inclusions in several different stainless steels (results not shown). Line profiles from an as-cast 316F sample and from a sample of the cast 316F annealed at 1,100 °C also showed the same sharp boundaries. The as-cast and annealed structures should provide the opportunity for chromium to segregate to the sulphide and cause depletion in the matrix[5], but this did not occur. Similar sharp boundaries were also evident at MnS inclusions in a standard commercial stainless steel (grade 304), indicating the absence of a chromium-depleted zone. Secondary-ion mass spectrometry (SIMS) mapping performed at MnS inclusions on polished surfaces of the 304 alloy and the 316F sample used by Ryan *et al.* also revealed no evidence of a chromium-depleted zone.

Figure 1c shows the results of a scan made along the line labelled 2 in Fig. 1a, traversing the sulphide, through the oxide, and then into the matrix. The chromium concentration is lower in the oxide than in the matrix, and even lower in the sulphide. The resulting chromium profile appears to have a chromium-depleted region, but this is really the effect of the oxide particle. The iron content in the oxide decreases more than the chromium content relative to the bulk concentration, resulting in a higher chromium/iron concentration ratio in the oxide. SIMS measurements at these particles showed that the Cr/Fe-ion yield ratio was similar or slightly higher in the oxides relative to the matrix. We therefore consider that the depleted zone described by Ryan *et al.* cannot be due to the effects of oxides adjoining sulphide particles.

Figure 1d shows the normalized ratio of raw EDS data for the linescan from the sulphide to the matrix in Fig. 1b. (This is analogous to the SIMS data shown in Fig. 1a in ref. 1.) There is little scatter and no evidence of a depleted zone near the sulphide (Fig. 1d). There is a sharp transition to the higher Cr/Fe ratio inside the sulphide particle.

In contrast to the findings of Ryan *et al.*[1], our evidence from high-resolution scanning TEM and SIMS mapping has failed to reveal the presence of chromium-depletion zones around MnS inclusions in any of the steels we investigated, at least within a nanometre-sized region.

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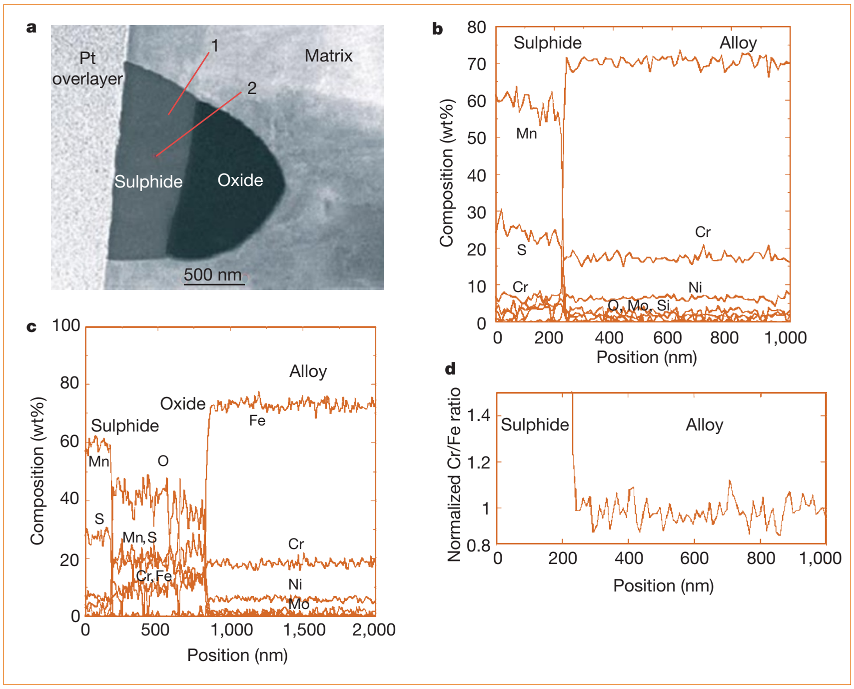

**Figure 1** Analysis of composition near an MnS inclusion by nano-EDS profiling. **a,** Dark-field image in the transmission electron microscope of a typical mixed sulphide/oxide particle in the 316F stainless-steel sample used by Ryan *et al.*[1]. The lines labelled 1 and 2 indicate the locations of the energy-dispersive spectroscopy (EDS) scans shown in **b** and **c**, respectively. **d,** Ratio of Cr/Fe signals from raw EDS data for the linescan shown in **b**. The ratio has been further normalized to unity to match the form of Fig. 1a in ref. 1.

*Ryan* et al. *reply* — Frankel *et al.* find no depleted zone adjacent to MnS inclusions in stainless steels, which contradicts our results[1] and raises important issues about pitting mechanisms. We have also used high-resolution electron microscopy and secondary-ion mass spectrometry mapping to study these systems, and our results are similar to those of Frankel *et al.*, giving a consistently large scatter in the analysis. With SIMS mapping in particular, we find that the flux required to generate a significant signal means that too much material has to be removed; in addition, the sputter rate of the inclusion is higher than that of the matrix, and sulphur 'smears' are observed that blur the interfaces. We conclude that this method is not useful in these systems.

By using the SIMS probe[1], we were able to analyse 25 inclusions within a reasonable time — in contrast to transmission electron microscopy, which involves complex sample preparation. Of these inclusions, some showed a large scatter in the data, and sputtering of the inclusion complicated interpretation of the results in a few other cases. Some 20% of the inclusions showed no depletion, consistent with the observations of Frankel *et al.*, but over 20% showed the type of depletion we reported earlier[1]. As with all pitting studies, there is a strong statistical consideration to be taken into account — although the initiation of pitting corrosion is confined to sulphide inclusions, not all inclusions nucleate pits. We are working to develop a method that correlates inclusions that have chromium depletion with subsequent pit nucleation.

Frankel *et al.* show an inclusion connected to an oxide particle. We did not analyse sites that appeared to be multiple or connected inclusions to avoid complications arising from such oxide particles[2]. The inclusion was always sampled to ensure that it was a sulphide particle.

As we pointed out[1], the final attack on the steel that leads to an observable pit is triggered through dissolution of the inclusion. The mechanism by which this unusual dissolution occurs is the key step in the chain of events. There is further evidence indicating that the interface between inclusion and matrix is critical[3,4], and that there may be several precursor stages in which the electrochemical current is small[5,6], and we have directly investigated these aspects of corrosion.

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