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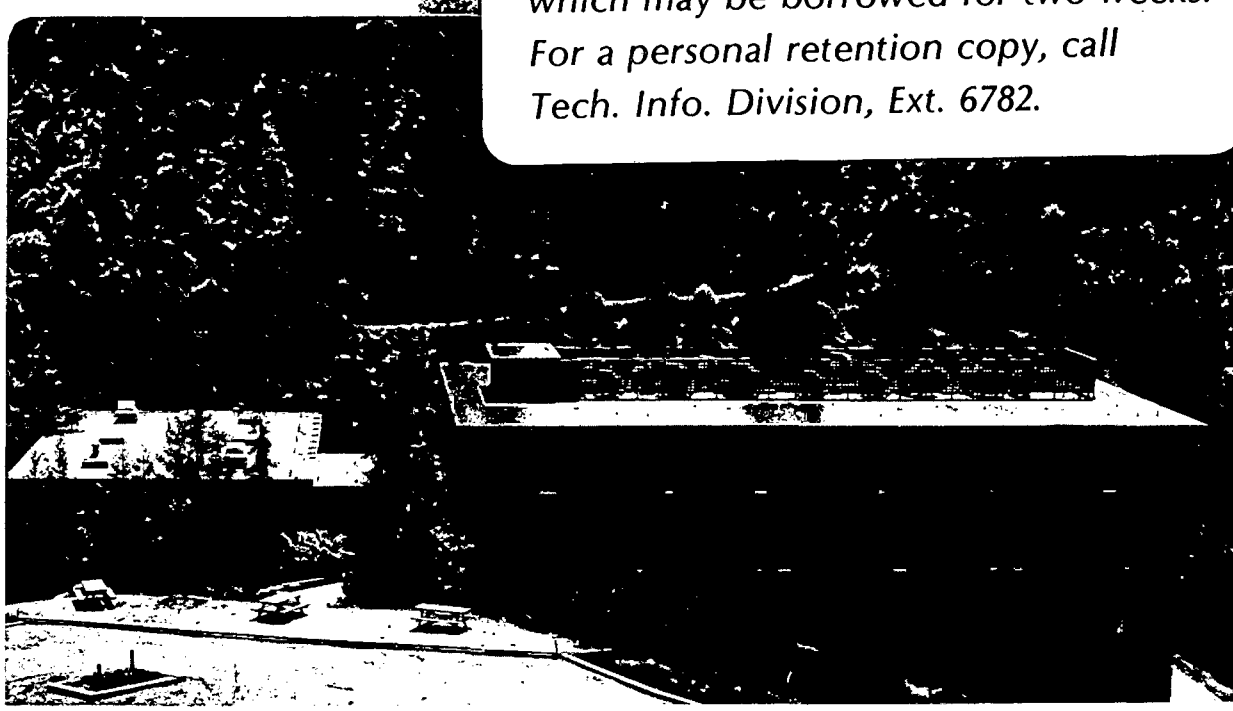

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SULFUR DIFFUSION IN OXIDE GRAIN BOUNDARIES

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ABSTRACT

Preferential sulfur diffusion down grain boundaries of the scale formed on pure iron has been identified using scanning Auger microscopy. A very high diffusion coefficient is implied.

This work was supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We would also like to thank Mr. K. Gaugler for assistance with the Auger analysis.

Virtually, all fossil fuels contain sulfur as an impurity and when they are burned - whether in a turbine, in fluidized beds, or in conversion processes such as coal gasification or liquefaction - they generate atmospheres that contain sulfur compounds. As a consequence, the use of metallic alloys in such environments unvariably leads to a "breakaway" phenomenon in which the oxide scale loses its protectiveness and unacceptedly high rates of metal wastage ensue. Generally, the cause of the breakaway is related to sulfur penetration through the growing oxide scale, resulting in formation of sulfides both within and below the scale, although the detailed mechanism has not been unequivocally demonstrated. Pre-forming of the protective oxide in a sulfur-free atmosphere may delay the breakaway, but does not eliminate it.

