MACROSTRUCTURE

1-1 INTRODUCTION

Macroscopic examination techniques are frequently employed in routine quality control, in failure analysis, and in research studies. These techniques are generally a prelude to microscopic examination; however, in quality control, they are often used alone as a criterion for acceptance or rejection. A great variety of destructive and nondestructive procedures are available. The most basic procedure involves simple visual examination for surface features such as seams, laps, or scale.

This chapter describes only destructive test procedures; nondestructive methods are not covered. These destructive methods include the following procedures:

- Macroetching
- Contact printing
- Fracturing
- Lead exudation

Proper implementation of these methods is fundamental to the manufacture of materials. In quality control, the manufacturing routine is usually established according to set practices, and the macroscopic methods are used to detect deviations from the norm. In failure studies, one often does not know specific details of the manufacturing process and practices, and the engineer uses these tests to judge quality, to locate problem areas for further study, and, in some cases, to determine how the component was produced. In research studies, the processing steps are often varied, and the macroexamination is designed to show differences due to changes in manufacturing practices. Thus for each type of study, the specific details of the macroscopic examination will vary somewhat, and
the practitioner must have a thorough understanding of the test method, its application, and the interpretation of test data.

Interpretation of the data from these tests requires an understanding of the manufacturing process, since the macrostructure is dependent on the solidification and hot- or cold-working procedures used. There can be pronounced differences in macrostructure because factors such as casting method, ingot size and shape, and chemical analysis will significantly alter the solidification pattern. In addition, the use of manufacturing techniques other than traditional ingot casting, such as continuous casting, centrifugal casting, electroslag remelting, or hot-isostatic pressing, produce noticeably different as-cast patterns. Also, there is a wide variety of metalworking processes that can be applied to material made by any of the above processes, and each exerts a different effect upon the material. All these factors influence the interpretation of the test results.

No material can be said to be entirely homogeneous either macroscopically or microscopically. The degree of heterogeneity can vary widely depending on the nature of the material, the method of manufacture, and the cost required to produce the material. Fortunately, the usual degree of heterogeneity is not a serious problem in the use of commercial materials as long as these variances are held within certain prescribed limits. Certain problems, such as pipe and hydrogen flakes, are in general, quite harmful. The effect of other features, such as porosity, segregation, and inclusions, can be quite difficult to evaluate, and one must consider the extent of these features, the amount of subsequent metalworking, and the nature of the application of the material.

Of the metallographic procedures listed, the macroetch test is probably the most informative, and it is widely used for quality control, failure analysis, and research studies. Classification of the features observed with the macroetch test is often confusing because of the use of "jargon" created since the introduction of this test procedure. The macroetch test is covered in considerable detail in this chapter, and numerous examples of its application to a variety of materials are presented.

1-2 VISUALIZATION AND EVALUATION OF MACROSTRUCTURE BY ETCHING

All quality evaluations should begin on the macroscale using tests designed to survey the overall field in a simple and reliable manner. After the macrostructure of a material has been evaluated, specific features can then be examined microscopically. Abnormalities observed on the etch disc can be studied by fracturing the disc or by preparing metallographic polished samples. Macroetching of transverse or longitudinally oriented samples, i.e., oriented with respect to the hot-working axis, enables the mill metallurgist to evaluate the quality of a relatively large area quickly and efficiently. Thus, macroetching is an extremely powerful tool and is a cornerstone of the overall quality program.
The earliest macroetchants were rather weak solutions used at room temperature. Reaumur (1683–1757) used macroetchants to distinguish between different types of steel and sketched the appearance of macroetched pieces of steel in his work. Rinmann promoted this technique in his book *On the Etching of Iron and Steel*, written in the late 1700s. Sorby, in his classic work published in 1887 "On the Microscopical Structure of Iron and Steel," showed "nature prints," which were inked contact prints of steel etched in moderately strong aqueous nitric acid solutions [1]. The early etching solutions have been reviewed in the classic text by Berglund [2].

