

1. ETCHING

Etching is used to highlight, and sometimes identify, microstructural features or phases present. Microscopic examination of a properly polished, unetched specimen will reveal only a few structural features. Only the non-metallic inclusions, porosities and cracks may be easily seen from the surface. Thus, it is beneficial to investigate the sample structure under the microscope after the polishing step. However the polished sample surface reflects the light equally, it would be too difficult to detect any differentiation on the sample surface; hence a generation of a contrast is highly required in that case. Thus the crystalline structure (grains and grain boundaries) of the polished surface is revealed by etching with a proper etchant. This process is named as “chemical etching” or “etching” in brief. It is based on the rate difference in chemical attack depending upon chemical composition, energy content, and grain orientation of the sample. Since the grain boundaries are attacked at a greater rate than the proper grain due to higher energy content of the grain boundaries. In addition, the presence of chemically different phases results in variations in the rate of chemical attack. These changes in the rate of chemical attack produce deviations both in angle and depth of certain portions of the surface. Thus the light is reflected in varying amounts depending on the angle and depressions of the portion of the surfaces resulting in light and dark regions. In this manner the crystalline microstructure of the specimens are revealed.

Etchants are usually dilute acid or dilute alkalis in a water, alcohol or some other solvent. Etching occurs when the acid or base is contacted with specimen surface because of the difference in rate of attack of the various phases present and their orientation. The etching process is usually accomplished by merely applying the appropriate solution to the specimen surface for several seconds to several minutes.

Nital, a Nitric Acid - Alcohol mixture, is the etchant commonly utilized with common irons and steels. Nital is dripped onto the specimen using an eye-dropper or cotton swab. Ten seconds to one minute is usually sufficient for proper etching depending on sample and nital concentration. The sample is immediately washed under running water, rinsed with alcohol and dried in an air blast. Do not touch, wipe or swab the specimen following etching; dry off the rinsing alcohol on the specimen with the air blast and then move on to the microscopic examination stage.

1.1. Macro-etching

This process is utilized to reflect the heterogeneity exist in the metals and alloys. Added to this,

- Different structural defects left from the solidification or mechanical process (differentiation in grain size, traces left from the deformation process, columnar or dendritic structures,...),
- Heterogeneities resulted from the carburization or decarburization processes, segregation and carbide-ferrite band formation,
- Physical defects (porosities, cracks,...) may be noticed by the macro etching process.

Moreover, to observe the welding, heat treatment and quenching effects (the depth of the affected region, the presence of cracks), on the sample microstructure we can also utilize macro-etching process.

In steel industry, this process is widely used for quality control. The structures of the ingot, segregation and inclusion presence are detected by this process. In hammered alloys, by following the traces left from the hammering, an optimization in hammering process is also achieved. In order to make macro-etching, grinding up to 400 numbered sandpaper is done. Mostly, there is no need to polish the sample surface before the macro-etching.

1.2. Etching of a sample having multi-phases structure

The etching mechanism of the multiphase structure has electrochemical properties. Once the sample is reacted with the reactive, a potential difference between the different phases is aroused. The phase having higher electropositive potential behaves like a positive electrode and starts to be dissolved during etching. The other phase behaves like a negative electrode (cathode) will stand out without any change. The concentrations of the etching solution and the process duration have to be optimized to prevent over etching effect of the sample. During etching the dissolution of the positively induced phase, will result in a crater formation. During the microscopic analysis, the light cannot reflect this region, thus darkness is detected. On the other hand, for the negatively induced phase a reflection of light occurs and bright appearance is detected (Figure 1).

