

Fig. 9—Structural changes in single-crystal bismuth after 50 pct completion of I-II transitions. (a) After 50 pct completion; (b) final structure in transformed region after repolishing. X100. Reduced approximately 42 pct for reproduction.

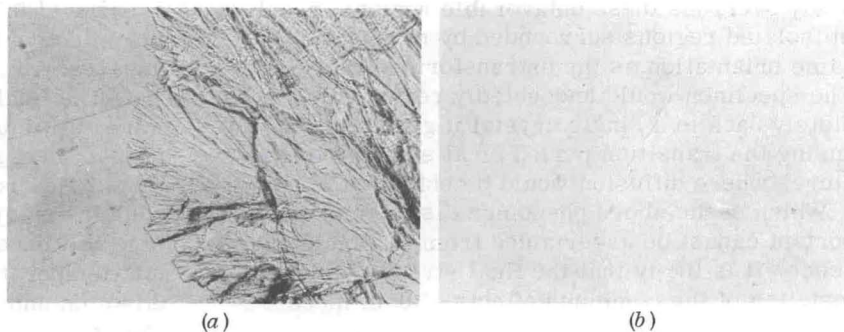
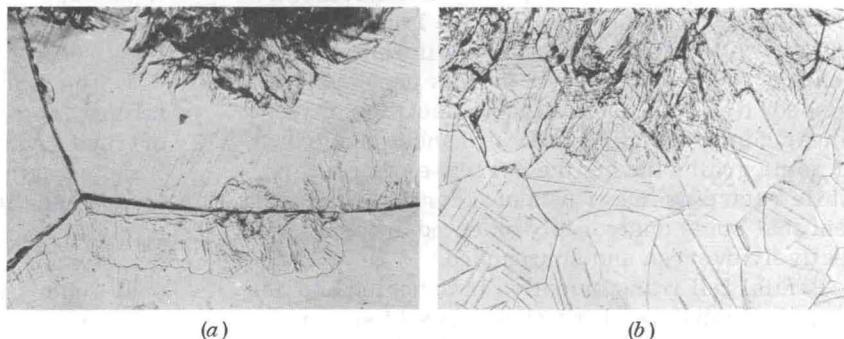


Fig. 10—Structural changes in polycrystalline bismuth after various stages of completion of I-II transition. (a) After 38 pct completion; (b) after 41 pct completion. X100. Reduced approximately 42 pct for reproduction.



to that of the residual structure after transition, required an annealing treatment of 220°C for 5 hr which resulted in ten to twenty grains intersecting an equivalent polished area as demonstrated in the original structure photomicrographs of Figs. 6 and 8.

Two factors that could contribute to the enhanced boundary migration are stored strain energy and preferential orientation of the structure as indicated by the difference in resistivity after pressurization. The stored strain energy arises from the fact that, just as increasing pressure progressively induces shear stresses in the grain boundaries of Phase I bismuth, so also will decreasing pressure once the material has transformed back from Phase II to I. Undoubtedly, substantial boundary migration and deformation occur progressively in Phase I reaching a maximum at atmospheric pressure. The available stored strain energy at atmospheric pressure due to this deformation could materially affect the rate of boundary migration.

A better understanding of how the transformations occur and the rather unusual residual structure can be gained from the examination of partially transformed specimens. For the purpose of obtaining partially transformed samples for examination, the I-II transition was interrupted after a certain percentage of voltage change, as indicated by the oscilloscopic recorder, by simply reducing the pressure by 100-atm increments. Partial transformation in a single-crystal sample is shown in Fig. 9.

Referring to (a) of Fig. 9, the boundary between the transformed and untransformed region is quite evident. The transformed region is typical of that observed in all cases for the I-II transition containing an image of the polycrystalline nature of Phase II. There is a small amount of slip in the untrans-

formed area, undoubtedly due to deformation induced by the volume change of the transformed portion of the sample. Photomicrograph (b), which is of the transformed area in the region of the initial transformed-untransformed boundary after repolishing, shows an interesting characteristic. The initial boundary is gone, and the only visible variation from the original single-crystal structure consists of a very few small isolated grains, one of which is shown in the center of the photomicrographs.

