The Study of the Structural and Transformation Characteristics of the Pressure-Induced Polymorphs in Bismuth

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It is known from the early work of Bridgman that the two lowest-pressure transitions (I-II and II-III) are accompanied by substantial and abrupt changes in resistivity and volume. However, unlike the temperature-induced allotropic transformations observed in such elements as lithium, cobalt, tin, and so forth, there is little actually known about many of the characteristics of the pressure-induced transitions. This current work involves an examination of the structural and transformation characteristics of the bismuth I-II and II-III transitions under hydrostatic pressures. The relationship of initial structure to the transformation pressure, rate, resistivity change, and resultant structure is discussed. It is shown that the transition pressure and transformation rate are independent of the presence of grain boundaries and associated anisotropy-induced deformation. An observed hysteresis in both the I-II and II-III transitions is shown.

BISMUTH is one of the most interesting of the elements exhibiting pressure-induced polymorphs since it undergoes several allotropic transformations at pressures below 90,000 atm. It is known from the early work of Bridgman[1,2] that the two lowest-pressure transitions (I-II and II-III) are accompanied by substantial and abrupt changes in resistance and volume. However, unlike the temperature-induced allotropic transformations observed in such elements as lithium, cobalt, tin, and so forth, there is little actually known about many of the characteristics of these pressure-induced transitions. It is the purpose of this work to examine some of the structural and transformation characteristics of the bismuth I-II and II-III transitions under hydrostatic pressures.

Another interesting characteristic of bismuth is that, in its polycrystalline form, hydrostatic pressures of sufficient magnitude will induce severe progressive plastic deformation in the region of the grain boundaries.[3] This deformation, which has also been observed in several other metals, is attributed to the high degree of anisotropy in the linear compressibility of bismuth, resulting in shear stresses in the grain boundaries when it is exposed to hydrostatic pressure.

Most thermally induced allotropic transformations in metals, whether of the diffusionless athermal (martensitic) or isothermal nucleation and growth types, are dependent upon structure and prior history,[4] viz., grain boundaries, deformation, and so forth. One logically wonders then whether the transformation characteristics of the pressure-induced polymorphs in bismuth might also depend upon initial structure, particularly with respect to the presence of grain boundaries and associated plastic deformation.

In this investigation, the role of grain boundaries and plastic deformation on the characteristics of the bismuth I-II and II-III transitions will be established. The rather unique residual microstructural changes associated with these transitions will be presented and discussed. The occurrence of a measurable hysteresis in both the I-II and II-III transitions will be demonstrated. The type of transformation mechanism based on the observed transformation rate will be discussed.

EXPERIMENTAL PROCEDURE

A) Apparatus. The hydrostatic pressure system utilized in this investigation is similar to that previously reported by Bridgman[1] and Birch and Robertson,[5] and has been previously described.[3]

For the purpose of this work, the pressure medium utilized was a 1:1 mixture of pentane and isopentane. Pressure measurement was by means of a manganin coil in conjunction with a Foxboro Recorder. The manganin coil was mounted in the bottom closure and inserted inside the pressure cavity. Based on calibration against a controlled clearance piston gage at approximately 10,000 atm, the estimated error in the pressure measurement was ±2 pct. Assuming the nonlinearity in the pressure coefficient of resistivity between 10,000 and 28,000 atm to be not greater than 1 pct, then the estimated error in the range of the I-II and II-III transitions was ±3 pct.

B) Specimen Material and Preparation. The bismuth utilized throughout this investigation was of

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