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in A Fe-0.04% P Alloys"

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PHOSPHORUS SEGREGATION TO GRAIN BOUNDARIES IN A Fe-0.04%P ALLOY

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In this paper, we report the successful application of a high-performance time-of-flight (ToF) atom-probe to the study of grain boundary segregation in a Fe-0.04%P alloy. The ToF atom-probe used in this investigation, which was developed by Müller (1,2), is capable of noise-free analysis of solute atoms with a mass resolution (m/Δ 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 $\frac{m}{\Delta m} = 100$. The factor accounting for the improved resolution is the incorporation of a curved (Poschenrieder) electrostatic focusing lens (shown in Figure 1)(3). In addition, atom probes have the intrinsic capability of providing analyses on an absolute scale and, thus, can yield useful information which can only be obtained indirectly, and usually with difficulty, by other techniques.

In another study (4), it was found for a Fe-0.15%Ti alloy that (i) titanium atoms are segregated to the surface and grain boundaries after heating to 1073 or 1273 K at 10^{-6} Pa (10^{-3}Torr); (ii) the titanium concentration profile extends over 20 atomic distances; (iii) in the subsurface atom-layer region, the Ti is present as randomly distributed titanium atoms and to a lesser degree as clusters of Ti around impurities, such as C, N, and O; and (iv) due to an unknown source of oxygen, titanium in the outermost surface atomic layers and along the atomic structure of the grain boundary itself is in the form of oxide, mainly TiO and TiO_2.

Phosphorus is known from Auger electron spectroscopy analyses to segregate to grain boundaries of ferritic steels at elevated temperatures

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and produce a deleterious effect on the mechanical strength (temper embrittlement)(5,6). This element has also been observed to enhance grain boundary corrosion (7,8) and stress corrosion (9) in these steels. However, AES analysis of grain boundaries is possible only if the specimen is embrittled and can be fractured intergranularly at least to a fraction of about 10%. For non-embrittled alloys, the FIM atom probe is the only micro-analytical instrument available for the study of grain boundary segregation at the atomic level.

PROCEDURE

An iron wire was doped with phosphorus by heating at 800°C in vacuum with Fe-P alloy and TiH_2. The wire was made into a sharp, needle-shaped tip by electrochemical etching. The tip was installed in the atom probe and baked at 150°C overnight during which time the system pressure decreased to 7×10^{-7} Pa (5×10^{-9} Torr). Following field evaporation to remove surface layers, compositional analysis was performed at 78 K. No phosphorus was detected.

Field ion images were observed using H_2 imaging gas at 78 K, 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.

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 470, 530, 660, 770, and 910 ±30°C, and then cooling to 78 K. After each thermal treatment at least 1,000 pulse 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

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 (6). The results provide unmistakeable evidence at a truly atomic level for grain boundary segregation of phosphorus.

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 (4).

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 Auger electron spectroscopy studies. The atom probe FIM offers unique opportunities for evaluating the segregation characteristics of many elements, including those which cannot be studies by AES and other methods which rely on grain boundary fracture for the analysis.