In order to design and use high temperature alloys effectively in these systems requires an experimental or theoretical prediction of the time at which breakaway will occur as a function of the temperature and the corrosion environment, so that the alloys can be operated only in regimes in which there is a high probability that breakaway will not occur during their required service lifetimes. At present, the mechanism for the transport of sulfur through the oxide scale is not understood, and as a consequence, alloys can only be safely used under the assumption that breakaway corrosion will occur from the beginning of operation. This, of course, leads to an uneconomical design.

Generally, two distinct mechanisms for sulfur transport through the oxide are considered (1):

(i) dissolution of sulfur in the scale and subsequent solid state diffusion inwards either via a lattice or grain boundary route to the alloy/scale interface;

(ii) penetration of sulfur in molecular compound form through physical defects in the scale such as pores, cracks, or even grosser defects such as might prevail if substantial spallation of the protective oxide occurred.

The details of the mechanism are important, since they dictate the appropriate remedy. This communication identifies a transport mechanism of sulfur transport through iron oxide scales, and thus helps provide a basis for the prediction of breakaway of alloys.

Pure iron samples in the form of 2 x 0.3 x 0.1 cm coupons were notched to assure the position of the fracture of the specimens. The samples were completely oxidized in air for 2 days at 870°C; this avoids the ductile fracture of iron on subsequent breaking. The completely oxidized samples were then exposed to a H_2-10% H_2S atmosphere ($P_{S_2} = \sim 10^{-5}$ atm) at 870°C for 1 min. This short exposure time was chosen so that sulfur could penetrate into the scale, but substantial sulfide formation would not be expected. After exposure, the sample was fractured inside the vacuum chamber of the scanning Auger microscope, to avoid any contamination.

Figure 1(a) shows the impact fracture cross section of the scale. The left side of the micrograph shows a region of intergranular fracture, whereas the right side shows areas where fracture has occurred intragranularly. Figure 1(b) is the sulfur Auger electron map of Figure 1(a). Comparing these two pictures, it is clear that sulfur is only present along the grain boundaries of the scale. This is further confirmed by Figure 2 which are the corresponding images and sulfur Auger electron map of the same area after argon ion sputtering for 5 minutes. It is clear that all the sulfur

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has been sputtered away and that it existed only right at the grain boundary. Figure 3(a), (b) are the Auger electron energy surveys at point 1 and point 2 shown on Figure 2(a) before argon ion sputtering. The 150 e.V. peak of sulfur existing only at point 2 confirms that sulfur exists at grain boundary, but not in the grain. Figure 4(a), (b) are the intensities of the sulfur, oxygen and iron peaks composition depth profiles at point 1 and point 2 of Figure 2(a) respectively, during the 5 minutes argon ion sputtering. They indicate that the sulfur at point 2 disappears after the first half minute sputtering, i.e., the thickness of the sulfur layer covering the grain boundary is less than 200 Å (Argon ion sputtering rate is approximately 400 Å/min.).

Based on these results, it is concluded that sulfur can penetrate through iron oxide scale via grain boundary diffusion.

Even in this very short exposure, 1 min. or a maximum of 2 min. if the time taken for the sample to cool from the reaction temperature is included, sulfur has managed to penetrate completely through the 1 mm thick sample. This indicates an effective diffusion coefficient of the order of at least 10^{-4} cm^2/sec. This is considerably higher than reported diffusivities of sulfur in wustite: 10^{-7} cm^2/sec. at 1300°C (2) and 4×10^{-8} cm^2/sec. and 10^{-6} cm^2/sec at 1050 and 1250°C respectively. Whether the value implied by the present result represents a grain boundary diffusion coefficient, or a gaseous coefficient through fine pores at the boundaries remains in question. If the latter is the case then presumably hydrogen is also able to penetrate the pores, and increase the iron activity in the oxide, thereby enhancing the sulfur penetration. This may also account for the rough appearance of the grain boundary fracture surface. Nevertheless, some fracture of the grains themselves does take place.

FIGURE CAPTIONS

Figure 1. Fracture section through completely oxidized Fe exposed to H_2-10% H_2S for 1 min. at 870°C.

Figure 2. As Fig. 1, but after 5 min. argon ion sputtering.

