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GRAIN BOUNDARY MIGRATION AND MORPHOLOGY OF VACUUM ANNEALED SURFACES OF HIGH-PURITY NIOBIUM (COLUMBIUM)*

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At SLAC, we are developing materials and processes that may eventually convert the present accelerator structure into one that performs in a superconducting mode. The ultimate result of this new superconducting accelerator will be to offer physicists a constant beam of electrons at high power which will be an improvement over the present duty cycle of only one part in 2000. The most promising of many candidate superconducting materials is high-purity niobium (columbium). This material will carry power from high-energy klystron tubes to the accelerator sections also constructed of niobium — both structures are extremely sensitive to surface imperfections. Although we knew that surface condition was important, it was unclear as to what degree surface imperfections will degrade the superconducting accelerator. Therefore, routine observations

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were made of the surfaces of high-purity niobium sections that had been annealed and these observations revealed some totally unexpected phenomena.

Most of the time when a metallurgist examines the microstructure of a metal, the procedures for preparing a metallurgical sample obliterate much of the prior thermal history of the metal. The surfaces of our niobium samples contained some interesting features that formed before, during and after recrystalization and these features remained on the annealed surfaces. Figure 1 is a photo of a typical surface (most of the surfaces examined were cylindrical, so "odd" lighting conditions existed, resulting in oblique lighting, uneven contrast across the sample, and out-of-focus areas in the photomicrographs) that was first seen. Disregarding the long grooves from machining and the gouges from handling, a twisted network reminiscent of grain boundaries can be seen. These were thought to be the actual grain boundaries of the material until another larger and sharper set of grain boundaries was seen to be superimposed upon the original network (Fig. 2). Several interesting items may be seen in this figure. Besides the large globs of dirt, the surface contains small craters (black dots). The main grain-boundary grooves (shown to be wide and dark in Fig. 2) disappeared when examined at high magnifications.

The true grain-boundary positions were determined by examining the surface at high magnification and pinpointing only those grain boundary lines which were sharp. Figures 3 and 4 will clarify this. Figure 3 is a high-magnification photomicrograph which shows a true (sharp) grain boundary passing below a former "triple point" intersection. (Again, please disregard the dirt — but not entirely, since they provide good orientation markers.) This same intersection is shown at low magnification in the lower right-hand corner of Fig. 4 — at this magnification, it is difficult to say which is the true grain boundary. The "false" lines I have termed "ghosts" or "vestigial" grain boundaries. The other portion of Fig. 4 shows extremely interesting phenomena too. There are at least twenty "ghost" patterns that lead up to the "true" triple point at the left of the photomicrograph. Apparently, these ghosts trace the former positions of the present grain boundary as it was heat treated.

Figure 5 shows four major grain-boundary positions — some 3 or 4 more ghost positions may be seen in the sample and on the original photo. These latter ghosts fall between the thickest ghost boundary in the middle of the photo and the true boundary near the black flaw at the left. This figure was included since it shows a clear progression of blunt-to-sharp boundary "ghosts" as the boundary moves.

Unfortunately, the thermal history (time, temperature and vacuum) of this piece is not available since this information was not recorded for each piece.

Figure 6 illustrates how surface imperfections (and impurities?) have retarded movement of a grain boundary from the bottom to the top of the picture. There are no true grain boundaries in this photo, but the ghost boundaries show an interesting sequence of movements. Marked on the photo are seven imperfections, some apparently subsurface, that disrupted grain-boundary movement. The first and oldest ghost-line may be faintly seen at the bottom as it connects and bows upwards from these points. The next, sharper, ghost line shows that the boundary "snapped" through positions 2 through 5, but were retained at positions 1 and 6. There are two more imperfections near point 7 which also retarded movement. The portion of the photo to the left of point 6 shows many events of interest also.

Figure 7 is similar to 6 and shows 4 ghost boundary positions leading upwards to a true grain boundary that is pinned at several points. Disregard the uniform background ridges which are machining grooves caused by a cutting tool.

Figures 8 through 11 illustrate some other points of interest. Point A, Fig. 8 is a small geometric scratch that can be seen in the next three photos (only the lower portion is shown in Fig. 11) and can be used for orientation. Figure 8 indicates that three parallel grain boundaries are present. However, Fig. 9 at a higher magnification shows that the top boundary, by "the scratch," now appears as a ghost and, of the lower two lines, the bottom one is sharper. Figure 10 clearly shows the ghost boundary near the scratch (A) and some detail in the thicker dark line. Figure 11 shows this line is also a ghost and that the true boundary is the sharp bottom one. The scratch (A) is now out of focus although the area below the true grain boundary is in focus — thus there is a good sized "step" down into the metal above the true grain boundary. Figure 12 is a photo, using oblique lighting, in an area similar to the wide ghost seen in Fig. 11. The large amount of light reflected from these two ghosts shows that there is an orientation difference in this region where most of the other areas remain dark.

Ghost-Grain Boundary Production Mechanism

The annealing conditions for our niobium test specimens are typically for eight (8) hours at 2100 to 2500 ^{o}K in vacuums about 10^{-8} Torr. The vapor pressure of niobium (see Table 1) is great enough at these annealing conditions to