1-2.1 Macroetching with Acid Solutions

The first "deep"-etching procedure for steel was developed by Waring and Hofamman using nine parts hydrochloric acid, three parts sulfuric acid, and one part water. Considerable adverse comment about the use of strong acids to evaluate highly stressed components was generated by this paper. Overall, the initial response to deep-acid etching was negative; however, numerous subsequent studies revealed the great value of such etchants.

After the initial work by Waring and Hofamman, considerable attention was devoted to the study of strong acids for deep etching steels. The most widely used deep etch consists of a 1:1 solution of reagent-grade hydrochloric acid and water heated to 160 to 180°F for 15 to 45 min. Etching can be conducted on a saw-cut face, but better resolution is obtained with ground faces. Gill and Johnstin found that this etch was more selective in its attack than similar solutions involving nitric acid and water or sulfuric acid and water [3]. An important feature of this etchant is that evaporation does not significantly vary its composition during use.

The following items should be considered in the development of a macroetchant:

- The etchant should produce good all-around results, should be applicable to the majority of materials, and should reveal a great variety of structural characteristics and irregularities.
- The etchant should be simple in composition, inexpensive, and easy to prepare.
- The etchant should be stable during use or storage.
- The etchant must be safe to use and should not produce noxious odors.

The widespread popularity of the 1:1 hydrochloric acid and water etch is due to the fact that it satisfies these requirements better than other etchants. Appendix A lists macroetchants for iron and steel as well as for other metals.

The 1:1 hydrochloric acid and water etch attacks manganese sulfides readily but does not attack aluminum oxides. Steels high in aluminum content, such as the nitriding alloys, are etched best with an aqueous solution containing 10% hydro-

\[†\text{The reagent grade contains 36.5 to 38\% HCl, whereas the technical grade contains 28\% HCl}\]
chloric acid and 2% nitric acid, developed by V. T. Malcolm. Etching is conducted at 180°F for 15 to 60 min.

As the alloy content increases, so does the degree of segregation and its associated problems. Etching is pronounced at the segregate-matrix interface, and segregate or matrix areas may etch out, leaving pits. Sulfides or carbides may also etch out, leaving pits. Before the investigator can distinguish between pits due to nonmetallic inclusions or segregates and carbides, the disc must be hardened and reetched. If the pits were due to nonmetallics, they will be present to the same degree in both the annealed and the hardened discs.

Watertown Arsenal [4] developed a variant of the standard etch that consists of 38 parts of hydrochloric acid, 12 parts sulfuric acid, and 50 parts water.† This reagent often produces a sharper definition of features than the standard etch, and like the standard etch, its acid concentration does not change markedly during use.

Macroetching provides an overall view of the degree of uniformity of metals and alloys by revealing:

- Structural detail resulting from solidification or working
- Chemical uniformity in qualitative terms
- Physical discontinuities due to solidification, working, etc.
- Weldment structure or heat-affected zones from burning operations
- Hardness patterns in non-through-hardened steels or patterns due to quenching irregularities
- Grinding damage
- Thermal effects due to service abuse

The first three features are best revealed by hot-acid etching, and the remaining four are best revealed by room temperature etchants. Macroetching is usually performed on ground surfaces, although in some cases, especially with cold etchants, better results are obtained when the surface is polished. Chemical segregation can be shown by certain cold etchants. The information obtained can be recorded by photographing the samples or, where possible, by contact printing.