Figure 3. Auger electron spectra at points 1 and 2 (Figure 2).

Figure 4. Intensity/depth profiles during argon ion sputtering at points 1 and 2.

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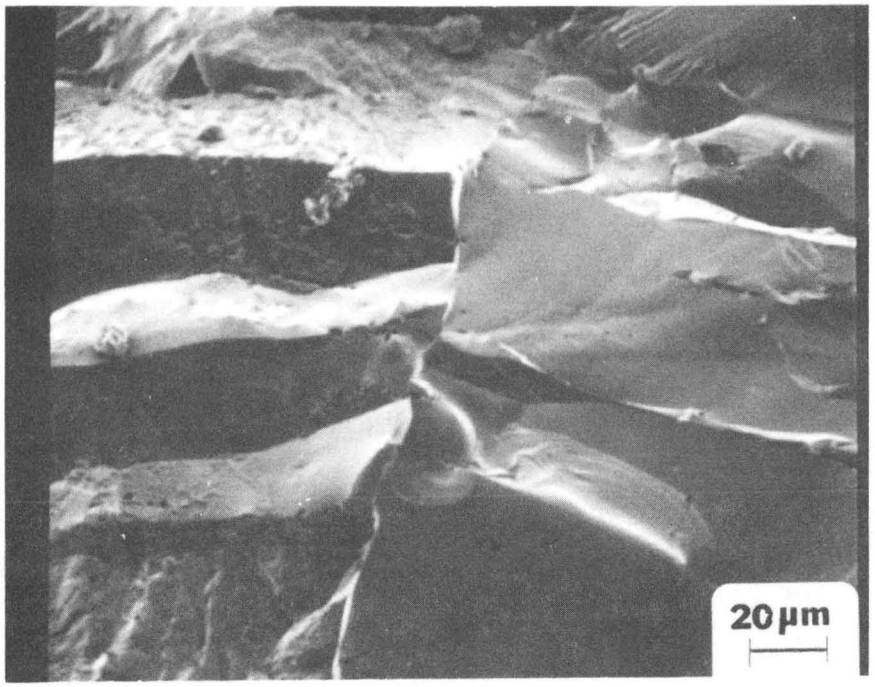