TABLE 1

VAPOR PRESSURE OF NIOBIUM AS A FUNCTION OF TEMPERATURE

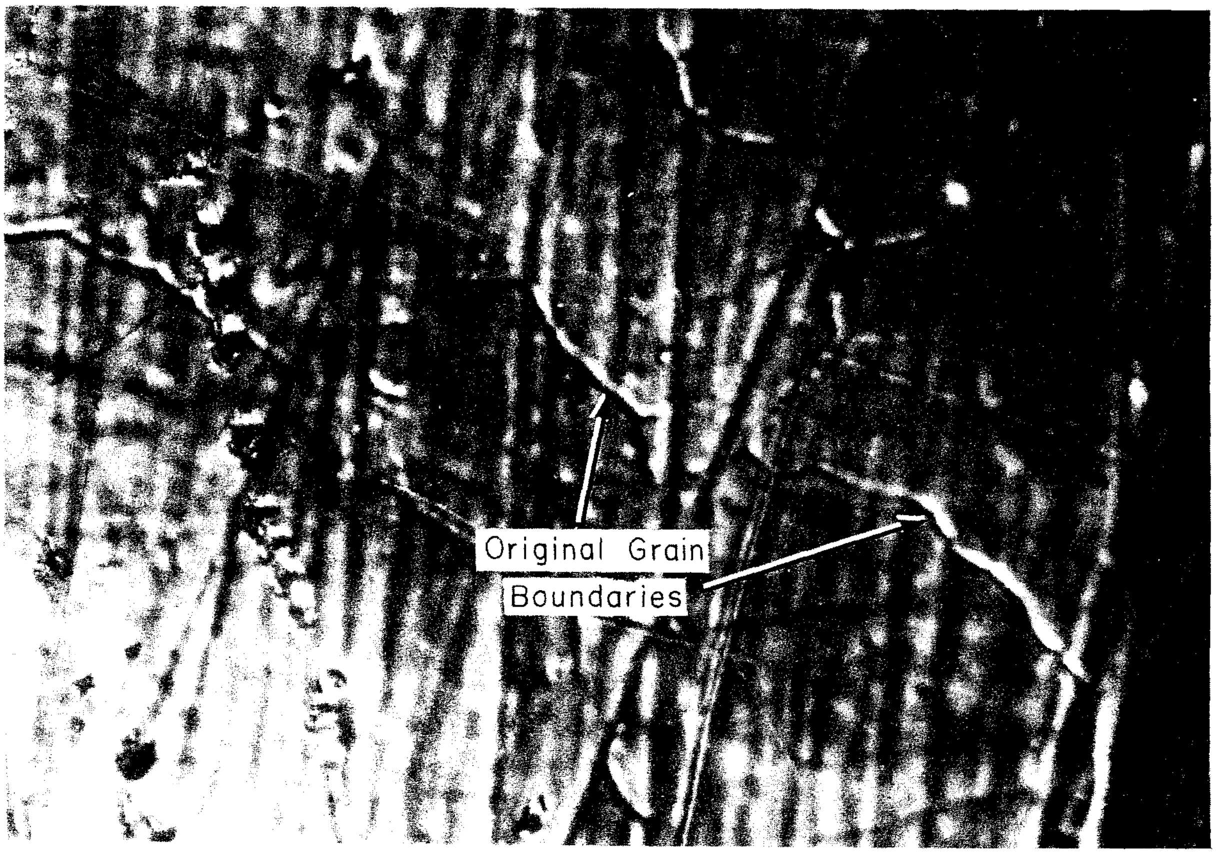
Temperature		Vapor Pressure
°C	°K	Torr
2287	2560	10^{-4}
2117	2390	10^{-5}
1977	2250	10^{-6}
1857	2130	10^{-7}
1737	2010	10^{-8}
1632	1905	10^{-9}

Reference: R. E. Honig and E. A. Kramer, "Vapor Pressure Data for the Solid and Liquid Elements," Techniques of Metals Research, R. F. Bunshah, Series Editor, John Wiley and Sons, Vol. 4, Part 1, R. A. Rapp, Editor, p. 510, 1970.

cause slow localized sublimation. Grain boundaries usually contain more imperfections than the body of the grain and will etch at a faster rate than the grain.

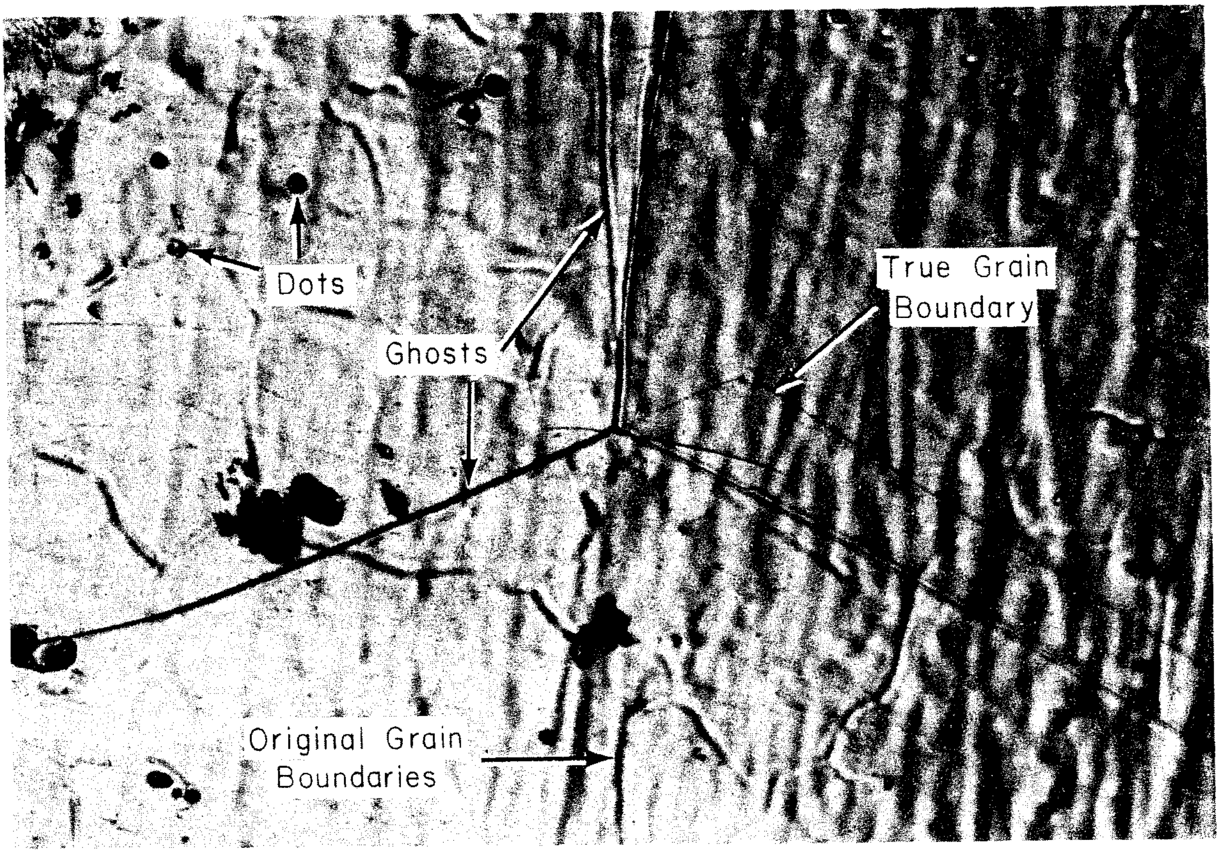
This brings up an interesting point. Grain growth and grain-boundary migration has been described at some length in many physical-metallurgy publications. We are told that boundary movements are diffusion controlled and thus it is implied that movement is steady when perturbing forces are ignored. Clearly, the entire length of the grain boundaries in these photos stopped long enough to produce a "ghost" image and since many of the boundary images are parallel to each other, local perturbations do not seem to be operative. This material is very high purity (99.99+ %) niobium with tantalum as the major impurity. Since niobium and tantalum produce a continuous solid solution at all temperatures, tantalum should not act as a disruptive force to smooth grain-boundary flow.

