Technical Note: Metallographic Sulphur Determination by SEM in Austenitic Stainless Steel Weld Metal

BY J. I. MORGENFELD, M. SOLARI AND J. OVEJERO-GARCÍA

Introduction

Sulphur distribution in weldments is of great interest, because it is associated with several phenomena: corrosion, mechanical resistance, intergranular brittleness, hot cracking, etc. (Ref. 1).

Probably the most common method to reveal segregated sulphur widely used in industry is the one developed by Baumann in 1906 (Ref. 2). This technique permits the detection of sulphur in a direct way. However, the silver bromide crystals of photographic paper are several microns in size, so that resolution achieved by this method is restricted.

Recently, a new metallographic technique — called microprint Baumann or sulphur microprint — was developed; this reveals sulphur in a direct way, even at the electron microscopic scale (Ref. 3).

In the CNEA's Materials Laboratory, the hot cracking of austenitic stainless steel was investigated using the solidification theory background and the Varestraint test. The aim of this work is to analyze the relationship between operative variables and the mechanism responsible for hot cracking, taking into account microstructural features. In this framework, the results of the investigation described here indicated that a sulphur microprint is useful for revealing sulphur segregation in austenitic stainless steel weld metal. As a consequence, it appears to be an excellent tool in the hot cracking research field.

Background

During welding, the molten weld pool does not freeze according to equilibrium conditions. Thus, during metal alloy cooling from the liquid state, a solute pile-up in front of the solid-liquid interface may appear. As a consequence an instability is originated that produces morphological changes. The constitutional supercooling criteria developed by Chalmers (Ref. 4) permit the determination of interface instability conditions, besides justifying the fact that the dendritic growth can develop towards the liquid pool center in a temperature gradient direction.

The first visible instability signals connected to the interface are depressions called nodes (Ref. 5), allowing its metallographic detection by special techniques.

In a typical fusion weld, the solid surface in contact with liquid metal grows adopting a cellular or dendritic shape, with the object of eliminating the constitutional supercooling by redistributing the solute in front of the interface. The result is a short range segregation — microsegregation — located in the interdendritic spacing.

Microsegregation can appear in connection with nonmetallic inclusions, microporosities and microshrinkage. On the other hand, the relationship between solidification structure and hot cracking is well known. In general, hot cracking is caused by the combination of two factors:

1. Mechanically and/or thermally induced strain.
2. Crack susceptible microstructure.

Welding parameter, rate of solidification, alloy composition and microsegregation are factors which play an important role in the control of hot cracking associated with welding.

Sulphur can appear in the solidified weld metal as a solid solution as well as nonmetallic inclusions. The strong sulphur segregation in the interdendritic spacing is due to its too low partition coefficient. Several authors showed that steels with the same chemical composition but with different sulphur content could have different behaviors in reference to their weldability.

The Fe-Cr-Ni stainless steels can solidify as austenitic dendrites as well as delta ferrite dendrites. Austenitic stainless steel weld metal normally has a duplex structure that contains varying amounts of ferrite. The delta ferrite can be associated with the interdendritic spacing as well as the cores of dendrites according to the cooling rate and composition. Extensive discussions have been published on the solidification behavior and origin of ferrite in austenitic stainless steel weld metal. However, no one has been able to clearly establish the solidification sequences leading to the observed final microstructure of the weld metal (Ref. 6, 13).

It is recognized that, if sufficient ferrite is in the weld, the ferrite will effectively prevent hot cracking (Ref. 7). The ferrite level that prevents cracking is found to be dependent on the impurity level, whereas for low P + S, little or no ferrite is required to prevent cracking. With ferrite contents greater than Ferrite Numbers 13 or 14, large amounts of P and S can be accommodated without cracking (Ref. 8). Compared to phosphorus, sulphur has a much greater effect on high temperature cracking (Ref. 9).

