

## Corrosion at Sulphide Inclusions in Stainless Steel

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### ABSTRAK

Analisis auger telah dilakukan menggunakan spektroskopi elektron auger dan mikroskop imbasan elektron auger berpeleraian tinggi. Peta kontur auger bagi unsur-unsur pada inklusi sulfida terkakis pada keluli karat disertakan. Didapati bahawa inklusi mangan sulfida terkaya kuprum mengalami kakisan sekata berkemungkinan disebabkan oleh pengendapan  $\text{Cu}_2\text{S}$  pada permukaan inklusi yang mengkakis. Sebaliknya bagi inklusi mangan sulfida yang kurang kuprum mengalami serangan kakisan secara tidak sekata, menyebabkan pembentukan mikrocelah yang dalam pada tepi-tepi inklusi tersebut.

### ABSTRACT

Auger analysis was performed using a high resolution scanning auger electron microscope and auger electron spectroscopy. Elemental auger contour maps for corroded sulphide inclusions in stainless steel were presented. It was found that the copper enriched-manganese sulphide inclusions were uniformly corroded, which might be due to  $\text{Cu}_2\text{S}$  deposition on the surface of corroding inclusions. In contrast, manganese sulphide inclusions containing less copper were non-uniformly attacked, resulting in the formation of deep microcrevices at their edges.

**Keywords:** auger electron spectroscopy, sulphide inclusions, corrosion

### INTRODUCTION

Generally, sulphur improves machinability in steel. However, the presence of sulphur also produces deleterious effects on some service properties such as forgeability, ductility, toughness, weldability and corrosion resistance.

It is known that solid solubility of sulphur in iron (Fe-S system) at temperatures below  $769^\circ\text{C}$  is very low (Smithells 1967; Brandes 1983). Since the solubility of sulphur in iron and steel is very low (less than 0.01% at room temperature), it is usually present as a sulphide (Wranglen 1969; Sedriks 1983). The sulphide inclusions formed during solidification of steel are predominantly manganese sulphide. Although in ordinary steels, S and

Mn are added to avoid formation of FeS along grain boundaries, the formation of MnS is detrimental since it acts as an active anodic site particularly in stainless surfaces in the presence of aqueous chloride ions (Sedriks 1983).

Studies on pitting at sulphide inclusions in steels using an electron microprobe had been carried out by Szklarska-Smialowska *et al.* (1970), while Eklund (1974) had used a scanning electron microscope to obtain pictures of corrosion pits at inclusion sites. However these two techniques are unable to give information on the profile of elements which are present in the outermost layer of an alloy surface.

This paper reports the use of a more refined technique, i.e. a combination of scanning auger electron microscope (SAM) and auger electron spectroscopy (AES) to study pitting corrosion at MnS inclusions in stainless steel. AES can give information on the chemical composition of the outermost layer between 5 Å to 20 Å depth.

## MATERIALS AND METHODS

### *Auger Mapping*

The instrument used in this work was the ultrahigh vacuum auger microprobe model VG MA500 made by VG Scientific, United Kingdom. The auger electron detector was mounted at 60° to the electron beam. The specimen was positioned in the analyser chamber at 45° to the electron beam.

A 10 KeV electron beam with beam current of 7.5 nA was used. This gave a spatial resolution of about 180 nm. For auger measurement, the hemispherical analyser was used with a 4-mm slit in the constant retard ratio (CRR) mode. In order to compromise between energy resolution, auger electron signal and mapping time, a CRR of 4:1 was used. Contour maps of elemental distribution were constructed using ratio of net peak height to background data of auger spectra. The contour lines represent 80 and 20% of the maximum intensity of elements.

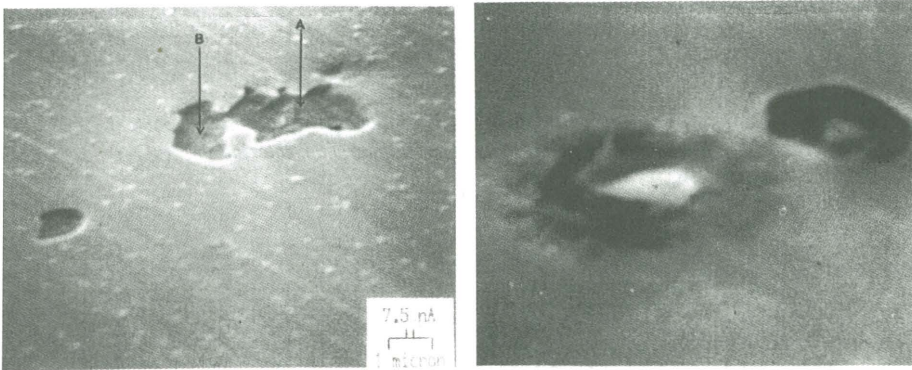
### *Specimen*

Specimens of stainless steel type 316 with dimensions 1.5 cm × 1.0 cm × 0.1 cm (composition wt. %: C < 0.08, Cr 18.60, Ni 11.70, Mo 2.20, Cu < 0.4, Mn 2.00, Si < 1.0, P < 0.04, S < 0.03, Fe rest) were wet-abraded with silicon carbide paper, polished with diamond paste to a 1-micron finish, and cleaned using detergent, distilled water and acetone. A metal to metal crevice was simulated by clamping two specimens across one another with a PTFE clamp in order to corrode the inclusions in the specimens naturally. The whole assembly was exposed in 1 M MgCl<sub>2</sub> solution for one week. The exposed specimens were then gently washed in distilled water and dried in a vacuum system.