An explanation to a step-wise movement of grain boundaries, instead of a smooth movement, probably can be made as follows: grain boundaries are triggered into movement when the entropy of the system finally reaches a threshold limit that upsets the stability of the present boundary. As the boundary starts to move, much of the energy in the system is used up and the boundary moves to another position dictated by the remaining energy of the system. Here, the boundary waits for another energy buildup before it can proceed again and starts to "boil away" at a slightly greater rate than the surrounding grain and thus produces a "ghost" boundary. Energy, loosely taken, is assumed to be the integrated heat, time, and grain-boundary length and morphology. Indeed, some recent observations performed on high-purity niobium samples shows a ghost boundary for each high-temperature anneal. These ghosts would reside in place until the energy (usually thermal, since annealing times remained relatively constant) of the system permitted the boundary to move to a more stable configuration. This mechanism can still be considered to be "diffusion-controlled" since prior dislocations and impurities will probably migrate out of the structure quite readily at these annealing conditions.



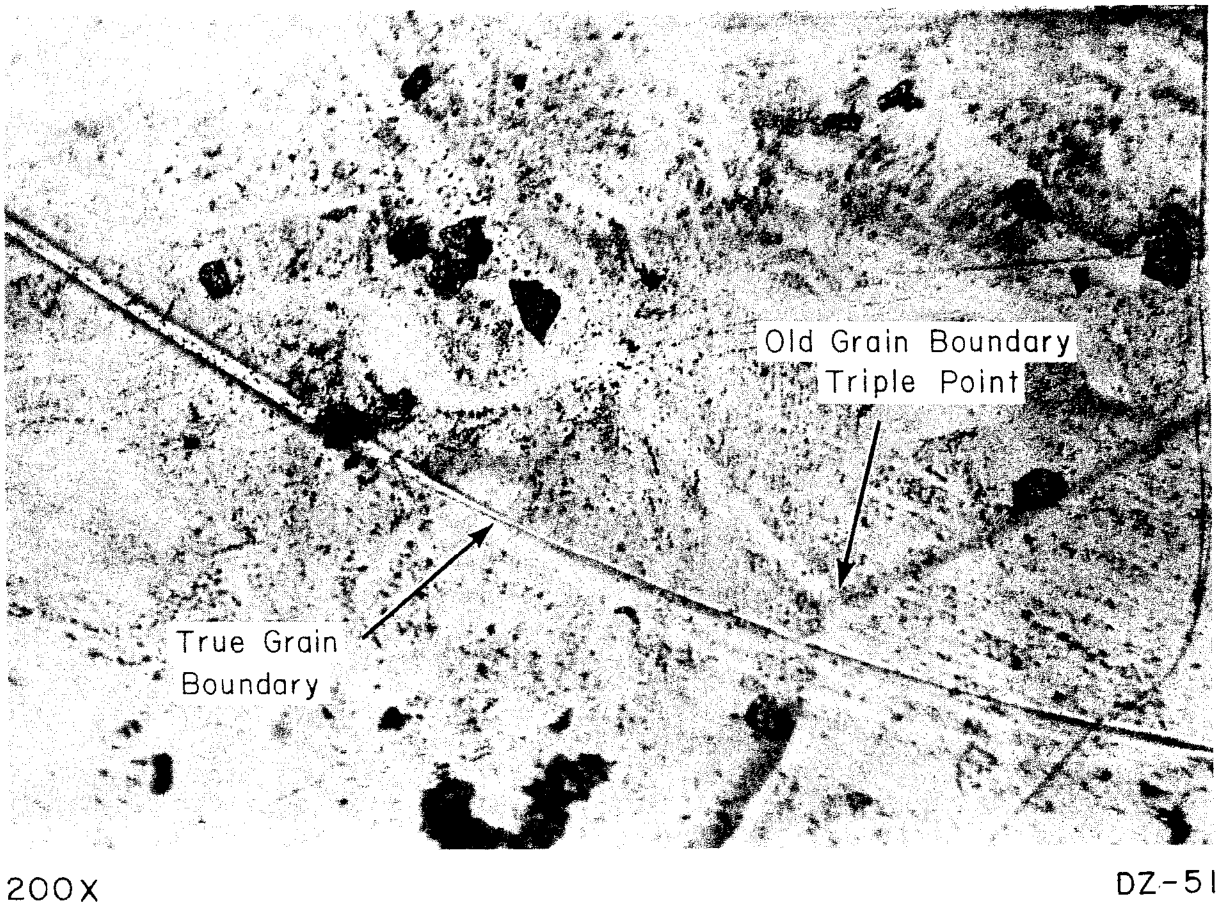
Grain boundary ghosts

Fig. 1



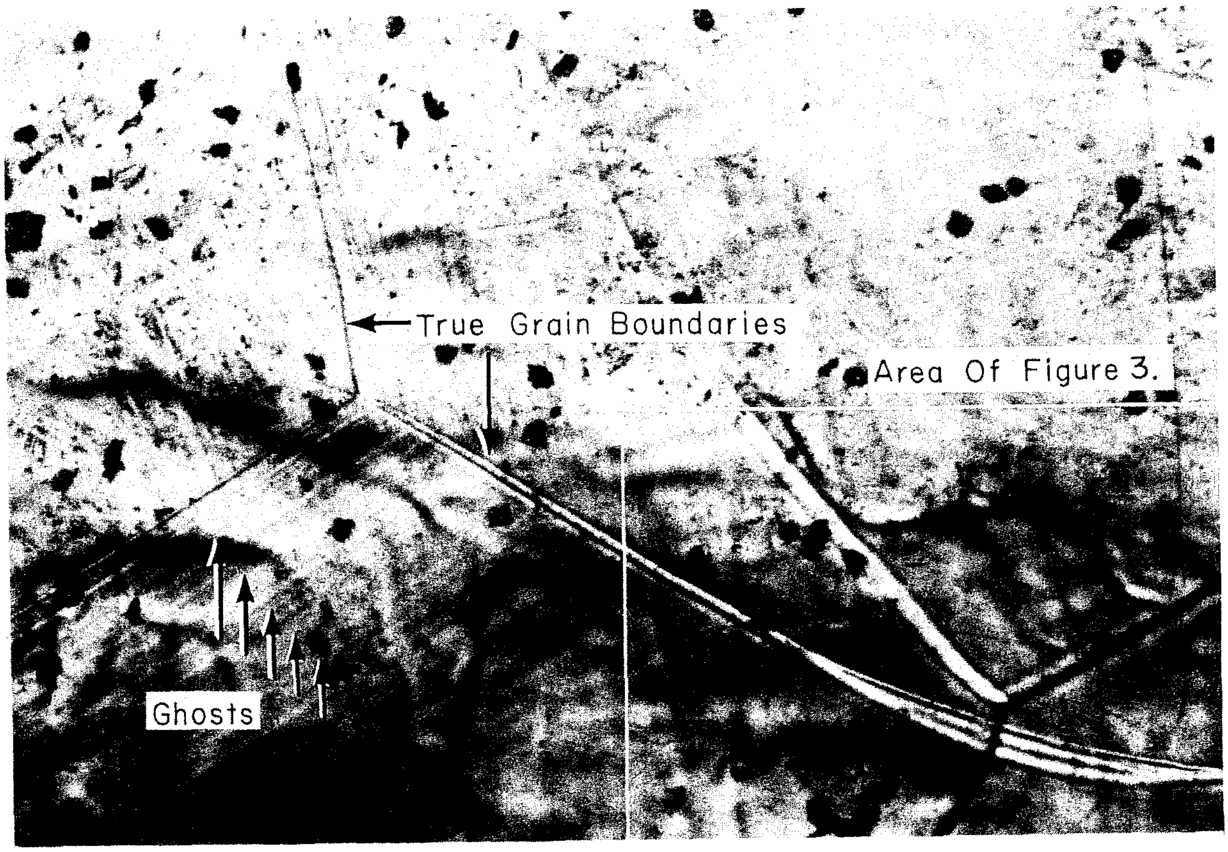
New grain boundary system superimposed on ghosts

