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# "Observation of Grain Boundary Segregation on an Atomic Scale in a Fe-0.04% P Alloy by Atom-Probe FIM"

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(Title of paper) Observation of Grain Boundary Segregation on an Atomic Scale in a Fe-0.04%P Alloy by Atom-Probe FIM


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(Type abstract in this area—double spaced.)


Grain boundaries introduced intentionally in a Fe-0.04%P alloy by cold-working were successfully observed using a field ion microscope (FIM), and the composition along a grain boundary was analyzed using a high-performance time-of-flight atom-probe. Phosphorus was found to segregate to the grain boundaries below 600°C, in agreement with previous Auger electron spectroscopy studies. In addition to P, it was found that several other elements, such as Ti, O, C and Mn segregate to the grain boundaries at different annealing temperatures.


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# OBSERVATION OF GRAIN BOUNDARY SEGREGATION ON AN ATOMIC SCALE IN A FE-0.04%P ALLOY BY ATOM-PROBE (FIELD ION MICROSCOPY)

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Phosphorus is known from Aüger electron spectroscopy analyses to segregate to grain boundaries of ferritic steels at elevated temperatures and produce a deleterious effect on the mechanical strength (temper embrittlement)(1,2). This element has also been observed to enhance grain boundary corrosion (3,4) and stress corrosion (5) in these steels. However, AES analysis of grain boundaries is possible only if the specimen is embrittled and can be fractured inter-granularly at least to a fraction of about 10%. For non-embrittled alloys, the field ion microscope (FIM) atom probe is the only micro-analytical instrument available for the study of grain boundary segregation at the atomic level.

In this paper, we report the successful application of a high-performance time-of-flight (ToF) atom-probe to the study of phosphorus segregation to grain boundaries in a Fe-0.04%P alloy. The ToF atom-probe used in this investigation, which was developed by Müller (6,7), is capable of noise-free analysis of solute atoms with a mass resolution ($m/\Delta m$) of over 1,000. This is to be compared with the conventional (straight drift tube) ToF atom probes which have resolutions on the order of $m/\Delta m = 100$. The factor accounting for the improved resolution is the incorporation of a curved (Poschenrieder) electrostatic focusing lens (shown in Figure 1)(8).

## PROCEDURE

An iron wire was doped with phosphorus by heating at 800°C in vacua with Fe-P alloy and $TiH_2$. The wire was made into a sharp, needle-shaped tip by electrochemical etching. The tip was field evaporated until a sharp field ion image characteristic of iron was observed. Compositional analysis was then performed at 78K and about $10^{-7}$ Pa ($10^{-9}$ Torr) by gradually field evaporating the surface atoms.

A series of analyses was then done at the grain boundary on this tip from exactly the same area after heating in vacuum to successively higher temperatures of 440, 470, 530, 660, 770 and 910 ±30°C, and then cooling to 78K. After each thermal treatment at least 1,000 pulse

*Permanent address: Max-Planck Institut für Eisenforschung, GMBH, Dusseldorf, Federal Republic of Germany field evaporations, removing and analyzing the surface atoms, were attempted in order to obtain statistically meaningful data. This corresponds to an analysis of approximately 30 atomic layers along the grain boundary.

## RESULTS

Field ion images were observed using $H_2$ imaging gas at 78K, Fig. 2. In this figure, a grain boundary, 1 to 2 atom distances wide, is seen running north to south. In some cases, grain boundaries were wider and rough.

Phosphorus was found to segregate to the grain boundary at temperatures below 600°C, Figure 3. The phosphorus content in the grain boundary is 15 ±3% at 440°C; it decreases to about 7.5% at 530°C and approaches 0% at or above 660°C. This atom probe observation agrees qualitatively with previous AES studies (2). The results provide unmistakeable evidence at a truly atomic level for grain boundary segregation of phosphorus. Ti, C, O and Mn were also detected to segregate to the grain boundary at different temperatures.

