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

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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 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 Number 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 μm², 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.
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 $^{35}S$, 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 specimens.

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.

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 cfm (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 was 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 Buticol-solve, 700 ml ethanol and 120 ml H$_2$O. 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 $\mu$m. 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

![Fig. 1](image1)
![Fig. 2](image2)
![Fig. 3](image3)
![Fig. 4](image4)
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

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