Fig. 2



True boundary near triple-point ghost

Fig. 3

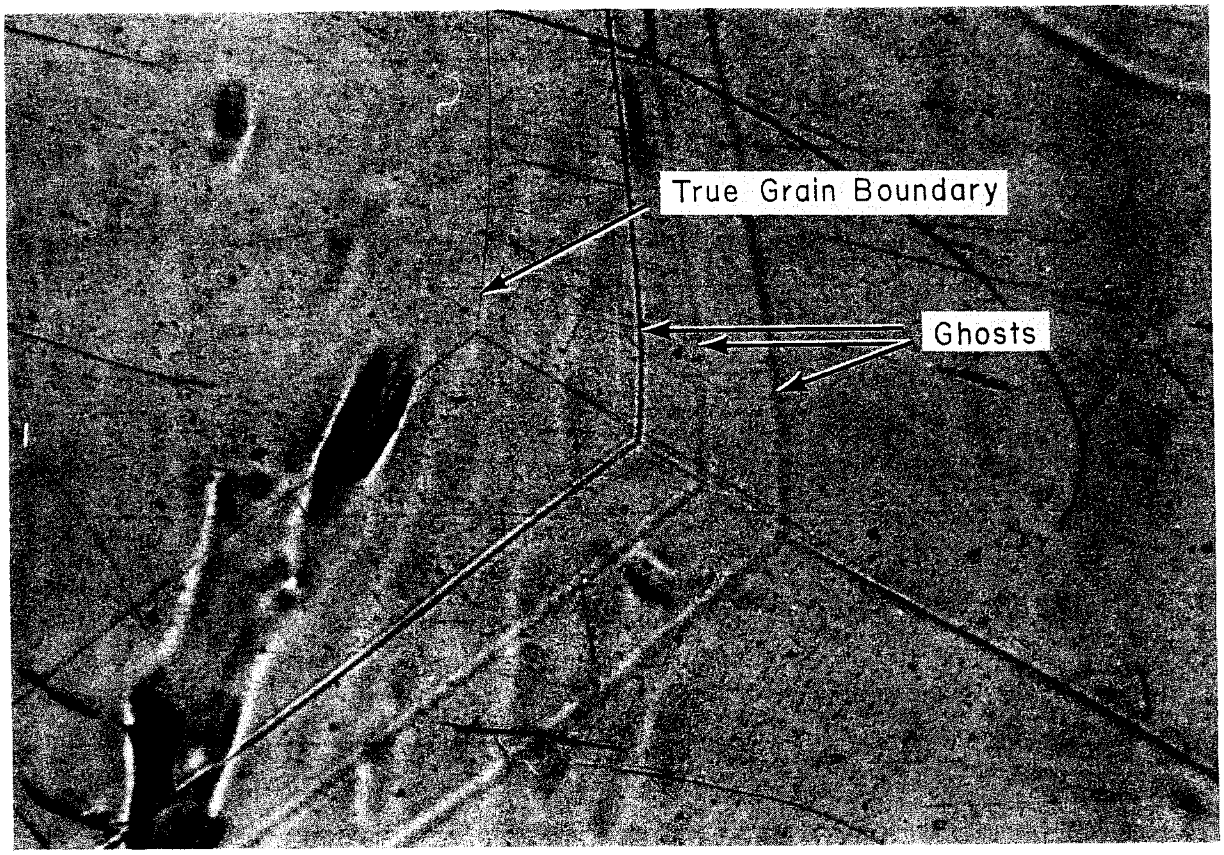


100X,

DZ-46
1863A4

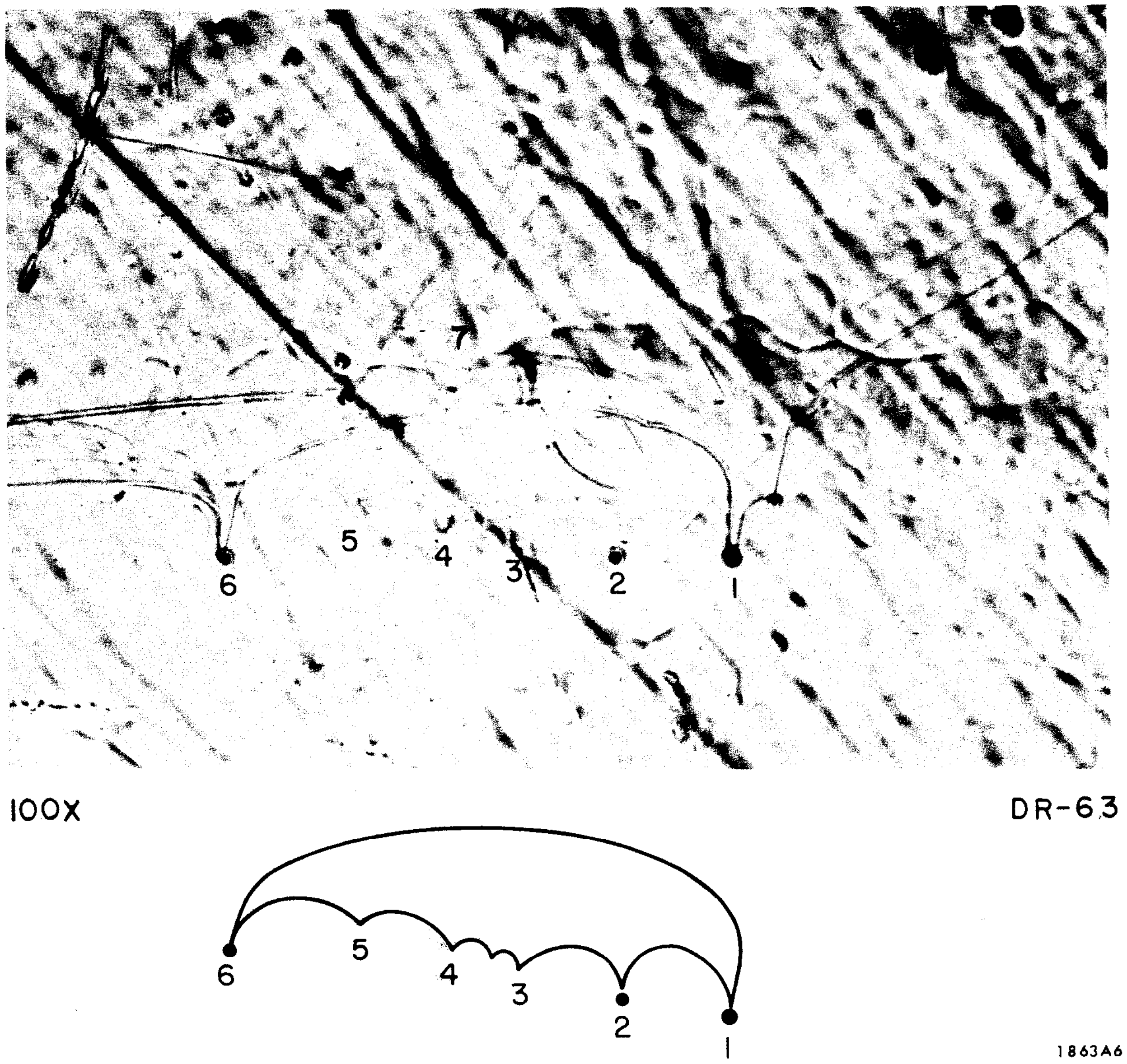
Appearance of surface at lower power
Also note numerous ghosts