The importance of sulphur in hot cracking corresponds to its association with low melting point films as well as a ductility diminishment near solidus.

Taking into account the complex distribution of austenite and delta ferrite (approx. 1 μm wide) as well as the microsegregation associated with a fine dendrite arm spacing (approx. 5 μm) typical in weldments, it results that the electronic microprobe technique (limited by the probe size to 1 μm^3, and sensitivity, doses higher than 0.3% in weight) is not capable of determining sulphur distribution on this fine scale. On the other hand, the epitaxial layers technique enables one to reveal segregation very accurately, but it is not possible to determine sulphur in a selective way.

Techniques for analysis of fracture surfaces with good depth resolution, such as Auger electron spectroscopy, are difficult

J. I. MORGENFELD is with the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, and M. SOLARI and J. OVEJERO-GARCÍA are with the Departmento de Materiales de la Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.

to apply to austenitic stainless steels which resist intergranular fracture. On the other hand, x-ray microanalysis of thin foil specimens appears to be the best technique currently available for high spatial resolution analysis of the heavy elements in austenitic steels (Ref. 10) (resolution of 30 nm). However, the applicability of this technique is limited by the method's complexity.

An alternative technique is high resolution autoradiography with radioactive sulphur S^{35} which is also limited to laboratory studies.

The originality of the sulphur microprint is based on the association of the classic Baumann test with high resolution autoradiography wherein a silver bromide monogranular emulsion is deposited on the surface specimen.

The technique used in this work can be applied not only to massive pieces, with a conventional metallographic specimen observable by SEM, but to thin foils observable by scanning electronic transmission microscopy with a 150 nm resolution. It is possible to reveal the sulphur distribution with a very high sensitivity. For example, it has been reported that sulphur monoatomic layers were revealed (Ref. 12).

This technique can be useful in the study and solution of many problems in basic as well as applied investigations, such as stainless steel hot cracking.

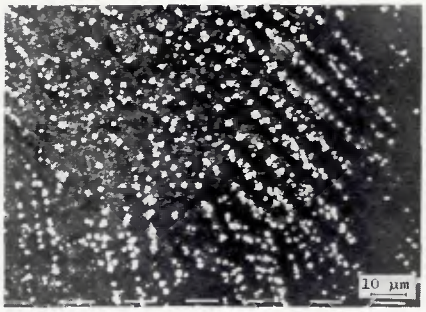

Fig. 1 — Cross section of a weld bead showing periodic sulphur segregation within columnar grains. X800 (reduced 50% on reproduction)

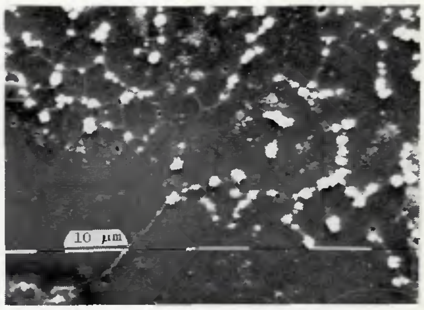

Fig. 2 — Sulphur inclusions in the segregated regions of an area close to the fusion line. X1200 (reduced 50% on reproduction)

Fig. 3 — Preferential segregation at the structure nodes. X3200 (reduced 50% on reproduction)

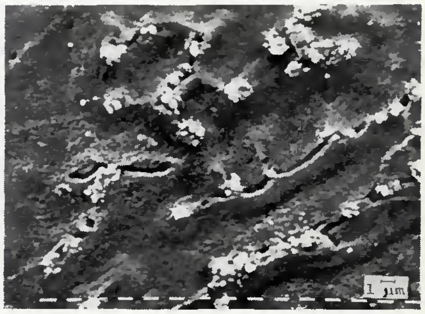

Fig. 4 — High magnification detail of sulphur inclusions. X3200 (reduced 50% on reproduction)

Materials and Procedures

AISI Type 304L stainless steel in the form of a 3 mm (0.12 in.) thick sheet was used. Experimental fusion welding performed semiautomatically using the GTA process with 11 volts (V) and 90 amperes (A) in an argon atmosphere with 30 cfh (14.2 L/min) flow and a travel speed of 30 cm/min (11.8 ipm).