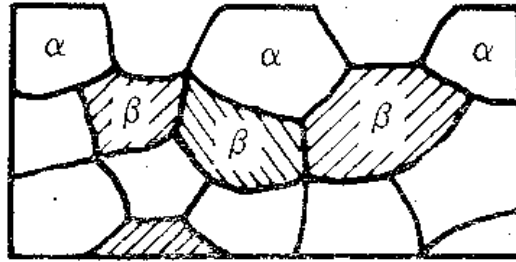


Figure 1. Etching of a sample having multi-phases structure

1.3. The etching of pure metals and one phase structured materials

The etching of homogenous one phase structured material is different than that of the multiphase structured samples. In this case, the etching mechanism is based on an electropositive process since the potential difference between the matrix material and inclusions or the bulk material and the grain boundaries are so small that it is highly difficult to detect any difference among them. Thus, it is aimed to notice the differentiation in the grain depending on their dissolution rate. The grains having the same orientation have the same brightness when the sample is observed under the optical microscope. This process is called as “oriented grain brightness”. This difference may be detected particularly in long etching process duration. In case of grain boundaries, since they exhibit high energy compared to the bulk material, they are preferentially dissolved when the sample contacts with the reactive resulting in the formation of cracks among the valleys (Figure 2).

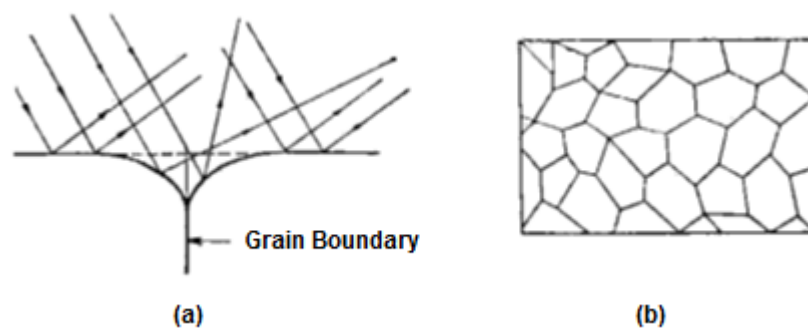


Figure 2. In grain boundaries a) the valley formation after the etching process b) view of the grain boundaries under the optical microscope investigation.

If the etching time exceeds a limit, the preferential dissolution of the sample ends up and the dissolution of the whole sample starts. This case is named as “excessive etching”. The

microscopic view of the over-etched sample is only dark. To be able to analyze this sample, it is recommended to make fine polishing and etching again.

1.4. Reactives used in etching

Generally the reactives used in metallographic etching are formed when the solvents (one or more) made of water, alcohol, glycerin and glycol mixed with different organic/anorganic acids, various alkalines and other complex compounds.

The reactivity and the effect of the reactives depend on,

- a) Hydrogen ion concentration
- b) Hydroxyl ion concentration
- c) The blackening effect of one or more components.

Each materials needs an appropriate reactive. The reactives used in steel and hammered iron are given in Table 1. For each application, the reactive must be prepared freshly and used immediately. Also, the etching solutions used for different materials are given in Table 2 The etching process is very easy but needs a particular attention. The main important point of this process is to choose the appropriate reactive. In order to achieve the desired effect, the application rules of the reactive where the concentration of the reactive, the process duration and conditions have to be obeyed.

Table 1.The etching solutions used in steel and hammered iron

<u>The reactive composition</u>	<u>The application</u>
1-10 ml HNO ₃ , 90-99 ml methanol or ethanol	It is known as Nital . This is the mostly used solution for the etching of iron, alloyed - pure steel and cast iron. It demonstrates the ferrite grain boundaries and phases within the sample structure.
4 gr picric acid, 100 ml ethanol	It is known as Pikral . It is recommended to be used for samples having ferrites and cementite phase. This reactive can not demonstrate ferrite's grain boundaries.
1-4 gr K ₃ Fe(CN) ₆ , 10 gr KOH, 100 ml water	It has to be used freshly. The sample is etched when the sample temperature arrives to its boiling degree. The Cementite phases are seen as black and the perlite phases are noticed as brown.
100 ml ethanol, 5 ml HCl, 1 gr picric acid	The reactive of Vilella . It is used for samples having ferrite and carbide structures. It gives information about the austenite grain size and notices the phases present in the stainless steel.
30 ml water, 25 ml ethanol, 40 ml HCl, 5 gr CuCl ₂	The reactive of Fry . It is used to demonstrate the defects in the steel resulted from the cold deformation process.
15 ml HCl, 20 ml water, 1 gr CuCl ₂ , 5 gr picric acid, 135 ml ethanol	The reactive of Noren . It is used to show the cracks formed in the region affected by the welding process.
10 gr oxalic acid, 100 ml water	This is an electrolytic etching reactive used for steel. The distance between the cathode and the anode material is kept as 25 mm, the applied voltage is set to 6V. The carbides become remarkable in 15-30 seconds, the grain boundaries become outstanding in 45-60 seconds.