Fig. 4



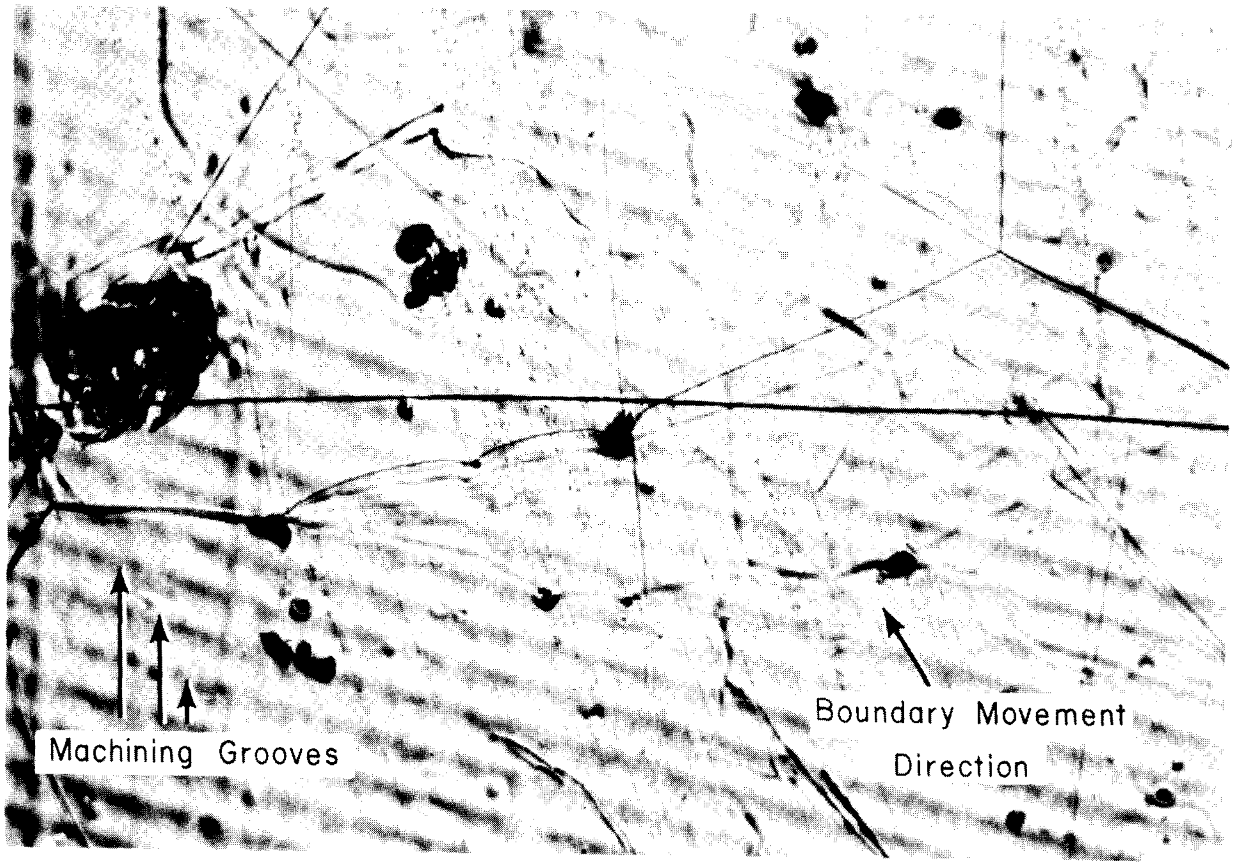
Blunting of old ghosts

Fig. 5



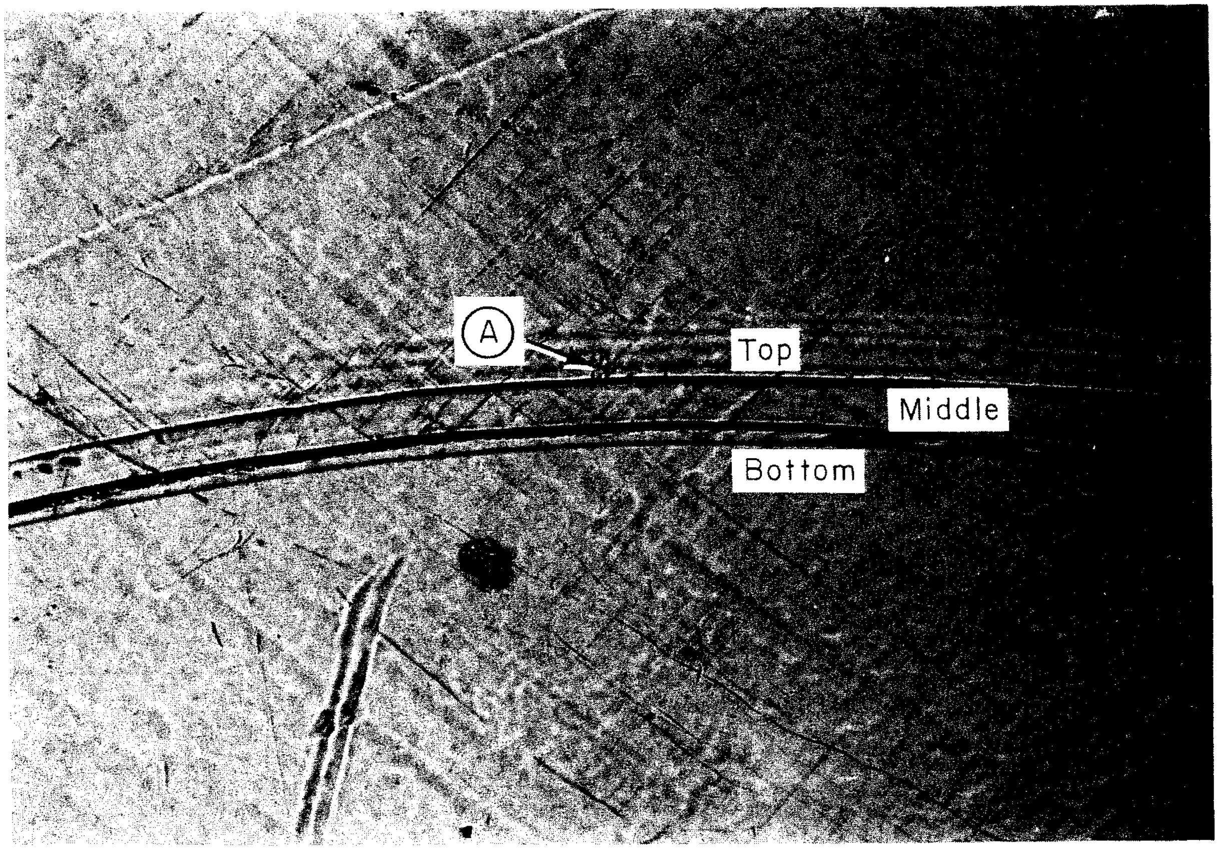
Grain-boundary pinning and movement

Fig. 6