At a distance of a few atom layers from the grain boundary the phosphorus content was virtually nil, indicating a very sharp gradient. This is to be contrasted with results presented for Ti segregation to grain boundaries in Fe-0.15%Ti alloy in which the decay of the Ti concentration was quite broad, extending over 20 atom layers into the bulk (9).

## CONCLUSIONS

Grain boundaries were successfully observed in a Fe-0.04%P alloy using a field ion microscope (FIM), and the composition along a grain boundary was analyzed using a high-performance time-of-flight atom-probe. Phosphorus was found to segregate to the grain boundaries below 600°C, in agreement with the previous Aüger electron spectroscopy studies. The atom probe FIM offers unique opportunities for evaluating the segregation characteristics of many elements, including those which cannot be studied by AES and other methods which rely on grain boundary fracture for the analysis.

## ACKNOWLEDGEMENT

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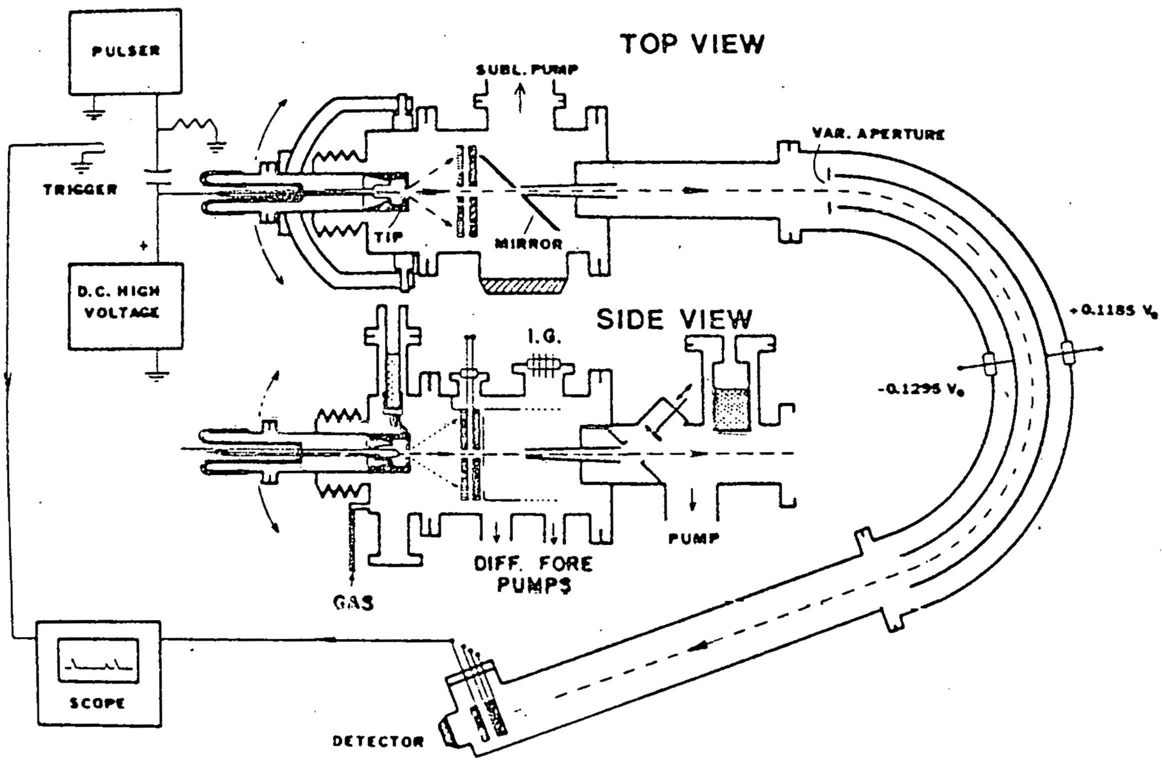


Fig. 1. A schematic of the high-performance time-of-flight atom-probe FIM equipped with a curved electrostatic focusing lens.

