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APPLICATION OF ANALYTICAL ELECTRON MICROSCOPY
TO THE STUDY OF INTERGRANULAR CORROSION IN 304 STAINLESS STEEL

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APPLICATION OF ANALYTICAL ELECTRON MICROSCOPY TO THE STUDY OF INTERGRANULAR
CORROSION IN 304 STAINLESS STEEL*

C. S. Pande and R. L. Sabatini

The technique of analytical electron microscopy in a scanning transmission electron microscope fitted with an energy dispersive X-ray spectrometer is used to measure the chromium depletion in sensitized 304 stainless steel along the grain boundaries. It is shown that such measurements could be misleading unless care is taken to properly choose the regions on the grain boundaries for such analysis.

Intergranular corrosion in sensitized stainless steel is supposed to be caused by the precipitation of chromium iron carbide $((Fe,Cr)_{23}C_6)$ at the grain boundaries, with a concomitant depletion of chromium in and around the grain boundaries, to the levels below that required for protection against corrosion.^{1,2} With the advent of the analytical electron microscope the first direct evidence in support of this theory was obtained by Pande et al.,³ and independently by Rao and Lifshin.⁴ These authors measured the chromium concentration across the grain boundary, and showed that the chromium concentration dropped drastically adjacent to grain boundaries in sensitized specimens. The results reported in this paper refer to measurements made along and adjacent to grain boundaries instead of across them.

Experimental Set-up

The experiments were performed on a JEOL-100C electron microscope with scanning and energy-dispersive attachments. When the scanning electron

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beam was made stationary it acted as an electron probe and the X-rays generated were detected by an NSI Si(Li) detector mounted on the electron microscope column. In order to improve the spatial resolution and yet obtain sufficient counts, it was necessary to optimize various parameters, such as the accelerating voltage of the electrons (120 kV), the detector area (30 mm²), the beam size (about 30Å), a constant counting time (30 sec), and tilt of 40°. For further details see refs. 3 and 5.

The following three improvements to the previous procedure³ were introduced.

1) The beam size was reduced to the smallest possible in our instrument for a 250 μ condenser aperture. The reason for this step was the following. It has been noted previously,³ that the depleted zone along the grain boundaries is of the order of 1000Å. Therefore, it is critical that the spatial resolution of the measurement be as good as possible. The spatial resolution could of course be improved by reducing the specimen thickness. However, it was found that in specimens less than 1000Å thick, that the Fe/Cr concentration ratio is a function of specimen thickness even when no such variation exists in the bulk.⁵ The only other alternative for improving the spatial resolution is to reduce the beam size. In our experiments the beam size was about 30Å, according to Romig and Goldstein⁶ this would give us a spatial resolution of 220-380Å for foils of thickness 1000-1500Å. 2) The spurious copper peak was virtually eliminated in the 304 stainless steel spectra by using a modified graphite-holder and an aperture over the specimen stage. This is important because it is known that the spurious copper signal enhances the chromium and iron peaks of the stainless steel spectra by fluorescence.⁷ 3) Specimen drift was minimized by the use of the modified graphite holder in which the specimen is clamped by screws, instead of just held together by friction.

Results

Figure 1 shows the grain boundary in a 304 stainless steel specimen used for analysis. The specimen has been 'sensitized' by heating it at 600°C for 24 hours. The measured concentrations of chromium, iron, and nickel for the various points indicated in Fig. 1 are given in Table 1. The concentrations have been measured both for points on and adjacent to the grain boundary (about 300Å from the grain boundary). It should be noted (Table 1) that a point on or adjacent to the grain boundary may or may not show a depletion in chromium. The reason for this becomes clear, when the grain boundary is tilted 45° along an axis parallel to the grain boundary direction (Fig. 2). It can be seen that some of the measured regions may have partially overlapped precipitates on the boundary. This is especially true for grain boundaries where the number of such precipitates per unit grain boundary area is relatively high. In such cases although the depletion of Cr near these precipitates may even be higher, the actual measurements may not reveal such a depletion. Table 2 shows results of the concentration measurements along the grain boundary in another 'sensitized' specimen at the points shown in Fig. 3. It should be noted that the Cr value never falls below 15%, as compared to the 14% measured in the previous grain boundary, although the number of precipitates are higher. In some cases the Cr values measured along the grain boundary are higher than that of the matrix indicating that the analyzed region contains a precipitate.

A careful selection of the areas of analysis is therefore necessary, before such results could be used to interpret a chromium depletion as a function of the angle of misorientation, or the heat treatment in this material.