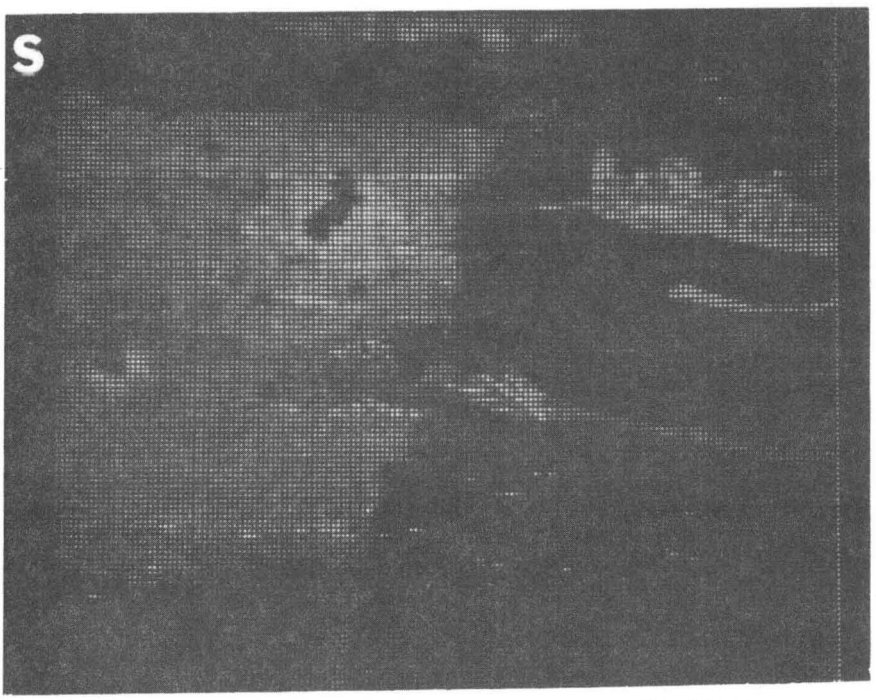

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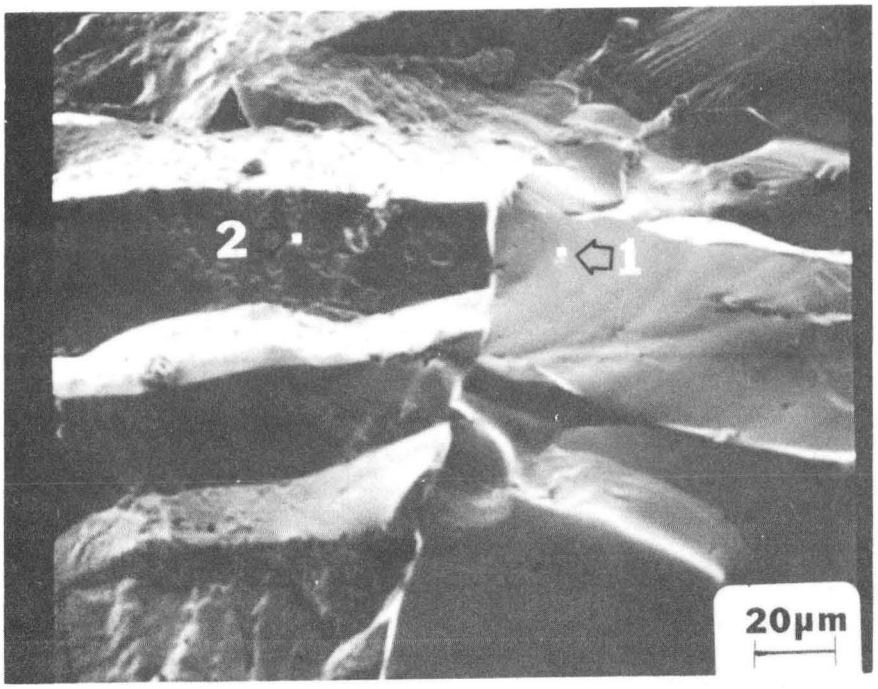
Figure 1.



