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Standard Practice for Preparing Sulfur Prints for Macrostructural Evaluation[1]

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1. Scope

1.1 This practice provides information required to prepare sulfur prints (also referred to as Baumann Prints) of most ferrous alloys to reveal the distribution of sulfide inclusions.

1.2 The sulfur print reveals the distribution of sulfides in steels with bulk sulfur contents between about 0.010 and 0.40 weight percent.

1.3 Certain steels contain complex sulfides that do not respond to the test solutions, for example, steels containing titanium sulfides or chromium sulfides.

1.4 The sulfur print test is a qualitative test. The density of the print image should not be used to assess the sulfur content of a steel. Under carefully controlled conditions, it is possible to compare print image intensities if the images are formed only by manganese sulfides.

1.5 The sulfur print image will reveal details of the solidification pattern or metal flow from hot or cold working on appropriately chosen and prepared test specimens.

1.6 This practice does not address acceptance criteria based on the use of the method.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 9.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E3 Guide for Preparation of Metallographic Specimens

E7 Terminology Relating to Metallography

E340 Practice for Macroetching Metals and Alloys

E381 Method of Macroetch Testing Steel Bars, Billets, Blooms, and Forgings

E407 Practice for Microetching Metals and Alloys

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, see Terminology E7.

4. Summary of Practice

4.1 The sulfur print provides a means for macroscopic evaluation of the sulfur distribution in steels and cast irons by contact printing using photographic paper soaked in an aqueous acid solution, for example, sulfuric acid, citric acid, or acetic acid.

4.2 The test specimen is usually a disk or rectangular section, such as used in macroetch evaluations, cut from an as-cast or wrought specimen with either a transverse or longitudinal orientation. The specimen is freshly ground smooth and cleaned to remove cutting oils, scale, abrasives, or other contaminants. The specimen should be at room temperature when sulfur printed.

4.3 A sheet of photographic paper with (usually) a matte surface finish of appropriate size is soaked in the dilute aqueous acid solution, any excess liquid removed, and the emulsion side of the paper is placed on the ground surface of the specimen. After a suitable time, the paper is removed, washed in water, fixed, washed again in water, and dried as flat as possible.

4.4 The distribution of sulfur in the specimen is revealed as a mirror image on the photographic paper as darkly colored areas of silver sulfide embedded in the emulsion.

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[1] This practice is under the jurisdiction of ASTM Committee E04 on Metallography and is the direct responsibility of Subcommittee E04.01 on Specimen Preparation.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5. Significance and Use

5.1 The sulfur print reveals the distribution of sulfur as sulfide inclusions in the specimen. The sulfur print complements macroetch methods by providing an additional procedure for evaluating the homogeneity of a steel product.

5.2 Sulfur prints of as-cast specimens generally reveal the solidification pattern and may be used to assess the nature of deoxidation, that is, rimming action versus killed steel sulfur distributions.

5.3 Sulfur prints will reveal segregation patterns, including refilled cracks, and may reveal certain physical irregularities, for example, porosity or cracking.

5.4 The nature of metal flow, such as in various forging operations, can be revealed using sulfur prints of specimens cut parallel to the metal flow direction.

5.5 The sulfur print method is suitable for process control, research and development studies, failure analysis, and for material acceptance purposes.

5.6 The intensity of the sulfur print is influenced by the concentration of sulfur in the steel, the chemical composition of the sulfide inclusions, the aggressiveness of the aqueous acid solution, and the duration of the contact printing between the acid soaked emulsion coated paper and the ground surface of the specimen (this time is the order of seconds rather than minutes). Very low sulfur content steels will produce too faint an image to be useful for macrostructural evaluations. Selection of appropriate printing practices including selection of type of emulsion coated media, acid type and strength, will yield satisfactory prints. Very faint images in the sulfur print can be made more visible by scanning the sulfur print into a PC, and using a photo editor to increase the color saturation. Steels with compositions that produce predominantly titanium or chromium sulfides will not produce useful images.

6. Interferences

6.1 The specimen must be properly cleaned, otherwise dark spots will be produced which may be incorrectly interpreted as a gross sulfide segregate.