## RESULTS AND DISCUSSION

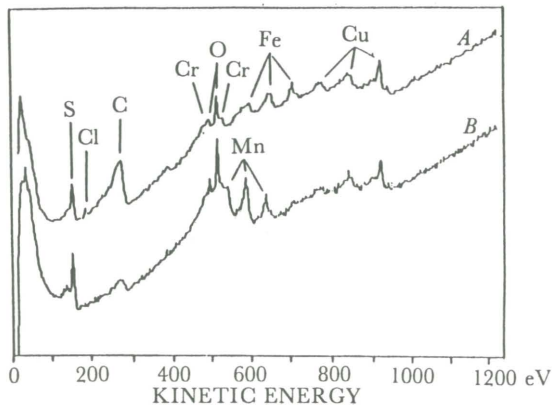
*Plates 1* and *2* show different types of corrosion attack at sulphide inclusions. The inclusion shown in *Plate 1* had undergone uniform attack whilst the inclusion shown in *Plate 2* had corroded extensively, especially at its edges. This may be due to the different concentrations of elements present at the inclusions. Inclusions in stainless steel can be pure manganese sulphide or complex sulphides and oxides (Baker and Castle 1992; Dowling *et al.* 1995).

Auger point analysis done prior to mapping indicates that the corroded inclusion contained different intensity of elements. This is shown in *Fig. 1* where auger spectra A and B are for points A and B respectively for the inclusion shown in *Plate 1*. The two points have different concentrations of Fe and Mn but both contain Cu. A better picture of the qualitative elemental distribution in the outermost layer of the inclusion is given by auger maps in *Figs. 2* and *3*.



*Plate 1.* Scanning auger electron micrograph of a corroded Cu-enriched manganese sulphide inclusion ( $\times 10000$ )

*Plate 2.* Scanning auger electron micrograph of a corroded manganese sulphide inclusion ( $\times 10000$ )



*Fig. 1.* Auger spectra for points A and B at the corroded sulphide inclusion shown in *Plate 1*

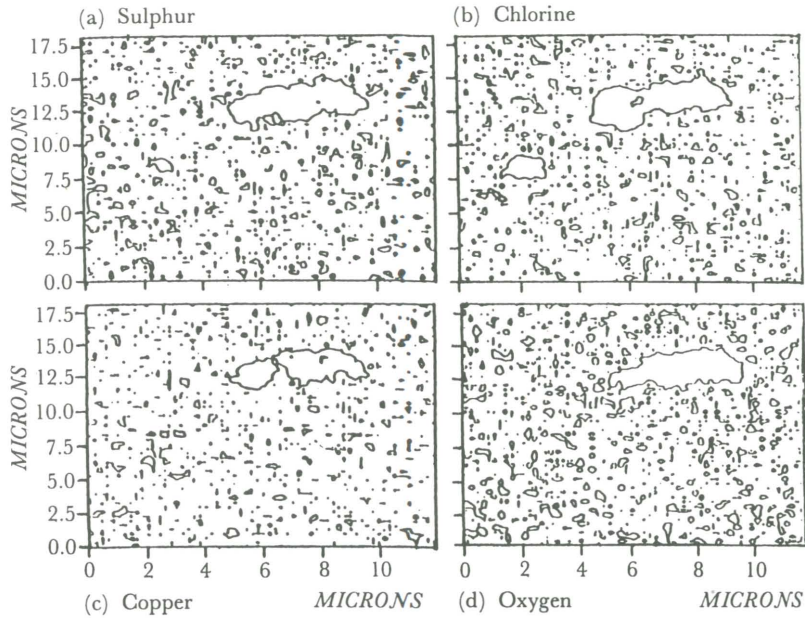


Fig. 2. Auger maps for the corroded sulphide inclusion shown in Plate 1 with contour lines 20% [—] and 80% [—] of the maximum intensity. (a) sulphur (b) chlorine (c) copper (d) oxygen