In order to observe these features, one must sample the material properly and use the macroetch test procedure correctly. Fortunately, these test procedures are straightforward and simple to use as long as a few precautions are followed. In practice, one must consider the following test variables:

- Selection of representation samples
- Choice of surface orientation
- Proper preparation of sample surface
- Selection of the best etch composition
- Control of etchant temperature and etch time
- Documentation of test results

†Add the sulfuric acid slowly to the water and allow it to cool; then add the hydrochloric acid.
For routine mill inspection, the metallurgist generally cuts a disc from the top and bottom (occasionally the middle) of billets rolled from the first, middle, and last ingots. For certain products, discs are prepared from all the ingots, after rolling to the required billet size. These discs should be cut so as not to include any of the shear drag which may be present after hot shearing the billets to length or removing the top and bottom discard material. In general, the thickness should be held to ½ to 1 in, since the weight of larger discs is prohibitive for handling. Both cuts should be relatively parallel. It is advisable to cut discs with large cross sections into two or more pieces; cutting directly through the center of the disc should be avoided. Transverse discs are used in most cases, although longitudinal discs can be useful in evaluating segregation and mechanical heterogeneity. For routine work with steels, the saw-cut face is generally satisfactory for etching. For detection of fine details, a smooth ground surface is preferred. Some etchants require a smooth ground or a polished surface for proper delineation of macroetch features.

It is not necessary to remove the as-rolled scale from the disc, but any grease, dirt, or debris on the cut face should be removed. It is not advisable to hot-acid etch hardened steel discs, since they can crack or fracture during etching. Similarly, billets should be soft prior to cutting to prevent surface damage during cutting which will obscure the true etch pattern. Proper cutting and grinding techniques must be employed to avoid any damage from these sources.

1-2.2 Copper-Containing Macroetchants for Primary Structure

Macroetching steels with etchants containing copper ions predates the development of hot-acid etching. These copper-containing reagents are listed in App. B. Heyn's reagent was the first to be developed; some of the others stemmed from efforts to produce better results. The reagents are used principally to reveal phosphorus or carbon segregation and dendritic structure. At the time these reagents were first introduced, phosphorus segregation was an important problem in Bessemer steels. Today, however, little Bessemer steel is produced and phosphorus segregation is not a major problem. However, carbon segregation is still widely evaluated, especially in high-carbon steels. These etchants are employed primarily now in research studies and occasionally in quality control. One of the uses of these etchants has been to reveal the primary structure of materials, that is the gross structure resulting from solidification rather than the secondary or tertiary microstructure. More recently developed copper-containing macroetchants have been used to study strain patterns in stressed metals.

Stead's no. 1 reagent is one reagent that has been widely used. Stead recommended that the etch be used in the following way: A small amount of the etching solution is poured on the surface, and etching is allowed to proceed for about 1 min. The solution is drained off, and fresh solution is added. This process is repeated until the desired etch pattern is obtained. Magnusson [5] states that this procedure produces uneven etching across the sample and results are better if the specimen is etched by immersion, which is contrary to Stead's comment that immersion should never be used.
Magnusson has performed an exhaustive study of the use of Stead's reagent for revealing the primary structure of welds [5]. Magnusson states that the influence of the secondary and tertiary structure must be reduced so that the primary structure can be clearly observed. This can be accomplished by heat treating the specimen prior to etching. While normalizing produces improved results, best results are obtained by quenching and tempering. He recommends austenitizing at about 125°F (52°C) above the upper critical temperature. After a short (5 min) hold, the sample is quenched fast enough to form martensite and is tempered between about 1025 and 1250°F (552 and 677°C) for 1 h. Tempering above 1250°F produces indistinct contrast.

Stead's reagent is used with polished surfaces. According to Magnusson, after heat treatment the sample should be polished using nital etching between the final polishing steps. After the final polishing stage, the sample should be etched about 5 s in 0.5% nital. The sample is rinsed and dried and then etched by immersion. Etching is started with a solution of one part Stead's reagent plus three parts alcohol and one-quarter part water for 45 s. The sample is rinsed, and 5 to 10 drops of a 50-mL solution of 10% ammonia plus 10 drops of H₂O₂ is poured on the surface. The copper precipitate is removed by wiping with cotton. The sample is then etched twice for 30 s (rinse and dry between etches) in one part Stead's reagent and two parts alcohol and then in dilute Stead's reagent (dilution not specified, probably one part alcohol) for 15 s. Preetching with picral produces softer contrast. Magnusson also recommends preetching with a solution of 10 mL of 0.5% HNO₃ plus three drops of 4% picral for improved contrast.