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TABLE 1.--Results of the microanalysis along the grain boundary in fig. 1.

Point	Cr	Fe	Ni
A	.144 ± .020	.726 ± .010	.105 ± .053
B	.172 ± .019	.708 ± .011	.095 ± .057
C	.160 ± .019	.716 ± .010	.099 ± .054
D	.142 ± .020	.736 ± .010	.097 ± .056
E	.160 ± .019	.720 ± .010	.094 ± .057
F	.186 ± .018	.700 ± .011	.090 ± .058

TABLE 2.--Results of the microanalysis along the grain boundary in fig. 3.

Points along the Grain Boundary	Cr	Fe	Ni
1	.198 ± .014	.684 ± .008	.093 ± .018
2	.180 ± .015	.704 ± .008	.091 ± .019
3	.153 ± .021	.719 ± .010	.103 ± .023
4	.175 ± .017	.702 ± .009	.097 ± .020
5	.174 ± .018	.705 ± .009	.096 ± .021
6	.273 ± .012	.628 ± .008	.074 ± .020
7	.149 ± .025	.736 ± .012	.089 ± .028
8	.174 ± .025	.702 ± .013	.099 ± .029

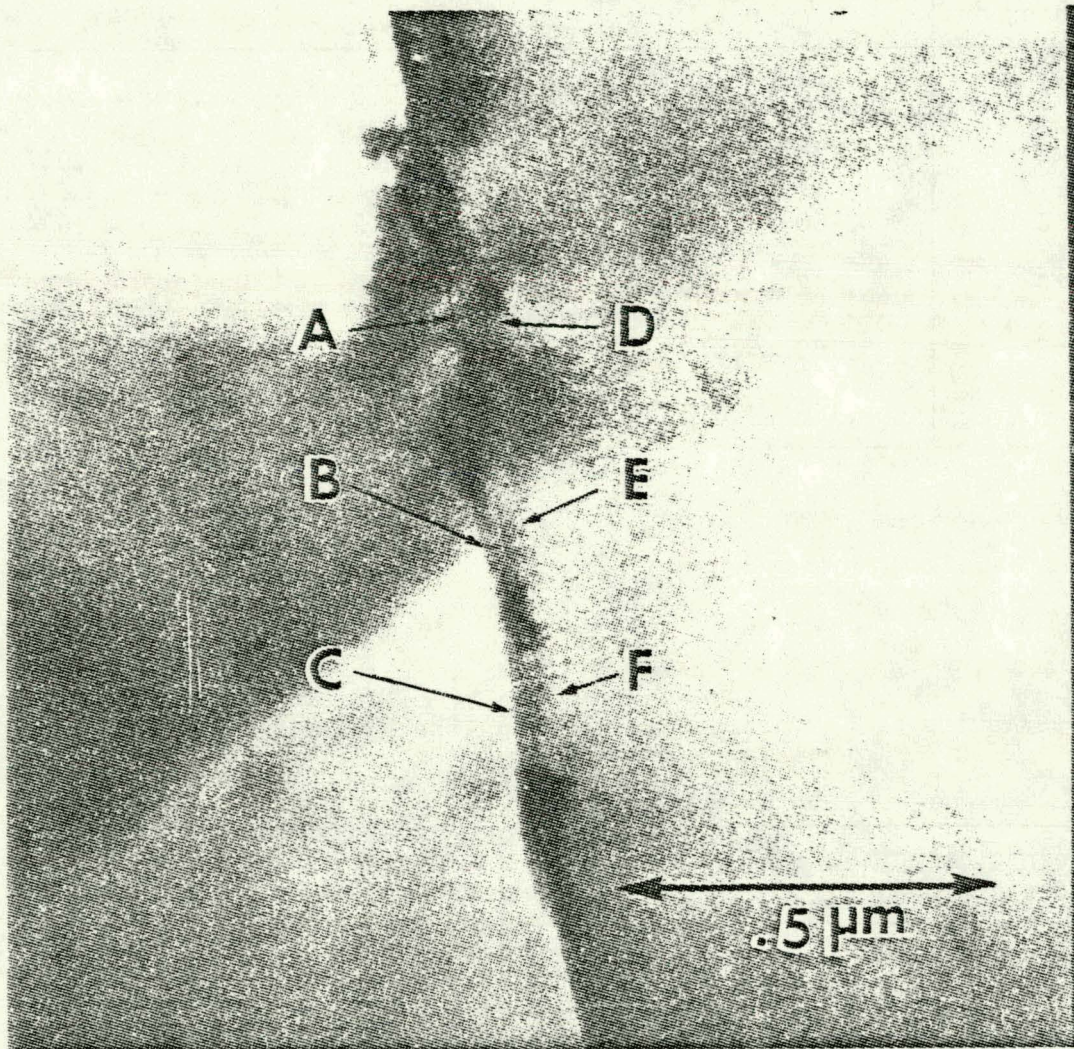


FIG. 1.--Scanning transmission electron micrograph showing precipitates along the grain boundary in a sensitized type 304 stainless steel specimen. The letters indicate the various points of analysis along the grain boundary (table 1).

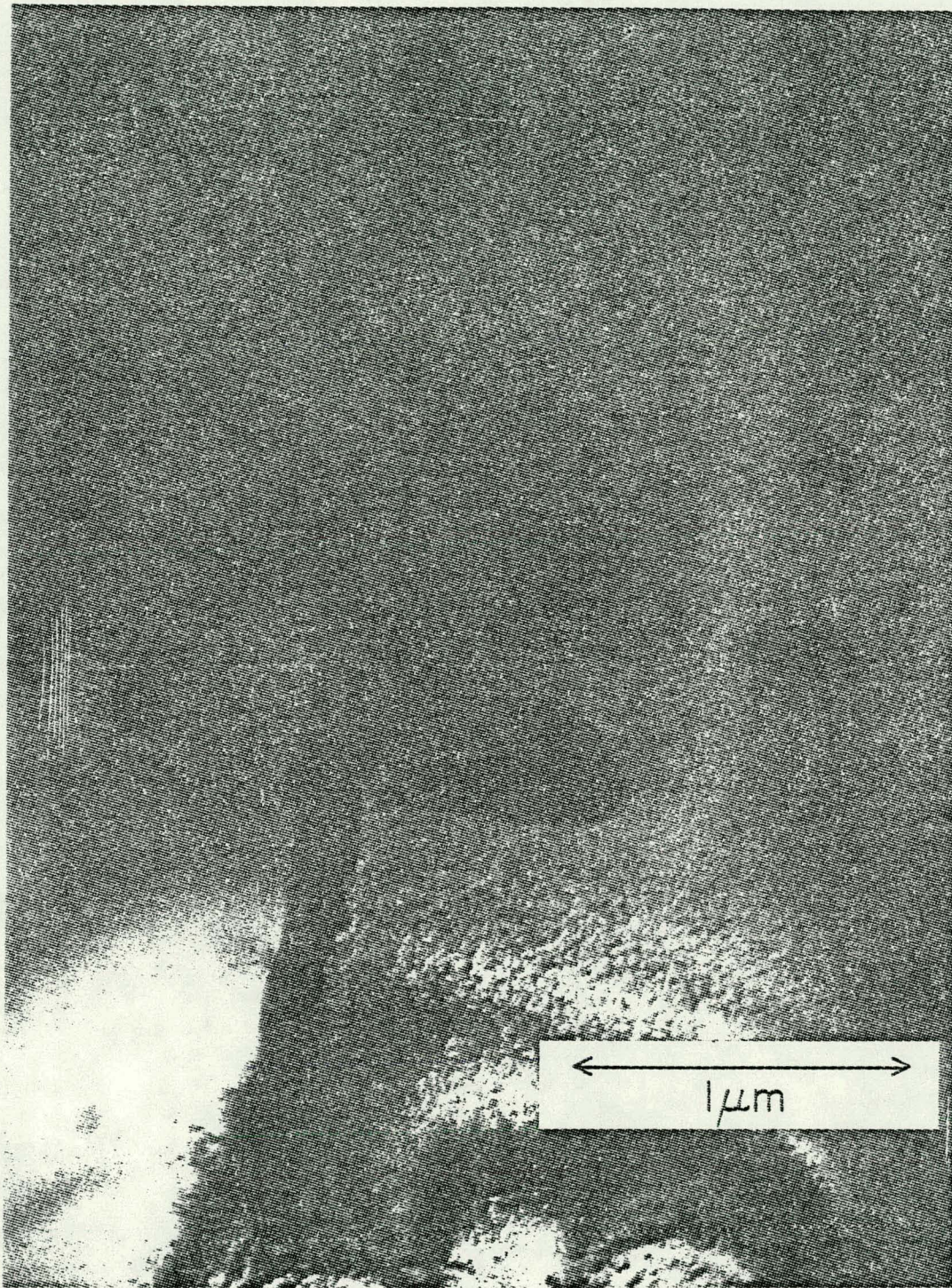


FIG. 2.--Transmission electron micrograph of the same area as in fig. 1 with the grain boundary tilted 45° along an axis parallel to the grain boundary direction. Note the contamination marks indicate the regions which were analyzed.