Metallographic specimens were prepared according to conventional practice. The upper surface of the welds were polished to the diamond stage. Then, two touches with automatic electrolytic polishing were performed using 20 V for 10 seconds(s); the reagent used was A2: 78 ml perchloric; 100 ml Butilcello-solve, 700 ml ethanol and 120 ml H_2O. Finally, an electrolytic attack with 10% oxalic acid and 8 V was performed.

Sulphur Microprint Experimental Method

The sulphur microprint principles were detailed in a previous paper (Ref. 3). Consequently, the following description is brief.

The metallographic prepared specimen is covered with a nuclear emulsion thin film Ilford L4. Then a 10% diluted sulphuric acid drop is deposited during 10 s with the aim of producing SH_2 detachment and SAg_2 formation. After fixing and washing with distilled water, the specimen-emulsion as a whole is observed by SEM. The SAg_2 appears superimposed on the microstructure as brilliant white grains. Thus it is possible to correlate the sulphur segregation with microstructural details.

Results and Discussion

As an initial step in the investigation of sulphur heterogeneity in weld metal, a study was carried out on AISI Type 304L austenitic stainless steel in order to observe sulphur microprint suitability.

Figure 1 is a photomicrograph of a transverse cross section of a weld bead showing a periodic sulphur segregation within columnar grains. This chemical heterogeneity corresponds to an interdendritic segregation resulting from a cellular dendritic growth. The SEM photomicrograph shows the SAg_2 brilliant white particles with a resolution of up to 300 nm. The presence of this type of particle is associated with sulphur microinclusions or sulphur in solution.

The dendritic arm spacing (DAS) is in the range of 5 μm. Flemings (Ref. 11) has pointed out that the mechanical properties of cast metals are strongly dependent on this parameter. The DAS is a function of cooling rate and composition. It should be noted that the DAS diminishes as the cooling rate increases. This parameter is a measure of the size and distribution of the structural elements.

Figure 2 shows an area close to the fusion line of the above mentioned weldments at higher magnification. This photomicrograph shows sulfur inclusions in the segregated regions.

Preferential segregation at the structure nodes is shown in Fig. 3. The nodes correspond to real solute enriched liquid channels. When the interface instability condition is present, a tendency to balance the solute rejection with a curvature change occurs. Note that the solute and temperature diffusion coefficients are very different; as a consequence, the heat and mass transfer are balanced for a curved interface due to the different flow directions. The degree of segregation depends upon solute pile-up and interface curvature effects, solid state diffusion and dendritic arm coarsening.

Figure 4 shows a high magnification detail of sulphur inclusions. A previous work (Ref. 3) reported the possibility of revealing sulphur microprecipitation in the delta ferrite — austenite interface. Now, a part of the present work in austenitic stainless steel weld metal is the study of sulphur segregation in a delta ferrite — austenite interface using thin foil sulphur microprint specimens, observed by TEM.

Conclusion

The experimental work performed reveals that the application of the sulphur microprint technique to the investigation of austenitic stainless steel weld metal allows the successful selective detection of sulphur segregation from the solidification process. This new technique promises to become an important tool in the study of weld metal solidification and hot cracking. Additionally, the thin foil sulphur microprint observed by TEM will offer higher accuracy in the detection of sulphur segregation.

References

1. Stout, R. D., and Doty, W. D. 1971. *Weldability of steels.* New York: Welding Research Council.

2. Baumann, R. 1906. *Metallurgie,* 416.

3. Moulin, G., Ovejero-Garcia, J., Haut, C., Dadian, M., and Acouturier, M. 1978 (Nov.). La micro-empreinte Baumann a haute résolution pour la mise en évidence de microsegregations de soufre a l'echelle de la microscopie électronique. *Rev. Met.* 11:627-632.