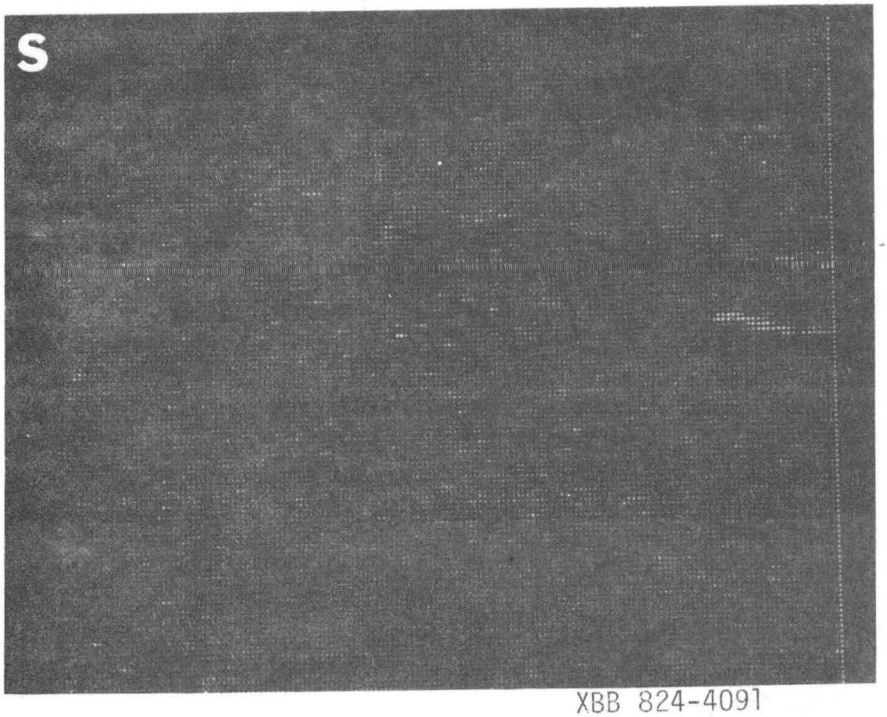


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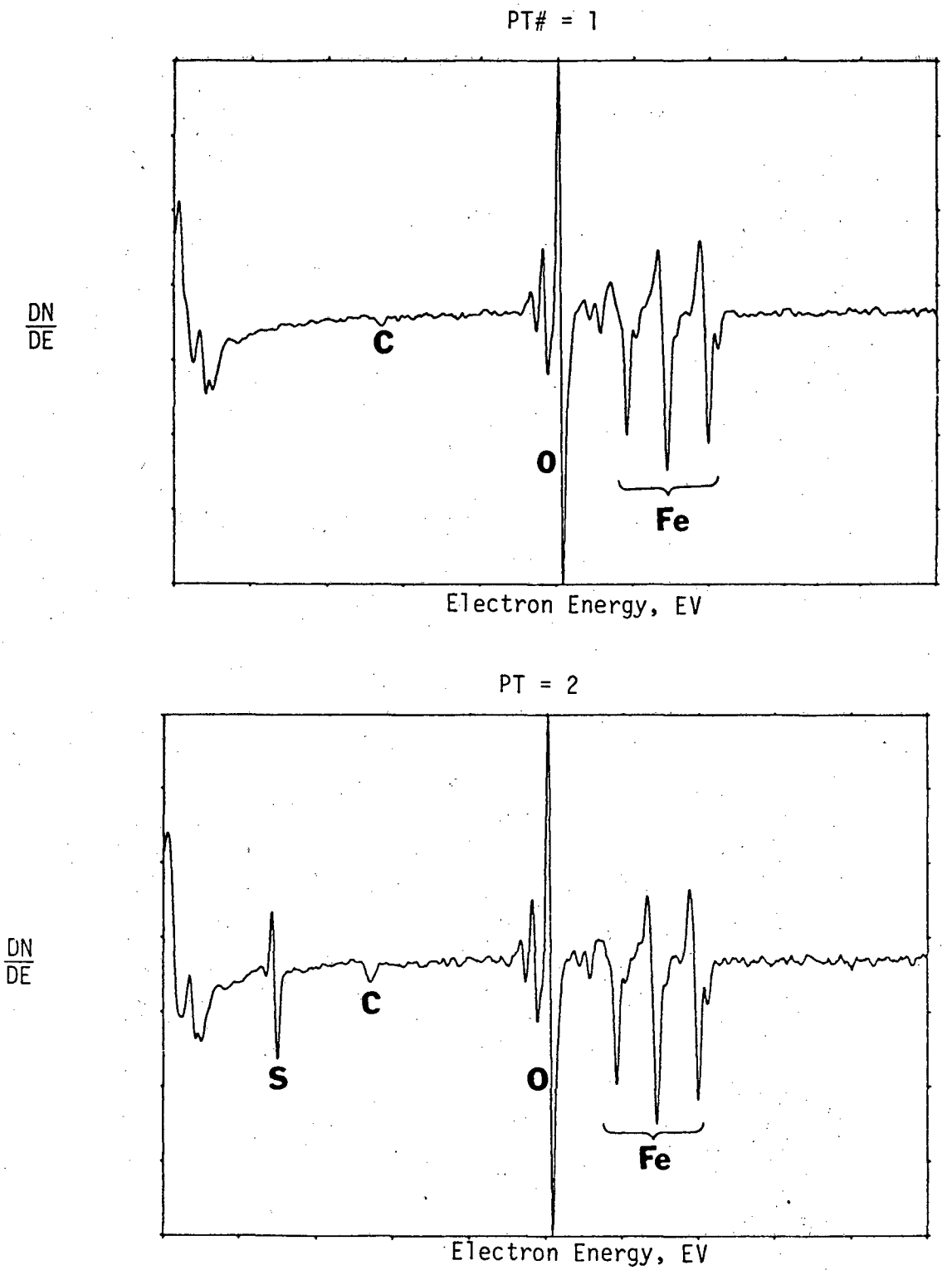
Figure 2.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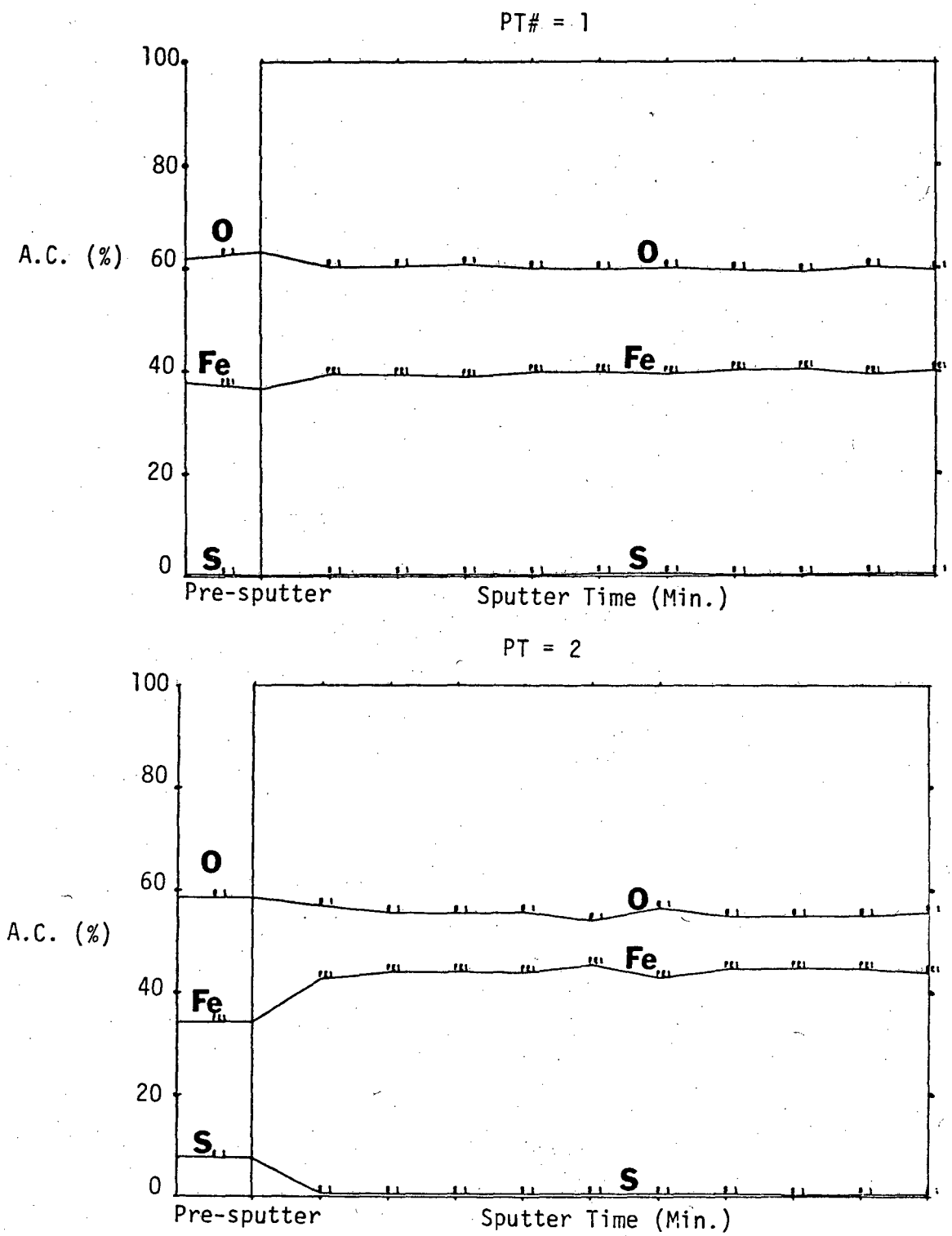
Electron Energy, EV

Figure 3.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PT = 2
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0
A.C. (%)
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Pre-sputter
Sputter Time (Min.)

Figure 4.

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