There appear to be at least two plausible explanations for this reversion back to near single-crystalline form and the presence of the isolated regions. First, substantial boundary migration occurs to reduce the progressively increasing shear stresses in the polycrystalline form of Phase I transformed from the Phase II region, as was previously described. The second possibility is that the untransformed Phase I region controls the direction of growth and possibly the orientation of the nuclei of Phase I transformed from Phase II, similar in effect to the growth of single crystals from a "seed" crystal. This is probably due, at least in part, to the large anisotropy of the linear compressibility of bismuth which, under pressure, could tend to enhance growth of nuclei similarly oriented to the untransformed volume and, due to the greater energy involved, retard the growth rate of those with a different orientation. This effect would be more prevalent in the region of the interface between the transformed and untransformed region. At a distance removed from the interface, nucleation and growth of unfavorably oriented material occur to a limited extent, as shown by the small isolated regions. However, the enhanced growth rate of the favorably oriented nuclei effec-



tively overruns these unfavorable regions, resulting in isolated regions surrounded by material of the same orientation as the untransformed region. The specimen would undoubtedly revert completely back to a single crystal if given enough time during the transition period or at elevated temperatures where diffusion would be enhanced.

Which of the above phenomena is the more important cannot be ascertained from available evidence. It is likely that the final structure is a manifestation of the combined effects of both mechanisms.

When the specimen completely transforms, as shown in Figs. 5 through 8, Phase I nucleates and grows from Phase II in many initially independent regions. However, as was previously discussed, it is felt that the high anisotropy of the linear compressibility again enhances the growth of some grains during the decrease of pressure, while retarding the growth of others to such an extent that some unfavorably oriented areas are effectively overrun and surrounded.

Partial I-II transformation in annealed and as-extruded polycrystalline structures is shown in Figs. 10(a) and 10(b), respectively. As can be noted, the original Phase I grain boundaries, including those along which severe anisotropy-induced deformation has occurred, do not appear to be preferential sites for Phase II nucleation. Although in photomicrograph (a) of this figure transformation appears to be associated with a Phase I boundary in one area, in another region it is independent. This lack of any significant dependency of the I-II transformation on Phase I boundaries is more clearly shown in (b) which bears out the insensitivity of the transition pressures and rate to initial structure. The formation of Phase III from II is even further removed from the original Phase I structure; thus one would not expect to encounter any structural sensitivity.

## CONCLUSIONS

1) The bismuth I-II and II-III transition pressure and transformation rate are structure-insensitive with respect to the presence of grain boundaries and associated localized plastic deformation.

2) The I-II and II-III transitions are completely isobaric for increasing hydrostatic pressures. The III-II also occurs isobarically but, at very slow pressurization rates, there is a tendency for the final stages of the II-I transition to extend over a narrow range of 200 to 300 atm.

3) Even under very slow pressurization rates consisting of 100-atm increments with 5-min stabilization periods, there is a measurable hysteresis in both the I-II and II-III transitions amounting to an

average of 0.71 and 0.55 k-atm, respectively. The magnitude of the hysteresis in the transitions increases with increasing pressurization rates.

4) The final structure is the same regardless of initial structure or whether the specimen had passed through the I-II or the I-II and II-III transitions. This residual structure is polycrystalline and contains many small isolated grains. This structure will become single crystalline as a result of a low-temperature short-time anneal that has little effect on unpressurized polycrystalline material. This enhancement of boundary migration is attributed, in part, to the release of stored elastic strain energy resulting from the anisotropy of the linear compressibility.

5) The formation of Phase II, which is polycrystalline, from Phase I occurs independently of any original grain boundaries. In the case of partial transformation, the orientation of Phase I formed from Phase II upon decreasing pressure is effectively the same as the original Phase I in the untransformed regions.

6) Under equilibrium, or near equilibrium, pressurization, there is a substantial waiting period at pressure before initiation of transformation. Under these conditions, the actual transitions will require up to several minutes for completion in a manner indicating a nucleation and growth-type transformation mechanism. Under faster pressurization rates, the transformation may be completed in as little as a few seconds.

## ACKNOWLEDGMENT

The assistance of Timothy Magila in the conduct of the experiments and sample preparation and of Messrs. D. P. Kendall and C. G. Homan in helpful discussions on instrumentation is gratefully acknowledged.

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