Oberhoffer's reagent has also been widely used because of the good, uniform results obtained. However, well-polished surfaces must be used and best results are obtained if the polished surface is left to sit in air for about 1 h before etching, as pointed out by Magnusson. Pokorny has made a detailed study of the influence of the surface condition, using copper-containing reagents as the macroetchant [6]. Polishing produces two surface effects, a mechanically deformed layer and a chemically absorbed layer. Pokorny claims that primary etching works best in the presence of these two layers. Most other studies claim that the mechanically deformed layer must be removed. The chemically absorbed layer was studied after diamond and alumina polishing using AES (auger electron spectroscopy) and SIMS (secondary ion mass spectrometry) techniques, which showed that this layer consisted of oxygen-metal compounds plus sulfur or ammonium compounds, depending on whether polishing was conducted in an urban or a rural atmosphere. The chemical layer can be removed by ion bombardment. A clean metallic surface is obtained after removal of about 4 nm.

Pokorny showed that etching of freshly polished surfaces produced average results, while samples etched after standing in air or in a vacuum for 20 h produced very good results. He recommends that diamond polishing be conducted only long enough to remove the scratches from grinding and then the samples be aged in air before etching.

Buhr and Weinberg compared the results obtained with the standard 1:1 HCl and H₂O hot etch and with Oberhoffer's reagent to autoradiographs of direction-
ally solidified AISI (American Iron and Steel Institute) 4340 doped with radioactive phosphorus [7]. This work stemmed from the statement of Kirkaldy et al. that Oberhoffer’s reagent was unsuitable as a detector of phosphorus segregation. Both studies agreed that Oberhoffer’s reagent would not produce a useful correlation between the rate of copper deposition and the alloy content. They observed that the hot-HCl etch brought out the outline of the dendrites but little else, did not reveal secondary branches, and attacked the phosphorus-rich regions. Oberhoffer’s etch deposited copper preferentially on the phosphorus-depleted regions and delineated the phosphorus segregation fairly well. The phosphorus-depleted secondary branches were barely revealed, and the widths of these branches were similar to those revealed by the autoradiograph.

Buhr and Weinberg observed that copper was initially deposited preferentially on the phosphorus-depleted regions [7]. Then, a secondary etching attack occurred in these regions that was apparently associated with the structure, producing deeply etched acicular dark areas. This attack produced the dark appearance of the dendrite branches.

These authors studied the influence of carbon content on the action of Oberhoffer’s reagent using the following steels:

<table>
<thead>
<tr>
<th>Code</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.01</td>
<td>0.001</td>
<td>0.39</td>
<td>0.33</td>
<td>0.004</td>
</tr>
<tr>
<td>B</td>
<td>0.01</td>
<td>0.061</td>
<td>0.37</td>
<td>0.33</td>
<td>0.004</td>
</tr>
<tr>
<td>C</td>
<td>0.46</td>
<td>0.001</td>
<td>0.52</td>
<td>0.31</td>
<td>0.007</td>
</tr>
<tr>
<td>D</td>
<td>0.45</td>
<td>0.053</td>
<td>0.10</td>
<td>0.28</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Steels A and C with low phosphorus content did not exhibit a dendritic pattern when etched with Oberhoffer’s reagent. Steel B showed a slight indication, while Steel D exhibited a well-delineated dendritic pattern. These results clearly showed that carbon must be present along with sufficient phosphorus for the dendritic structure to be revealed. The influence of phosphorus level was also examined using AISI 4340 castings with 0.006, 0.020, 0.043, and 0.090% phosphorus. All four samples exhibited dendrite patterns after etching, with the pattern being more pronounced as the phosphorus level increased. According to Karl, the lower limit of phosphorus detection using Oberhoffer’s reagent is 0.003% [8].