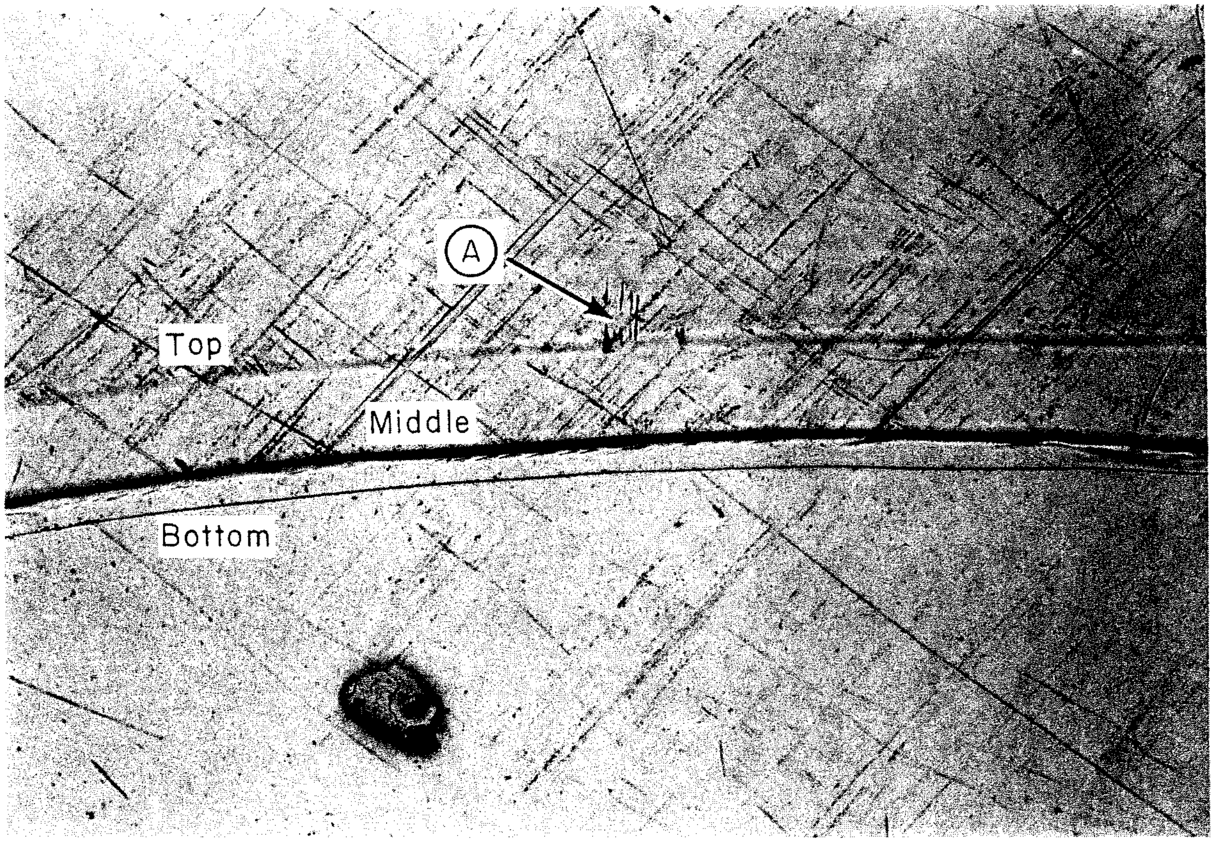
Grain-boundary pinning and movement

Fig. 7



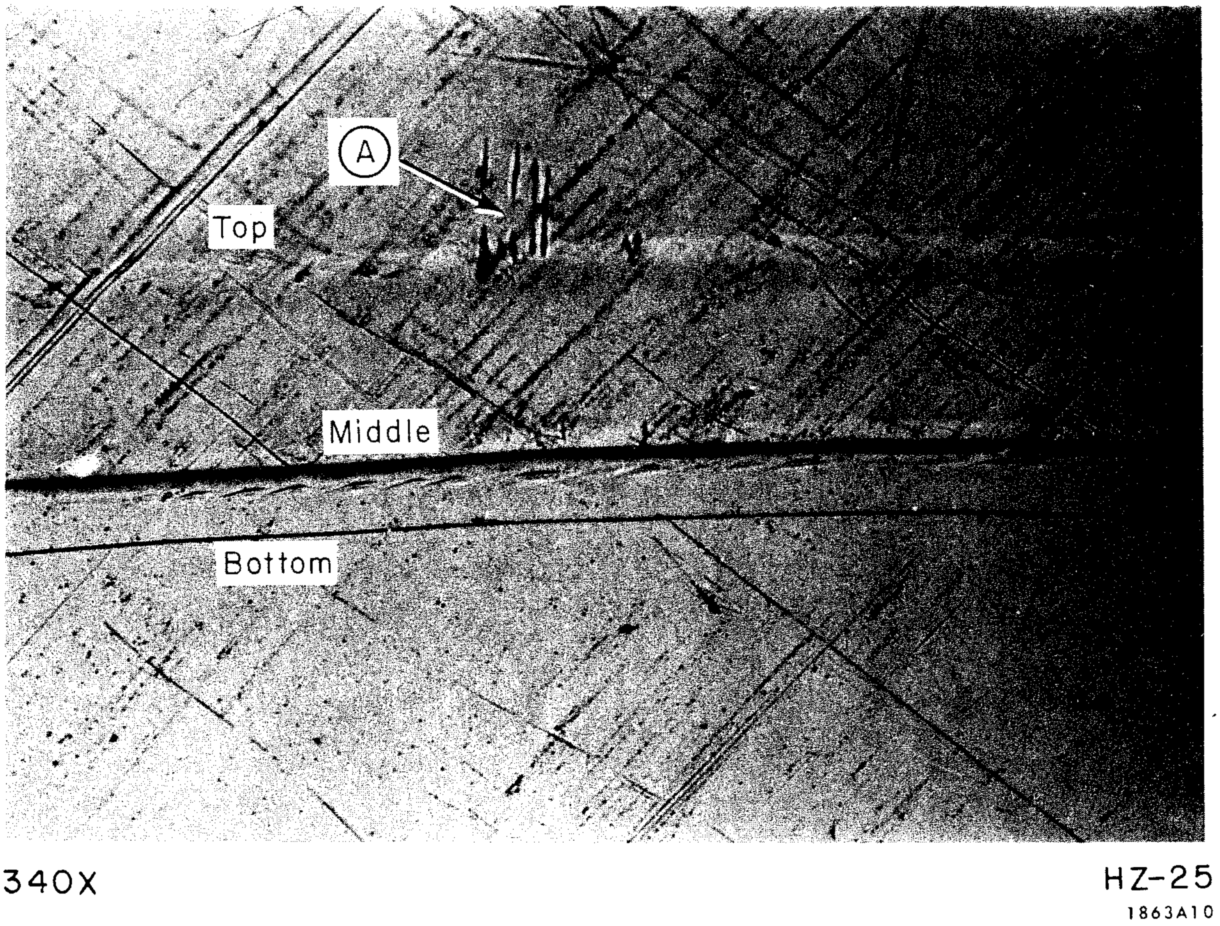
Parallel grain-boundary formations