4. Chalmers, B. 1962. *Principles of solidification.* New York: J. Wiley & Sons.

5. Biloni, H., Bolling, G. F., and Cole, G. S. 1966. *Trans.* TMS-ASME 236.

6. Fredriksson, H. 1972 (Nov.). The solidification sequence in an 18-8 stainless steel, investigated by directional solification. *Metal. Trans.* 3(11):2989-2997.

7. DeLong, W. T. 1974. Ferrite in austenitic stainless steel weld metal. *Welding Journal* 53(7):273-s to 286-s.

8. Brooks, J. A., and Lambert, F. J. 1978. The effects of phosphorus, sulfur and ferrite content on weld cracking of type 309 stainless steel. *Welding Journal* 57(5):139-s to 144-s.

9. Homma, H., Mori, N., and Shinmyo, K. 1979. A mechanism of high temperature cracking in steel weld metals. *Welding Journal* 58(9):277-s to 282-s.

10. Lyman, C. E., Manning, P. E., Duquette, D. J., and Hall, E. 1978. STEM microanalysis of duplex stainless steel weld metal. *Scanning Electron Microscopy* 1:213-220.

11. Flemings, M. C. 1974. *Solidification processing.* New York: McGraw-Hill.

12. Larere, A., Moulin, G., Ovejero-Garcia, J., Haut, C., and Roques-Carmes, C. (1980) Detection of intergranular sulphur segregation in commercial nickel by high-resolution sulphur microprint. *Scripta Met.* 14(7):703-708.

13. Lippold, J. C., and Savage, W. F. 1979. An investigation of duplex weld solidification in austenitic stainless steels. *Welding Journal* 58(12):362-s to 374-s.

AN INVITATION TO AUTHORS

Gentlemen:

The American Welding Society will hold its 65th Annual Convention and 1984 AWS Welding Show in Dallas, Texas, during April 9-13. One of the most important events of our 65th Annual Convention will be its Professional Program.

It is indeed a pleasure to invite you as Authors to be participants in the Professional Program of our 65th Annual Convention. On this occasion, the Society is offering an opportunity to Authors to bring the results of outstanding work on their part to the attention of our entire membership, the welding industry, and the nation's metalworking industries.

To this end, the Society's Technical Papers Committee will be happy to receive your application for participation in our 65th Annual Convention Professional Program; the Committee is inviting 500-word summaries for, basically, two categories of papers:

1. *Applied Technology*—unusual industrial or field applications of welding, new process or significant equipment developments, surfacing, unique welding case histories, education, safety and health, cost studies—also related topics such as nondestructive testing of weldments as well as maintenance and repair.

2. *Research Oriented*—results of significant laboratory research and/or development projects, welding metallurgy, weldability studies, weld cracking or fracture, new test methods, arc physics—also related topics such as fracture mechanics.

To apply for participation in our 65th Annual Convention Professional Program, please complete both sides of the Author Application Form on the facing page. Also, please prepare a 500 to 1,000 word summary of what you intend to say in your paper and mail with the completed form to AWS.

The Technical Papers Committee will screen all Author applications and summaries (also the manuscripts of completed papers if included), and Authors will be notified during late October or early November concerning acceptance. Completed Author Application Forms and accompanying 500-word summaries must be mailed by August 15, 1983, to ensure consideration for the 65th Annual Convention Professional Program.

Please note that, as it screens Author Applications and summaries, the Technical Papers Committee will be looking for: (1) the newness of information and need for the information in its field, (2) technical accuracy, (3) clarity of presentation, and (4) adaptability for oral presentation (a paper consisting basically of complicated tables would not be suitable for oral presentation).