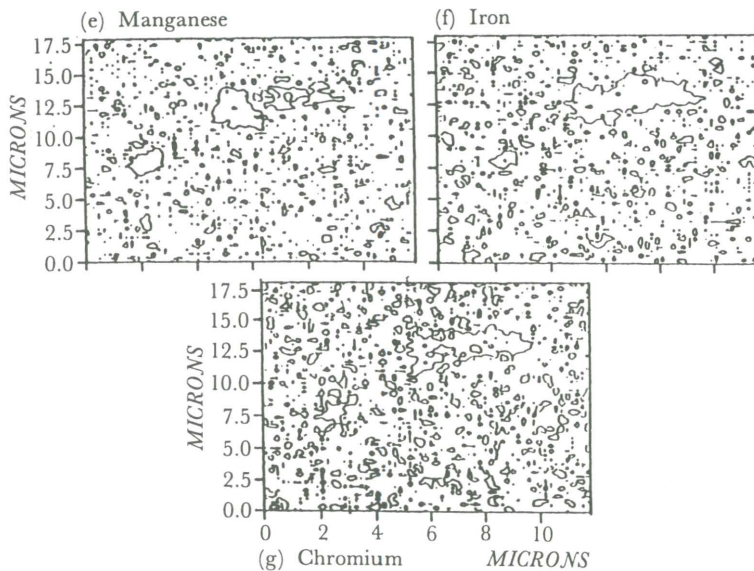


Fig. 2. (Cont.) Auger maps for the corroded sulphide inclusion shown in Plate 1 with contour lines 20% [—] and 80% [—] of the maximum intensity. (e) manganese (f) iron (g) chromium

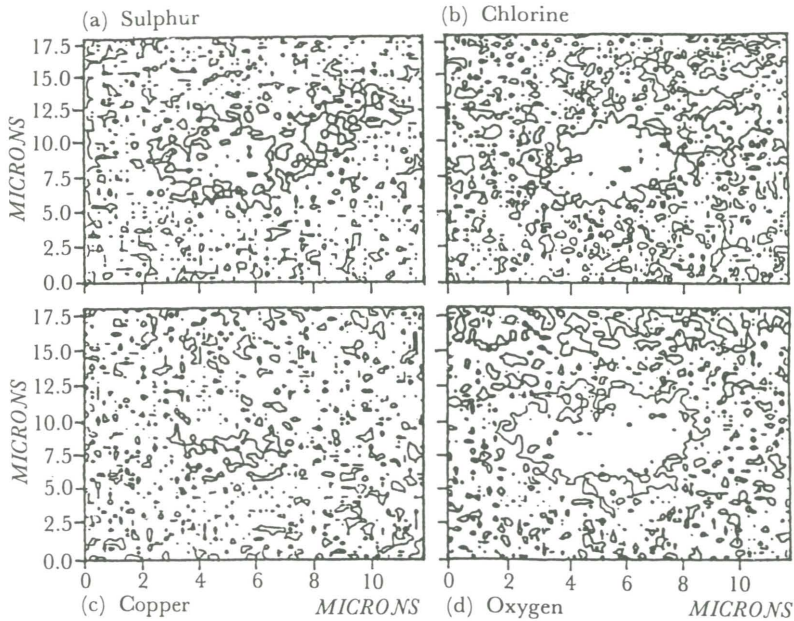
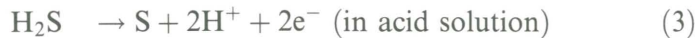


Fig. 3. Auger maps for the corroded sulphide inclusion shown in Plate 2 with contour lines 20% [---] and 80% [—] of the maximum intensity. (a) sulphur (b) chlorine (c) copper (d) oxygen

The chlorine auger maps (Fig. 2(b) and 3(b)) substantiate the statement that chloride ions preferentially adsorb into the surface of inclusions (Wranglen 1974) resulting in the breakdown of the surface layer, thus exposing the inclusion to an aqueous environment. This will lead to the dissolution of MnS. According to Eklund (1974) the reactions which take place are as follows.



Sulphur and manganese auger maps suggest that the above reactions were taking place at corroding inclusions. That is why S was found deposited on the entire surface of the corroded inclusions (Fig. 2 and 3).

For copper-containing manganese sulphide inclusions, copper reacts with hydrogen sulphide (Zakipour and Leygraf 1981) to form  $\text{Cu}_2\text{S}$ ,



The presence of S and Cu in the top layer of the inclusion surface (Fig. 2(a),(c) and 3(a),(c)) and indicates that the above reaction has taken place.

It is believed that some enrichment of Cu in the sulphide inclusions does take place, as suggested by Wranglen (1969).

The existence of  $\text{Cu}_2\text{S}$  on the surface of the inclusion seems to reduce corrosion attack, especially pitting. The scanning auger micrograph of the Cu-enriched inclusion shown in *Plate 1* indicates that the entire surface of the inclusion was attacked almost uniformly. By contrast, the inclusion shown in *Plate 2* which has less copper underwent serious corrosion where deep microcrevices were formed at its edges.

The beneficial effect of  $\text{Cu}_2\text{S}$  is understood to be due to its insolubility in highly acidic solutions. The solubility product of  $\text{Cu}_2\text{S}$  is  $10^{-48}$  and  $\text{MnS}$  is  $10^{-13}$ , as quoted by Wranglen (1974). Therefore the formation of  $\text{Cu}_2\text{S}$  will reduce the deleterious effect of sulphur on the steel. This finding suggests that an addition of Cu to stainless steels not only improves the steels passivity as reported by Lizlovs (1966), but also reduces pitting tendency at sulphide inclusions in the steels.

### CONCLUSION

Auger electron spectroscopy (AES) has been used successfully to identify the chemistry of the corroded manganese sulphide inclusions in stainless steel. The elemental composition of corroded manganese sulphide inclusions reveals that the corrosion attack might be slowed down for the inclusion rich in copper.

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