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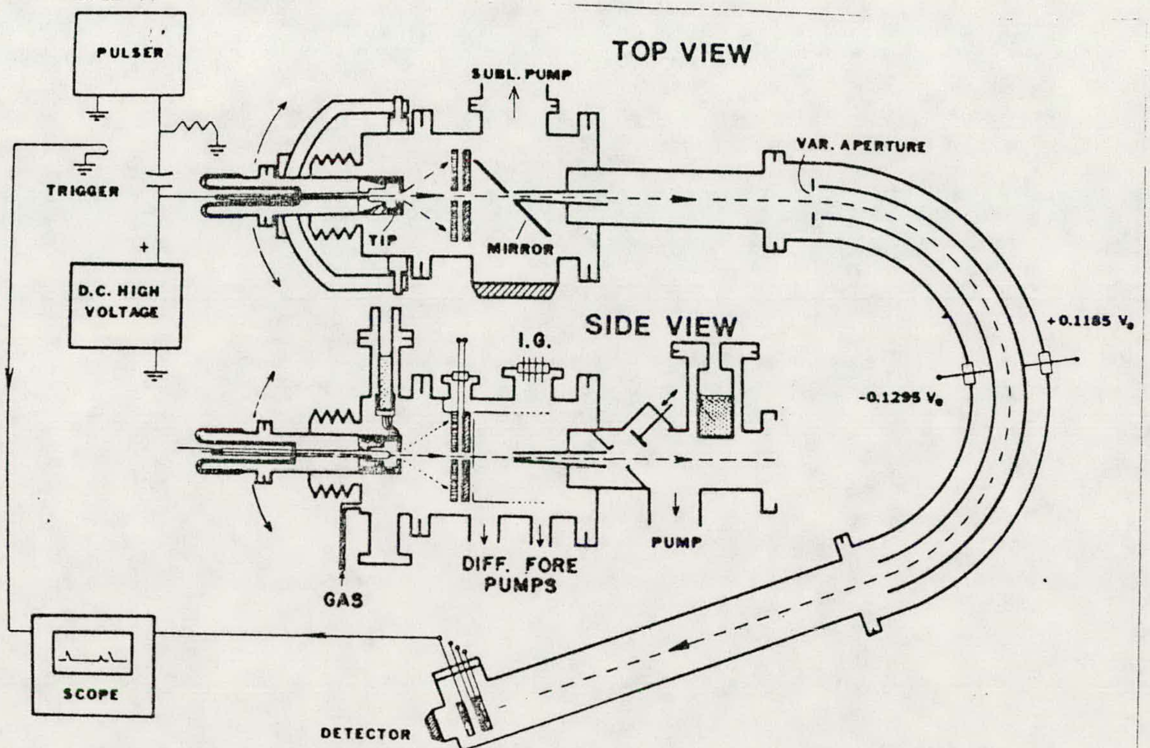
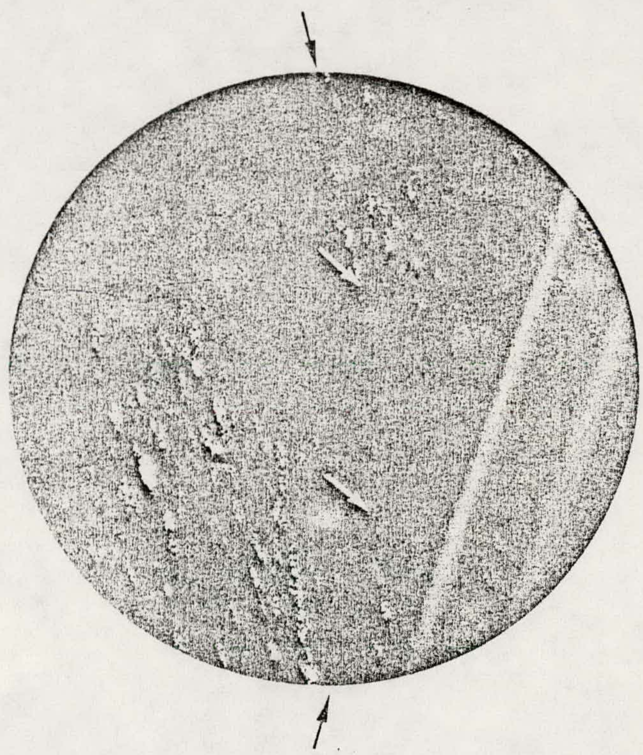


Fig. 1. A schematic of the high-performance time-of-flight atom-probe FIM equipped with a curved electrostatic focusing lens.

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.



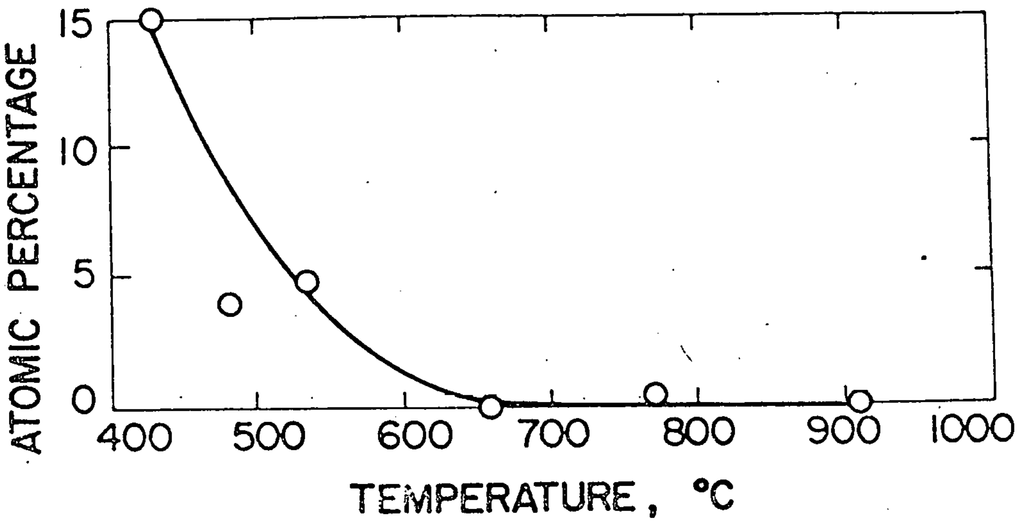


Fig. 3. Phosphorus content at a grain boundary in Fe-0.04%P alloy as a function of the annealing temperature.