Sincerely yours,

Paul W. Ramsey

P. W. Ramsey
Executive Director

May 2, 1983

AMERICAN WELDING SOCIETY
P.O. Box 351040, Miami Florida 33135

AUTHOR APPLICATION FORM
—FOR—
65th Annual AWS Convention
Dallas, Texas, April 9-13, 1984

COMPLETE ***BOTH*** *SIDES AND MAIL WITH 500-1000 WORD SUMMARY TO:*

American Welding Society
P.O. Box 351040
Miami, Florida 33135

Date Mailed ....

Author's Name ....

Company or Organization ....

Title or Position .... Telephone: Area .... Number ....

Mailing Address ....

City .... State .... Zip ....

If there are to be joint Authors, give name(s) of other author(s)

Name ....

Address ....

Name ....

Address ....

PROPOSED TITLE (10 words or less): ____________

SUBJECT CLASSIFICATION:

Classify your paper by placing a check mark in the two appropriate boxes:
Applied Technology ☐ Research Oriented ☐ Other ☐ / An Original Contribution ☐ A Review ☐ Progress Report ☐

SUMMARY:

- Type, double spaced, a summary of *not less than 500—but preferably not more than 1000*—words and attach to this form.
- Be sure to give sufficient information to enable the Technical Papers Committee to obtain a clear idea of content of the proposed paper; confine background to about 100 words. Also be sure to *emphasize Results and Conclusions* since this material, together with information on what is *NEW,* will have a very important bearing on the decision of the Technical Papers Committee.
- If complete manuscript is available, in addition to summary, please attach two copies to this form.
- Application Form and summary *must* be postmarked not later than August 15, 1983, to ensure consideration for inclusion on the 65th Annual AWS Convention Professional Program.

MANUSCRIPT DEADLINES:

- All manuscripts *should* be in the hands of the Technical Papers Committee not later than February 29, 1984. If received prior November 30, 1983, every effort will be made to publish them in advance of meeting.
- It is expected that the Committee's selections will be announced sometime in October or November 1983.
- If your paper is made a part of the program, which of the following manuscript deadlines will you be able to meet?
  November 30, 1983 ☐ January 31, 1984 ☐ February 28, 1984 ☐

PRESENTATION AND PUBLICATION OF PAPERS:

- Has material in this paper been previously presented in meeting or published?
  Yes ☐ No ☐ When? ____________
  Where? ____________
- Following presentation at the 65th Annual AWS Convention, would you accept invitations to present this paper before AWS sections? Yes ☐ No ☐
- Papers accepted for presentation become the property of the Society with original publication rights assigned to the *Welding Journal.*

RETURN TO AWS HEADQUARTERS. MUST BE POSTMARKED **NOT LATER THAN AUGUST 15, 1983,** *TO ENSURE CONSIDERATION.*

____
Author's Signature

Author(s) of Proposed Paper:

____

____

SUMMARY CODE ______________
(For AWS Headquarters Use Only)

Title of Paper (may be abbreviated) ______________________________

____

TO AUTHOR(S): Please briefly answer questions in spaces provided below—also please note that answers given below are required in addition to 500 to 1,000 word Summary. Please use typewriter.

(1) WHY WAS THE WORK DONE? ______________________________

____

____

____

(2) WHAT WAS DONE? ______________________________

____

____

____

(3) WHAT WAS FOUND? ______________________________

____

____

____

____

(4) WHAT ARE YOUR MOST IMPORTANT CONCLUSIONS? ______________________________

____

____

____

____

____

(5) TO WHOM DO YOU THINK YOUR PAPER WILL BE IMPORTANT? HOW? ______________________________

____

____

____

____

____

OTHER COMMENT (Optional) ______________________________

____

____

____

____

RETURN TO AWS HEADQUARTERS. MUST BE POSTMARKED **NOT LATER THAN AUGUST 15, 1983,** *TO ENSURE CONSIDERATION.*

Be sure to attach 500-1,000 word Summary when mailing completed Author's Application Form to AWS Headquarters.