Table 2.The etching solutions used for different materials

<u>Materials Composition</u>	<u>Application</u>	<u>Procedure</u>
Iron & Steel	1-5 Parts Nitric Acid 100 Parts Alcohol 1 Part Ammonium Hydroxide 1 Part 3% Hydrogen Peroxide 1 Part Water	Immerse/Swab Swab
Copper & Brass	5 g Ferric Chloride, 10 ml Hydrochloric Acid 100 ml Water 5-10 g Ammonium Persulphate 1 ml Hydrofluoric Acid 99 ml Water	Immerse Immerse
Aluminum	10 g Sodium Hydroxide, 100 ml Water 10 g Oxalic Acid 100 ml Water	Immerse Use Electrolytically
Stainless Steels	5 ml Sulfuric Acid 100 ml Water	Use Electrolytically

1.5. Electrolytic etching

The electrolytic etching of a sample is done in an electrolysis cell. This process is particularly used for the electrolytic polishing of stainless steel. The solution used in electrolytic polishing may be acidic/basic or salt contained. The samples will be anode in most cases. D.C. current is applied generally on the specimen. The etching process is controlled by varying the applied potential value and process duration.

2. MICROSCOPICAL EXAMINATION

The microstructural study of a material can provide information regarding the morphology and distribution of constituent phases as well as the nature and pattern of certain crystal imperfections. Optical metallography is a basic tool of material scientists, since the equipment is relatively inexpensive and the images can be obtained and interpreted easily. Distribution and morphology of the phases can be studied and, if their properties are known, a quantitative analysis of the micrographs provides some information about the bulk properties of the

specimen. A limited study of line and surface informations is also possible with the optical microscope.

In order to obtain reproducible results, with good contrast in the image, the specimen surface is polished and subsequently etched with appropriate reagents before microscopic examination. In a polished specimen, the etching not only delineates grain boundaries, but also allows the different phases to be distinguished by differences in brightness, shape, and color of the grain. Differences in contrast may result from differences in light absorption characteristics of the phases. Etching results in preferential attack or preferential colouring of the surface. The preferential attack is electrochemical corrosion; it is well known that different materials corrode at different rates. Grain boundaries are often anodic to the bulk metal in the interior of the grain and so are etched away preferentially and delineated. Staining is produced by the deposition of solid etch product on the specimen surface. This is formed by chemical reaction between the etchant and the specimen. Under favorable conditions the use of a proper etchant enables the identification of constituents. Failure analysis depends a great deal on metallographic examination.

Microstructural examination can provide quantitative information about the following parameters:

- 1) The grain size of specimens
- 2) The amount of interfacial area per unit volume
- 3) The dimensions of constituent phases
- 4) The amount and distribution of phases.

2.1. Metallurgical (Optic) Microscope

The microstructure of the metals and alloys is investigated by metallurgical microscopes. An optic microscope has the maximum 2000x magnification and 1000Å separation efficiency (lateral resolution). For higher magnification analyses, electron microscopy has to be used, which is not in the scope of this study. Unlike biological microscopes, metallurgical microscopes must use reflected light. Figure 3 presents a simplified ray diagram of the illuminating and imaging system of a metallurgical microscope.