6.2 Hydrogen sulfide gas is produced while the paper is in contact with the specimen. The hydrogen sulfide is readily absorbed by the wet emulsion. The hydrogen sulfide reacts with the silver halides in the emulsion to lay down insoluble silver sulfide. If the specimen contains pores or cracks, hydrogen sulfide gas may become entrapped in these openings and may produce a brown color on the paper which may be incorrectly interpreted as a gross sulfide segregate.

6.3 If air is entrapped between the contacting paper and specimen, and is not removed, a white spot may be produced on the print. Air entrapment must be quickly removed by the use of a rubber squeegee or roller to move bubbles to the edge of the specimen.

6.4 Image blurring may result from movement of the paper during contact.

6.5 Specimens with low sulfur contents are often pre-etched before printing to expose more sulfides and enhance the image. If the pre-etchant contains sulfate ions (for example, a stainless steel specimen etched with Marble's reagent), the print will be lightly colored, even if sulfides are not present in the steel. Such etchants should not be used for this purpose.

6.6 If chromium replaces some of the manganese in the sulfide inclusions, the print intensity for a given sulfur level will be reduced. An image will not be obtained, irrespective of the sulfur content, if titanium or chromium sulfides are present.

7. Apparatus

7.1 *Lighting*—If the chosen photographic paper when exposed to the existing room light for 15 min changes from white to light blue and then clears back to white when processed in the sequence of solutions, there is no need to turn off the existing white lighting, and work under amber bulb lighting; never expose the paper to sunlight.

7.2 *Shallow Container,* such as a photographic tray, is required to contain the dilute aqueous acid solution. The container must be large enough to soak the emulsion coated paper without wrinkling.

7.3 *Timing Device,* such as used in a photographic darkroom, is helpful for timing the contact printing time, and the washing and fixing periods.

7.4 *Tank,* of suitable size with cool flowing water, is required for washing the print.

7.5 *Tank, or Covered Tray,* to hold the fixing agent and the print; two can be used sequentially for faster fixing when using emulsion coated double weight fiber based paper.

7.6 *Drying*—Heated drum dryers are no longer made. Heated drying cabinets are available for fiber base prints laid horizontally on a screen. Resin coated papers can be dried with an infra red dryer very quickly. Clothes lines and cork peg boards will also work but the prints do not dry perfectly flat.

8. Reagents and Materials

8.1 Photographic paper is a multilayer paper coated with a gelatin emulsion containing about 80 mg per square meter of silver as a halide (Cl and/or Br) supported by a paper base that is nominally single or double weight (110 g/sq. m or 235 g/sq. m). The speed and contrast characteristics are of no importance when sulfur printing. The paper base may be fibre base or resin coated. A thin layer of baryta may separate the emulsion and the base in order to provide a more visible image. A glossy emulsion is preferred to a matte emulsion if image sharpness is important; the problem is that a glossy emulsion may slide on the steel surface and cause blurring. A fibre base is preferred to a resin coated base because the fibre base tends to better conform to the steel surface; in addition it has less tendency to slip when smoothing the paper over the steel surface. Note that photo paper for digital photo printing contains no silver halide emulsion and is not suitable for sulfur printing. The advantage of resin coated photographic paper, over fibre base paper, is that the paper base is sealed from contact with the dilute acid, the rapid fixer, and the water during washing; hence the processing time, including drying time, is much less, especially if double weight paper is used. Photographic paper is available in cut sheets and rolls of various widths. Cut sheets are ideal if the specimen size matches the sheet size. Roll dispensed paper can be fed from a "safe" box and cut as needed. The paper sheet should be 12 mm to 20 mm larger than the specimen around the perimeter of the specimen. If the overhang of the paper is too great then the paper will not lie tight to the edge of the specimen.

8.2 Technical or reagent grade acids, sulfuric acid, acetic acid, citric acid, etc., are used to make the solution in which the paper is soaked prior to contact printing; typical concentrations of acid are 2 % to 10 % sulfuric acid, 10 % to 15 % acetic acid, and 10 % to 15 % citric acid.

8.3 A commercial photographic fixing solution (rapid fixer contains ammonium thiosulfate rather than sodium thiosulfate) is used to fix the sulfur print image after contact printing and washing. The fixer should be tested periodically to ensure that it is still active; set aside a print in the sunlight and if the appearance changes then the fixer is depleted and should be replaced. Used fixer contains silver and should be disposed of in concordance with local regulations. There is not enough silver to justify having the silver recovered from the used fixer.