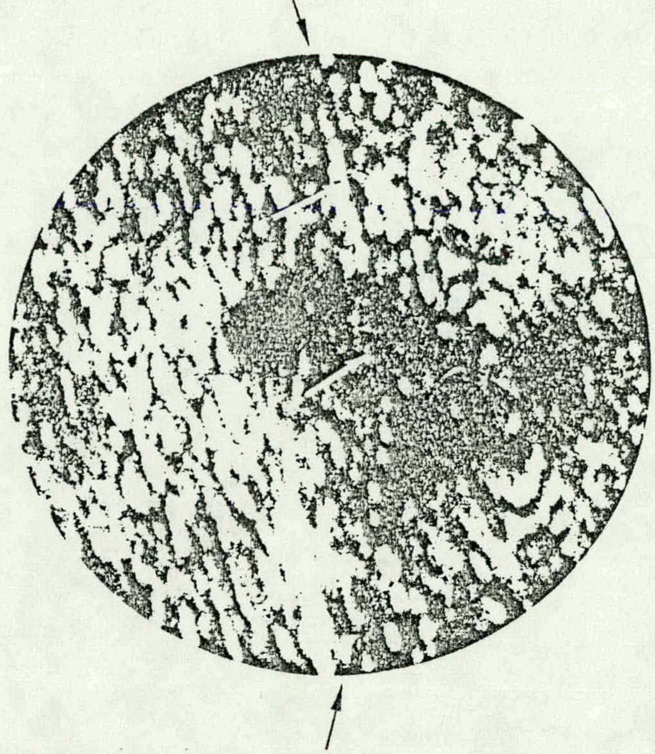

Fig. 2. A field ion micrograph of Fe-0.04%P alloy tip with a narrow grain boundary running north to south. $H_2$ imaging gas was used.

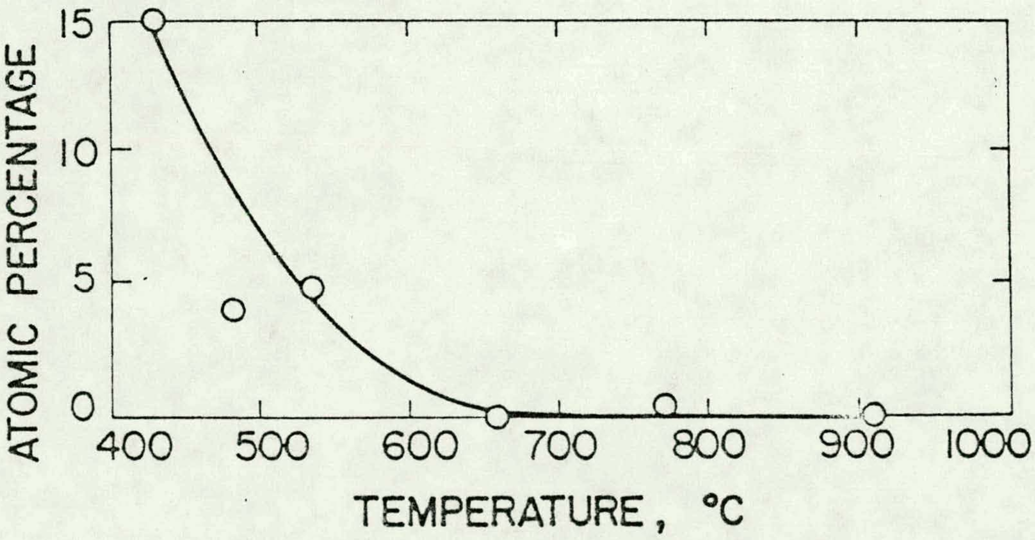


Fig. 3. Phosphorus content at a grain boundary in Fe-0.04%P alloy as a function of the annealing temperature.