No. 21

LECO MET-TIPS Ideas for Metallographic Procedures

Sulfur Printing

Sulfur printing is somewhat of a lost art in modern day metallographic practices, but it should not be because much information can be obtained from a sulfur print that is not available with highly sophisticated sulfur analyzers. Although these sophisticated instruments are extremely accurate (to the fifth decimal place), very rapid (less than 30 seconds), and very reliable, the results represent the sulfur content of just the small piece used for analysis and will not indicate whether the sulfur is randomly dispersed or is confined to segregated areas.

Sulfur is a yellow, brittle, crystalline solid which does not exist in its pure state in ferrous alloys but rather combines chemically with manganese to form manganese sulfide inclusions, or with iron to form iron sulfide inclusions. In the molten state, the sulfur inclusions are almost uniformly distributed, however, on cooling and due to difference in density and fusion temperature between these inclusions and the metal, they may segregate, causing some areas in the solid state to have a higher sulfur content. Sulfide inclusions can have a beneficial or a deleterious effect on steels, depending on type and distribution.

In free-machining steels, sulfur is deliberately added, along with an increase in manganese, to form globular manganese sulfide inclusions (Type I) which are usually randomly distributed. If there is not enough manganese to tie up the sulfur, it will unite with iron to form iron sulfide inclusions. Iron sulfide has a relatively low melting point, and when the metal is worked at elevated temperatures the iron sulfide will form a continuous film in the grain boundaries and cause the metal to crack along grain boundaries. This phenomenon is called hot shortness.

While sulfur printing cannot differentiate between manganese or iron sulfide inclusions, it can show the sulfur distribution on a macro scale. Sulfur printing is a technique applied to as-ground or polished sections from ingots, forgings, or a hot rolled product to reveal sulfur segregation. The technique is simple, requiring no special skills or equipment, but care must be exercised to avoid smearing the print during contact with the sample. Although photographic paper is involved, the procedures can be done in a well lighted room, but unused paper must be kept in a light-tight box and individual sheets taken from the box in a darkened room. Any grade of print paper (contact or enlarging) can be used, however, one with a matte or semi-matte finish is recommended to minimize the danger of slippage when the specimen is placed in contact with the paper.

A representative cross-section is obtained from the material by any means that will produce a relatively flat surface; however, a cut-off machine with an abrasive cut-off wheel will produce the best surface, requiring minimal grinding steps to obtain a finely ground and flat surface. Sulfur printing can be done on either an as-ground surface (600 grit silicon carbide) or an as-polished surface (diamond polish), but the latter will require less time and less chance of smearing the print.

A 3% aqueous sulfuric acid solution is placed into a shallow basin, and ordinary photographic print paper with a sensitized silver bromide surface is placed into the sulfuric acid solution for several seconds until thoroughly wetted. The paper is removed with tongs or tweezers and held over the basin to allow excess solution to drain off, then placed emulsion side up onto a flat surface such as a glass or baked bakelite sheet. The prepared surface of the sample is pressed and held against the paper surface for approximately 20 to 30 seconds (shorter time for as-polished surfaces and longer time for as-ground surfaces). One end of the sample is lifted off the paper first, taking care to avoid a twisting or sliding motion that will cause smearing.

The print is rinsed in water, fixed in a hypo solution, thoroughly washed, and dried. The brown pattern revealed (silver bromide deposits) indicates sulfur distribution. The best results are obtained from only one contact; if a second print is required because the first print is smeared or contact was not long enough, the sample must be reground and/or polished.

If darkroom equipment is not available for washing and drying prints, washing can be done by placing the prints in a large container (e.g. plastic bucket) and putting the container under a water faucet and running water into the container. A coarse mesh screen placed over the container keeps the prints confined.

Drying prints can be accomplished by placing the emulsion side down on a flat surface (ferro-type plates, glass sheet, smooth formica tops, etc.), covering with a paper towel, and running a roller over the towel to remove and absorb excess water. When the prints are dry, they will raise from the flat surface.

If commercial fixing solutions are not readily available, one can be made by combining the following in the order listed, making sure each is completely dissolved before adding the next.

