, Stainless steel cathode
Nickel superalloy 718, Inconel 718 alloy (20)	10 ml H <sub>3</sub> PO <sub>4</sub> 40 ml H <sub>2</sub> SO <sub>4</sub> 10 ml HNO <sub>3</sub> 10 ml DI H <sub>2</sub> O	3-5 s, 5 V DC, Stainless steel cathode
Nickel superalloy 718, Inconel 718 alloy (20)	1 part HCl 1 part H <sub>2</sub> O	3-5 s, 5V DC, Stainless steel cathode
Nimonic alloys - Nimonic PK 31 (21)	45 parts of HCl 15 parts of HNO <sub>3</sub> 40 parts of glycerol	5-15 s, 2-4 V DC, 0.5 A/dm <sup>2</sup> , Nickel, stainless steel or 80Cr-20Ni cathode
Nimonic alloys - Nimonic PK 33, PK 50 Nimonic 901 (21)	20 % KOH solution	5-15 s, 2-4 V DC, 0.5 A/dm <sup>2</sup> , Nickel, stainless steel or 80Cr-20Ni cathode
Nimonic alloys (Ni) - Nimonic alloys 75, 80A, 90, 93, 105 (21)	5 parts of HF 10 parts of glycerol 85 parts of DI water	5-15 s, 2-4 V DC, 0.5 A/dm <sup>2</sup> , Nickel, stainless steel or 80Cr-20Ni cathode

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Osmium, palladium , iridium -Os base alloys, pure Pd and Pd alloys, Pt-Au alloys, Ir (22)	90 ml ethanol (96 %) 10 ml HCl	90 s, 10 V dc, Graphite cathode
Plutonium (Pu) - Pu and Pu base alloys (23)	20 ml methanol (95 %) 50 ml ethylene glycol 5 ml HNO <sub>3</sub>	2 min, 0.05 A/cm <sup>2</sup> , Stainless steel cathode
Silicon carbide (24)	10 % aqueous oxalic acid	0.5 min, 10 V DC, 1 A/cm <sup>2</sup> , Stainless steel cathode
Silicon carbide (25)	10 ml DI water 2 gm KOH	20 s, 6 V dc, 1 A/cm <sup>2</sup> , Pt cathode, Move specimen
Silver (Ag) - Ag alloys (26)	10 ml DI water 10 gm citric acid	15 s to 1 min, 6 V DC, Ag cathode.; possibly 2-3 drops nitric acid
Sintered carbides with high content of Ti and Ta carbide; the carbides are etched (27)	2 gm KOH 10 ml DI water	2-30 s, 2 V, 30-60 A/cm <sup>2</sup> , Pt cathode; agitate specimen or electrolyte
Austenitic stainless steels and high-alloy nickel steel (28)	8 gm oxalic acid 100 ml DI water	5-60 s, Pt or stainless steel cathode

Table II. Electrolyte Solution Guidelines (Continued)

Material	Etchant	Procedure
Titanium (Ti) - Pure Ti and Ti base alloys (29)	80 ml glacial acetic acid 5 ml perchloric acid (70 %)	1-5 min, 20-60 V DC, Stainless steel cathode, Toxic
Titanium (pure) (30)	25 ml DI water 390 ml methanol (95 %) Ethylene glycol 35 ml perchloric acid (70 %)	10-40 s, 5-10°C (40-50°F), 30-50 V DC, Stainless steel cathode, Toxic

**7.5 ETCHING**

The purpose of etching is to optically enhance the microstructural features such as grain size, phase identification and other microstructural features. Etching selectively alters these microstructural features based on composition, stress, or crystal structure. The most common technique for etching is selective chemical etching, and numerous formulations have been used over the years. Other techniques such as molten salt, electrolytic, thermal, plasma and magnetic etching have also found specialized applications.

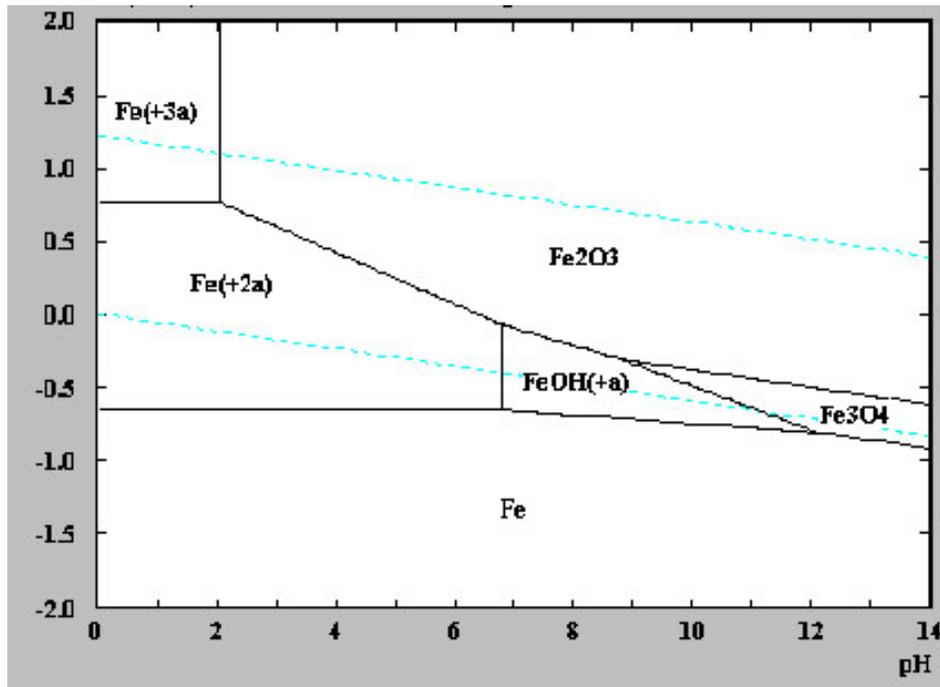


Figure 7-3 Pourbaix electrochemical diagram for iron.

## 7.6 ELECTROLYTIC ETCHING

*Electrolytic etching* is another fairly common etching technique. It is similar to chemical etching in that acids and bases are used for modifying the pH. However, the electrochemical potential is controlled electrically by varying either the voltage or current externally as opposed to chemically. Electrolytic etching is often used for harder-to-etch specimens that do not respond well to basic chemical etching techniques. Electrolytic techniques require that the specimen be conductive and therefore they are limited primarily to metals.

The most common electrolytic etching equipment uses a two-electrode design (anode and cathode) with acids or bases used for the electrolyte. Procedures for this type of electrolytic etching are fairly common and can be found in Section 7.4.

Another type of electrolytic etching requires a more sophisticated electrochemical potentiostat. This equipment uses a three-electrode configuration (anode, cathode and reference) which allows the current and voltage to be adjusted independent of each other. In comparison, for the two-electrode system, the voltage is generally adjusted with the electrochemical instrument, whereas the electrolyte type and composition establishes the etching current. One of the advantages of the three-electrode configuration is that it only requires a conductive solution, such as KCl, instead of highly-corrosive acids or bases.