9. Hazards

9.1 Sulfuric acid, H_2SO_4, is a highly corrosive, dangerously reactive, strong oxidizing agent. It reacts with water releasing substantial heat. Add sulfuric acid very slowly to the water with constant stirring. Contact with concentrated sulfuric acid must be avoided. The dilute solution used to soak the prints is not particularly dangerous but exposure to it should be minimized and hands should be washed after any contact. The use of rubber gloves should be considered. Use tongs to handle the paper in the soaking solution. The other acids recommended for sensitizing the paper are less aggressive than sulfuric acid, however, appropriate care should be taken in mixing and handling.

9.2 The reactions during sulfur printing are as follows:

$$H_2SO_4 + MnS = H_2S + MnSO_4 \tag{1}$$

$$H_2SO_4 + FeS = H_2S + FeSO_4 \tag{2}$$

(there may be some ferrous sulfide in the steel)

$$H_2S + 2Ag\,Cl = Ag_2S + 2HCl \text{ or} \tag{3}$$

$$H_2S + 2AgBr = Ag_2Br + 2HCl \text{ or both.}$$

Warning—Note that hydrogen sulfide is released into the room. Hydrogen sulfide is toxic and needs to be exhausted from the room if more than a few samples are sulfur printed per 8 hour time period. If you can smell the hydrogen sulfide then an exhaust system is needed.

10. Sampling and Specimens

10.1 Samples are generally selected in the same manner and extent as for macroetching, as described in Methods E3, E340, and E381. Specimens are frequently prepared to represent the entire transverse cross section, in addition, depending on the purpose of the evaluation; the longitudinal plane may be selected, and while it is usually vertical, it may be horizontal, when required, for example, checking near the edge of a slab.

10.2 The number, orientation, and location of specimens may be subject to producer-purchaser agreement.

10.3 Specimens should be cut in a region away from any effects from hot shearing or burning; unlike macroetching, the sulfur print appearance is not affected by being within the heat affected zone (HAZ) which results from the torch cutting of cold steel.

10.4 Specimens can be thin enough for ease of handling, generally 12 mm to 25 mm thick, but may be thicker, especially if being prepared on only one side for electrolytical macroetching after sulfur printing (40 mm to 50 mm thick). The surface to be contact printed should be freshly ground until smooth, and carefully cleaned. Edges should be free of flash, burrs, or scale.

10.5 Very smooth surfaces, such as produced by polishing, will promote slippage between the paper and disk resulting in blurred images. A 250 micron (60 grit as packaged) finish provided by dry grinding with a hand held abrasive grit disc sander, or a contact wheel belt sander is satisfactory. Using a face mill may leave tool marks that show up in the sulfur print. Using a (single) wiper insert for the final pass may leave the surface so smooth that it must be sanded to make it rough enough for sulfur printing. A vitreous bonded abrasive surface grinder may be used as long as the final pass is very light and removes only 5 micrometer. The surface should be cleaned with methanol to remove oils and other soils. The final surface roughness Ra should be no less than 0.4 micrometer and may be as large as 1.6 micrometer if the paper tends to slip too easily on a smoother surface.

10.6 Surface preparation (see Methods E3, E340 and E381) should not produce excessive cold work at the test surface that can close up voids and cracks.

11. Procedure

11.1 Soak the photographic paper in the selected aqueous acid solution. The strength of the solution will depend upon the acid selected, the sulfur content of the steel and the desired printing time (the reaction is very rapid). AISI 10XX steels with sulfur contents between 0.015 wt % and 0.035 wt % are typically printed using a 2 % sulfuric acid solution. AISI 11XX series steels are more successfully printed with a 15 % citric acid solution. Steels with low sulfur contents (under 0.010 wt %) may be printed using 5 to 10 % sulfuric acid solutions. When large size prints are desired, a longer working time may be required, necessitating a weaker acid solution.

11.2 Soak the paper in the solution for 1 min to 5 min. A 3 min soak time is commonly used. Periods in excess of 5 min may cause swelling of the emulsion. The tendency of the paper to curl must be removed and the paper must become very limp.

NOTE 1—Only fiber base papers permit the paper to become truly limp; this is the main disadvantage of resin coated papers; the paper will not conform with any low spots in the sample surface.

11.3 After soaking the required time, remove the paper from the solution and allow excess solution to drip off the paper into the bath. To minimize paper movement during printing, it may