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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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E3 Guide for Preparation of Metallographic Specimens

E7 Terminology Relating to Metallography

E340 Test Method 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.

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.

[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.

5.3 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 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 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:

$$H_2SO_4 + MnS = H_2S + MnSO_4 \quad (1)$$

$$H_2SO_4 + FeS = H_2S + FeSO_4 \quad (2)$$

(there may be some ferrous sulfide in the steel)

$$H_2S + 2Ag\ Cl = Ag_2S + 2HCl \text{ or} \quad (3)$$

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

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 to 25 mm thick, but may be thicker, especially if being prepared on only one side for electrolytical macroetching after sulfur printing (40 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 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 be advisable to place the paper on a glass plate and remove excess liquid with a rubber roller or non-rubber elastomer roller or squeegee.

11.4 When the paper surface is relatively dry, lay the paper, emulsion side down, on the clean, ground surface of the specimen.

NOTE 2—Hold the loop of paper between the left and right hands near the outer edges and allow the bottom of the loop to first touch the center of the sample so that the paper will overhang the sample equally on all sides.

11.5 Any air bubbles between the test piece and paper must be carefully moved off to the edge of the sample using a roller,

squeegee, sponge, or paper towel soaked in the aqueous sulfuric acid solution. This must be done carefully so that the paper does not move.

11.6 The emulsion side of the paper is kept in contact with the ground surface of the test piece for 30 s to 10 min, depending on the acid selected, the concentration of the acid solution, and the sulfur content of the steel.

11.7 When comparing test results for relatively similar specimens, it is best to standardize the selection of acid and the concentration of the bath, the soak time, and the contact time.

11.8 After the required contact time, peel off the print carefully from the disk. Avoid excessive handling of the print before washing, fixing, washing, and drying.

11.9 Wash the print in clear running water for about 15 min.

NOTE 3—5 min may be long enough to remove any residual dilute sulfuric acid from the sulfur print even if fiber base paper is used; if resin coated paper is used then 10 s may be adequate.

11.10 Fix the print in the photographic fixing solution for 15 to 20 min, or as long as it takes to complete the fixing.

11.11 Wash the print in clear running water for about 30 min, or as long as it takes to get all the fixer out of the paper. (Use of a fixer clearing agent, according to its instructions, permits use of a shorter wash time.) (Use of two trays of fixer solution will ensure that the second tray is not depleted; this is an important point if using double weight fiber base paper.)

11.12 Dry the print using an appropriate method for the paper used.

11.13 All of the above steps can be conducted under ordinary room illumination. Avoid strong sunlight. The unused paper stock should have minimal exposure to light. All solutions and washes should be at room temperature.

NOTE 4— If the precaution concerning excessive light exposure is not followed, a bluish or purplish tint will appear on the paper after printing.

11.14 In most cases, only one sulfur print can be made without regrinding the surface. For steels with high sulfur contents (above 0.100 weight % sulfur), the first print is generally very dark and a second print may give better results. For steels with ordinary sulfur contents, a second print can generally be made if the ground surface is superficially macroetched at room temperature (not deep etched with hot acid etchants, or even with cold dilute acid as with electrolytic macroetching). A room temperature macroetch with 10 % aqueous nitric acid, or a general purpose microetchant (see Methods E407), may be used.

11.15 For steels with low sulfur contents (less than 0.010 wt. % S), the initial print quality is usually enhanced if the disk surface is first superficially macroetched as described in 11.14.

11.16 A specimen that has been sulfur printed can be immediately macroetched with no further preparation. The same is not true in the reverse situation where aggressive macroetching has been done ahead of sulfur printing.

12. Interpretation of Results

12.1 The presence of sulfides is revealed on the print by the brown coloration produced by silver sulfide, Ag_2S. This coloration is produced wherever manganese sulfide, or more generally, (Mn, Fe)S, is present in contact with the treated paper.

12.2 The greater the sulfur content of the steel, the darker the image under controlled test conditions, except as noted in 6.6.

12.3 Localized sulfur segregation is revealed on the print as a concentration of darker spots. Dark spots may also be formed at cracks or holes (as discussed in 6.2) or due to improper cleaning (as discussed in 6.1).

12.4 White spots are usually due to entrapped air between the paper and the disk (see 6.3).

12.5 Comparison of the sulfur print with the aggressive macroetch should be made, keeping in mind that the segregation coefficient for sulfur is higher than for carbon. Refilled cracks can contain both sulfides and carbides, and not necessarily both.

13. Report

13.1 The test report should include the actual sulfur print(s), or a photographic reproduction, depending on the circumstances. The orientation of the sulfur print relative to the specimen should be shown on the sulfur print.

13.2 The report should include the complete identity of the sample(s) tested and the chemical analysis of the specimen or its parent sample, if known.

13.3 The report should state the sulfur print variables used, acid selected, and concentration of the acid solution.

14. Keywords

14.1 Baumann print; ferrous alloys; macrostructural evaluation; photographic paper; specimen preparation; sulfur print