1-2.3 Macroetchants for Revealing Strain Patterns

In 1921, Fry published a method for revealing strain lines in iron and steel using both microscopic and macroscopic etching reagents. The macroetchant, Fry’s
no. 4 (see App. B), has been widely used. This solution contains considerable hydrochloric acid, which keeps the free copper from depositing on the sample during etching. A polished specimen is immersed in the solution for 1 to 3 min. It is then removed from the solution, and etching is continued by rubbing with a cloth moistened in the solution and covered with CuCl$_2$. This is continued for 2 to 20 min. The surface should be washed in alcohol (water should not be used for washing) and dried periodically for inspection. If the surface is not bright, rubbing is continued. Etching produces a pattern of light and dark bands corresponding to the location of the maximum shear stresses.

It is recommended that the samples be aged between 400 and 500°F for about 30 min prior to etching. If the etched surface appears dirty, it should be wiped with a cloth saturated with the etching solution. After etching, it is helpful to rinse the specimen in a fairly concentrated solution of hydrochloric acid. The sample can then be safely washed with water and dried. In addition to strain lines, the etch may produce grain contrast.

The studies of Koster [9] and MacGregor and Hensel [10] were instrumental in showing why some steels respond to Fry's reagent while others do not. Koster claimed that the variability in etch response was due to the effect of the aging treatment. Koster believed that Fry's reagent worked only after iron nitride was precipitated during aging. The nitrogen content and the form in which nitrogen is found is critical. Steels high in nitrogen content, such as Bessemer steels, etch readily in a few minutes, while open-hearth steels with lower nitrogen content require several hours or more to reveal the strain pattern. Steels with still lower nitrogen levels cannot be successfully etched. MacGregor and Hensel state that mild steels with 0.01 to 0.05% nitrogen are readily etched with Fry's reagent. They showed that a steel with low nitrogen content that would not respond to Fry's reagent could be successfully etched after light nitriding of the polished surface.

Bish has developed a method to reveal strain patterns in mild steel with low nitrogen content using a modification of Fry's reagent on mild steel plates deformed by punching [11, 12]. The surface is ground to remove about 1 mm of metal and then ground on coarse emery cloth with paraffin lubrication and then with 150-, 220-, 400-, and 600-grit SiC paper with water for the lubricant. The surface is next chemically polished in a solution consisting of 60 mL of H$_2$O$_2$, 140 mL of water, and 10 mL of HF. The sample is first degreased and then swabbed in the chemical polish for 10 s. It is then rinsed in water and dipped in a 20 to 50% solution of HCl in water, rinsed and dried. The specimen is then etched in the modified Fry's reagent by swabbing and immersion using a solution consisting of 36 g of CuCl$_2$, 144 mL of HCl, and 80 mL of water. A black deposit forms on the specimen and is removed by immersing the sample in the chemical polishing solution. This procedure also increases the contrast between the deformed and undeformed regions. The sample is next rinsed in water and dipped again in the dilute HCl solution, then rinsed and dried. Only analytical-grade HCl should be used for making up the solutions described by Bish. Bish claims that successful

† Use plastic gloves when performing this step of the process.
etching requires the removal of any surface damage produced during sectioning and grinding and the use of the chemical polish to remove damage from fine grinding. The chemical polish also appears to produce an active surface. Bish states that this procedure produces etching of the undeformed regions rather than the deformed regions, as is normally observed.

Macroetching procedures have also been developed to reveal strain patterns in nonferrous metals. Procedures for aluminum and nickel-base superalloys are given in App. C.

The strain pattern in most metals can be revealed by annealing the specimen after deformation so as to obtain recrystallization [13]. In the region that receives a critical amount of strain, generally 5 to 8 percent, grain growth is more rapid. This area shows up quite clearly upon macroetching.