Fixing Bath
600 ml Water
240 g Sodium Thiosulfate (hypo)
15 g Sodium Sulfate
45 ml Acetic Acid (28%) *
7.5 g Boric Acid
15 g Potassium Alum
Enough water to make one liter

**To make 28% acetic acid from glacial acetic, dilute 3 parts glacial acetic to 8 parts water. Store unused fixing bath in a dark place.*

Following are two sulfur prints made by the technique described.

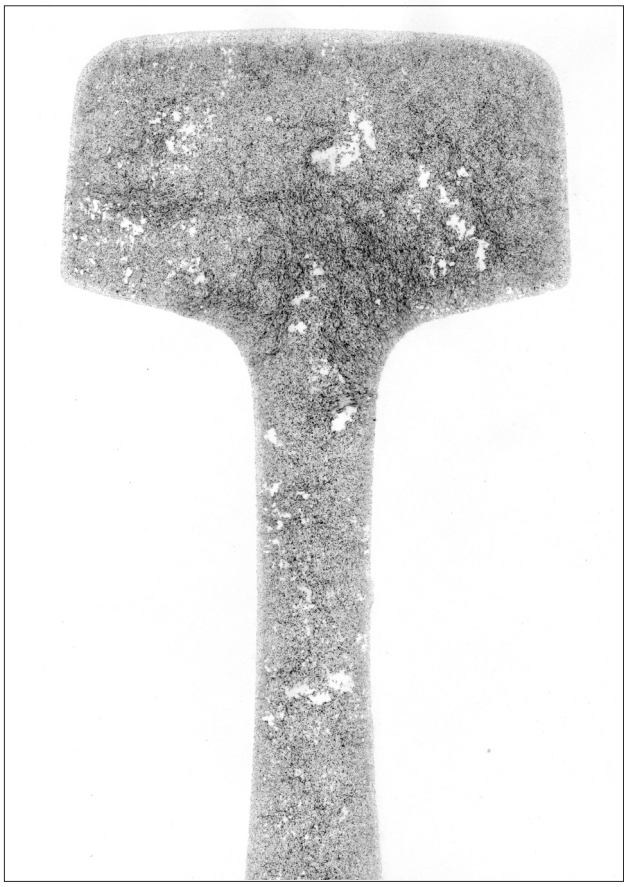

Figure 1. Cross section of a railroad rail.

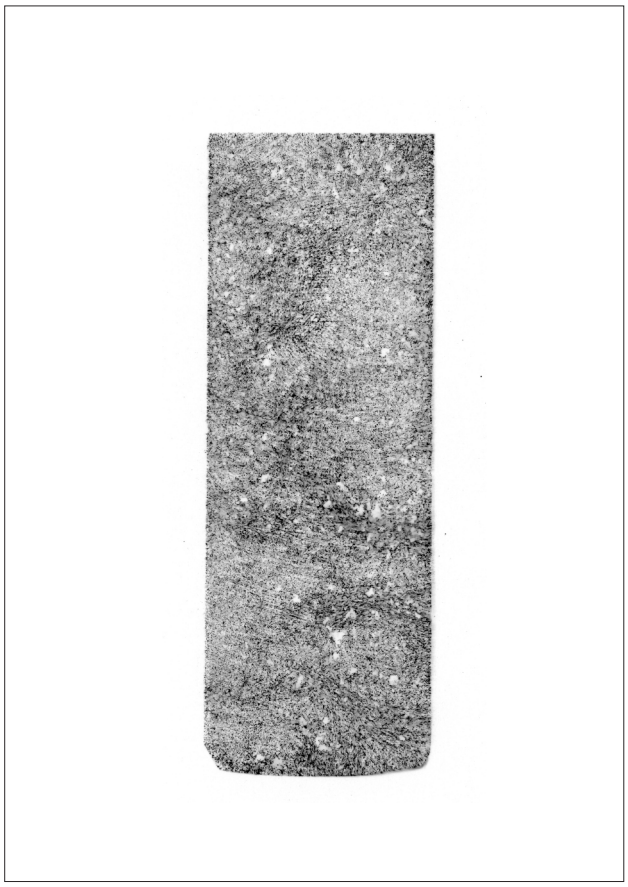

Figure 2. Cross section of a gray iron ingot.

LECO Corporation would like to thank Dr. Lee Dillinger for his contributions to this project.

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