Fig. 8



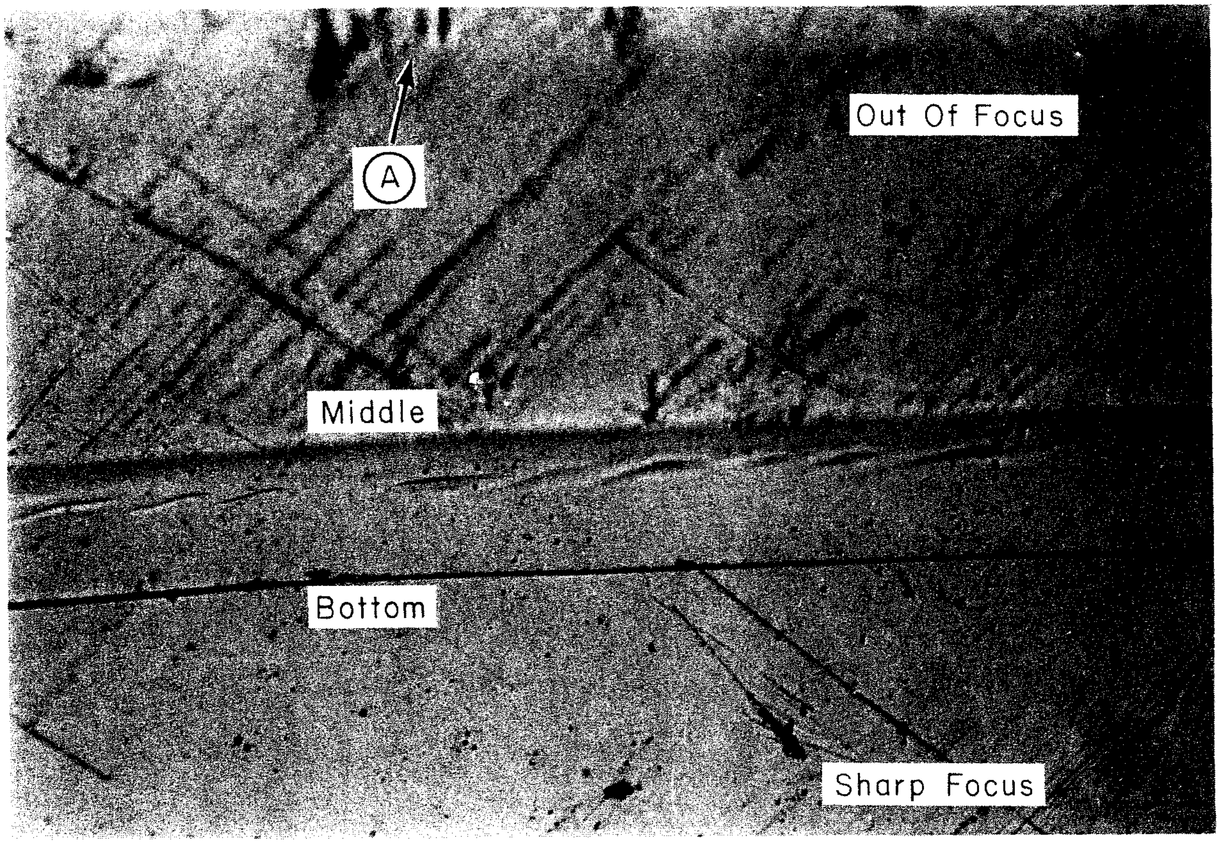
Parallel grain boundary - shows 1 ghost

Fig. 9



Parallel grain boundary - shows 2 ghosts

Fig. 10