1-2.4 Macroetch Specifications

The classification of macrostructures as a basis for acceptance or rejection of materials has been worked out and is now fairly straightforward. Serious defects and very good macrostructures are easily interpreted. In the case of the questionable macrostructure, however, the investigator must have experience and knowledge of the manufacturing procedures and the intended application before the macrostructure can be correctly classified. If the tested section is to be hot-worked to a smaller cross section, the mill metallurgist must know whether the additional hot work will improve the macrostructure sufficiently. Alternatively, rolling the bloom to a smaller size than originally desired in order to obtain a salable product must occasionally be recommended.

The American Society for the Testing of Materials (ASTM) has had a long involvement with macroetching techniques. The macroetching solutions for both ferrous and nonferrous metals were recently incorporated in a single specification, ASTM E340. ASTM has also developed specifications for evaluating the macrostructure of steels. In 1948, ASTM Specification A317, "Standard Method of Macroetch Testing and Inspection of Steel Forgings," was proposed. This specification showed macrographs that illustrated common features revealed by macroetching.

The first rating chart for macrostructure was published in 1957 as MIL-STD-430, "Macrograph Standards for Steel Bars, Billets and Blooms." This rating chart consisted of four series with eight macroetch pictures arranged in increasing order of severity:

<table>
<thead>
<tr>
<th>Code</th>
<th>Type indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Center defects</td>
</tr>
<tr>
<td>B</td>
<td>Subsurface defects</td>
</tr>
<tr>
<td>C</td>
<td>Ring defects</td>
</tr>
<tr>
<td>D</td>
<td>Miscellaneous defects (inclusions, flakes, and bursts)</td>
</tr>
</tbody>
</table>
The D category contained independent examples of particular types of imperfections. This chart is used in MIL-STD-1459A (MU), "Military Standard—Macrograph Standards for Steel Bars, Billets and Blooms for Ammunition Components."

MIL-STD-430 was revised, and the rating chart was changed in MIL-STD-430A. Two charts are used; the first chart shows three series of macroetch pictures with five picture per series:

<table>
<thead>
<tr>
<th>Code</th>
<th>Type indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Subsurface conditions</td>
</tr>
<tr>
<td>R</td>
<td>Random conditions</td>
</tr>
<tr>
<td>C</td>
<td>Center segregation</td>
</tr>
</tbody>
</table>

The second chart shows an example of a ring pattern which is judged acceptable in any degree and five examples of defects which are unacceptable in any degree (flute cracks, gas, butt tears, splash, and flakes). Both of these charts were adopted in 1968 in ASTM E381, "Standard Method for Rating Macroetched Steel."

In 1971, ASTM approved Specification A561, "Standard Recommended Practice for Macroetch Testing of Tool Steel Bars." This specification has a rating chart with two categories—ring pattern and center porosity—with six pictures per category. Another recently developed macroetch standard is ASTM A604, "Standard Method for Macroetch Testing of Consumable Electrode Remelted Steel Bars and Billets," adopted in 1970. This chart was developed to categorize and rate macroetch imperfections that are unique to these materials. Five examples of each class of macroetch imperfection are provided, with the severity increasing from A to E.

<table>
<thead>
<tr>
<th>Class</th>
<th>Type indication</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Freckles</td>
</tr>
<tr>
<td>2</td>
<td>White spots</td>
</tr>
<tr>
<td>3</td>
<td>Radial segregation</td>
</tr>
<tr>
<td>4</td>
<td>Ring pattern</td>
</tr>
</tbody>
</table>

These macroetch rating methods can be applied in a variety of ways. Steels made according to specific ASTM standards can be tested according to ASTM-agreed limits, implied industry limits, or producer-purchaser limits. Some ASTM standards state the chart method that is used but do not list macroetch limits. Other ASTM material specifications require macroetch tests but do not recommend a specific chart method.