Light incident upon the specimen is reflected back from the specimen surface. Any light that reflects back from specimen features which are approximately normal to the optical axis (i.e. features that are perpendicular to the incident light beam) will enter the objective, pass through the plane glass reflector, travel on to the eyepiece, and will form the bright portion of

the image one sees. Any light that is reflected back from features inclined to the optical axis (i.e. features that are not perpendicular to the incident light beam) will be scattered and will not enter the objective. Such features will thereby appear dark in the image one sees. The final image of the specimen, formed by the eyepiece(s) of the microscope, is thus bright for all features normal to the optical axis and dark for inclined features. In this way, the various microstructural features of a metallographic specimen (such as grain boundaries that have been etched to produce grooves with inclined edges, precipitate particles, and non-metallic inclusions) are all revealed in the image of the specimen. Figure 4 presents a schematic diagram showing bright and dark image areas corresponding to reflection from normal or inclined features on the specimen surface.

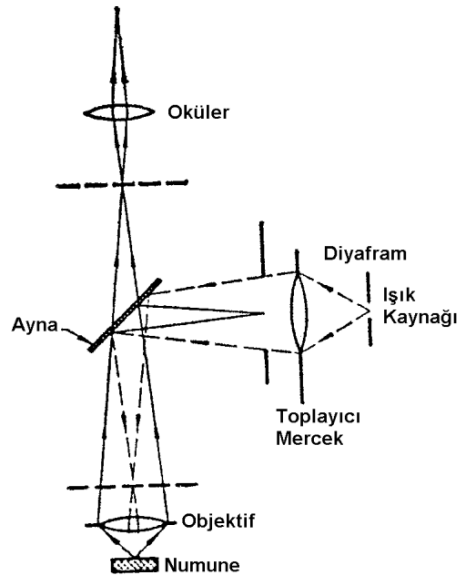


Figure 3. Specimen image under bright-field illumination.

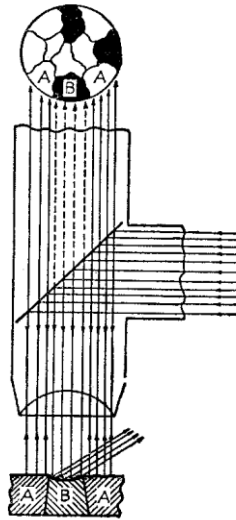


Figure 4. Schematic representation of an etched sample having two phases.

Lab Procedure- Etching Steel Specimens

1. Once the polishing step is end up, the sample is rinsed with distilled water. The sample will be rinsed with alcohol and and let it dry using the hot air gun.
 2. The sample will be observed by using an optical microscope with 100X magnification to decide if the polishing is enough or not. (If it's not enough then you can continue to polish the sample)
 3. Place the specimen on the table under the Fume Hood with the polished surface up.
 4. Some amount of cotton is kept by using pincers. The cotton is immerged into Nital solution then applied on the sample surface. This process continues up to a limit where the surface of the sample is not polished anymore (becomes opaque). (be careful, not over-etched the sample!!)
- Nital = % 1-5 Nitric acid (HNO_3) + %95-99 Alcohol(CH_3OH)
- when the sample is etched, it has to be rinsed with water then with alcohol, finally the sample is dried under the hot air gun.
5. Proceed to Microscopic Examination at 50X, 100X and 200X magnificaitons; if further etching is required you may return the last two steps will apply once again.
 6. If the specimen has many scratches and marks or the microstructure cannot be seen after several etches, return to fine grinding and go back through the necessary steps.

HOMEWORK

- 1.** What was the reactive you used during the etching process? What is the procedure that you applied while making etching process (indicate the process duration particularly)? Please indicate schematically how to get a view of an etched surface when it was investigated by an optical microscope.
- 2.** Draw schematically the view of the sample detected under the optical microscope with 100x magnification, before and after the etching processes.
- 3.** Please indicate precisely the problems that you faced while preparing the your sample for the microscopic examination. Moreover, explain in detail the solution that you find to resolve all those problems.