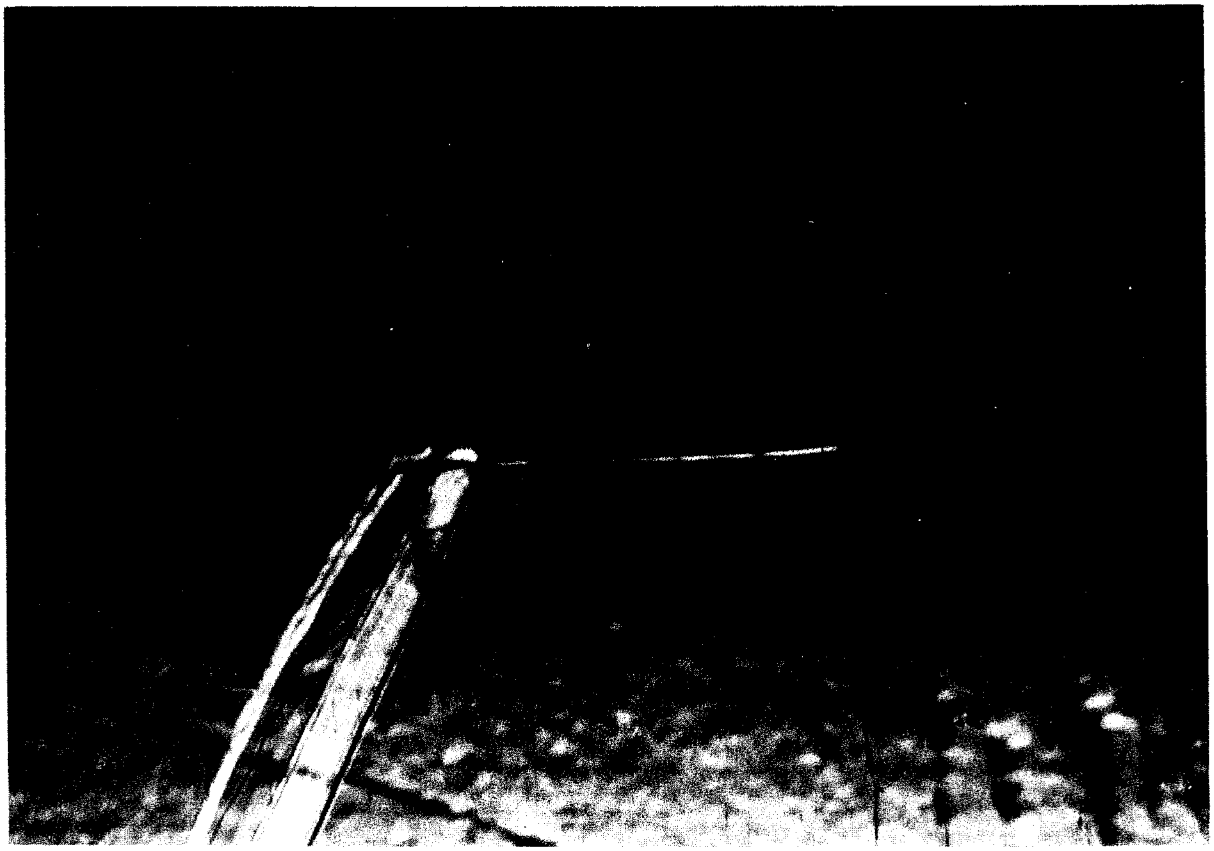
680X

HZ-26

1863A11

Parallel grain boundary - shows true boundary

Fig. 11



Orientation of groove - showing "step" between grains

Fig. 12