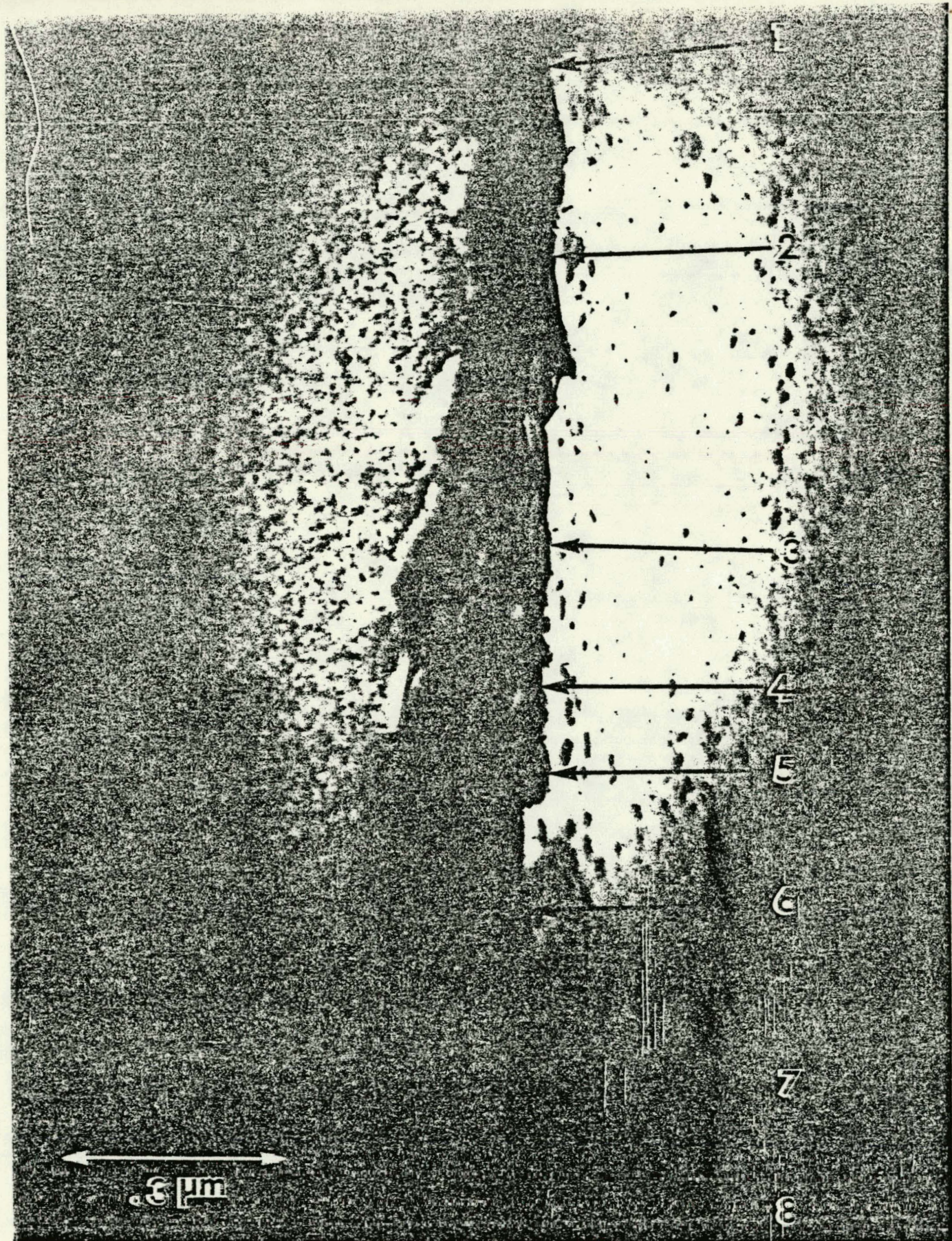


FIG. 3.--TEM micrograph of another sensitized type 304 stainless steel specimen along which 8 points were analyzed before tilting (table 2). Note that depending on the region selected for analysis one might actually be exciting x-rays from a small precipitate somewhere in the plane of the grain boundary.