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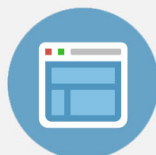
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Comparison of the Bismuth I-II Phase Transformations in Liquid and Solid High-Pressure Systems

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Bismuth specimens exposed to liquid and to solid pressure-transmitting media were examined simultaneously in a hydrostatic pressure system, and the measured initiation and equilibrium pressures of the I-II and II-I transitions were compared. The hydrostatic pressure-transmitting-medium was an equivolume mixture of normal- and iso-pentane, and the solid pressure transmitting media investigated were AgCl and Epoxy resin. Encapsulation by AgCl and Epoxy resin caused a lower I-II initiation pressure, but did not alter the equilibrium pressure. The bismuth I-II transition initiated near the equilibrium pressure in each of the solid pressure media. In the liquid pressure medium the equilibrium pressure was also found to be asymmetrically located toward the high-pressure side of the initiation pressure hysteresis. The region of indifference was 30 bar wide. The transformation behavior is explained in terms of the strain and kinetic dependences of solid-state nucleation. The solid pressure media accelerate the nucleation kinetics so that the transition initiates at the boundary of the strain hysteresis which is small for the forward transformation. For standard calibration of solid-media systems on increasing pressure, experimental justification is provided for the practice of calibrating the initiation of the I-II transition with the equilibrium pressure. The pressure of initiation is defined, and the importance of the pressurization rate is illustrated. Several common calibration methods used in solid-media systems are shown to be incorrect.

INTRODUCTION

There has been considerable interest and controversy relative to the calibrant polymorphic phase transitions of bismuth, thallium, barium, etc., particularly in regard to the type of high-pressure system used and the solid or liquid nature of the pressure-transmitting medium.¹⁻¹³ In some apparatus both the forward and the reverse transitions of a particular calibrant are measured; but in most apparatus, only the forward transition can be utilized for calibration. For the latter, particularly with solid pressure media, there is uncertainty with regard to the calibration pressure assigned to initiation of the forward transition. Originally, the equilibrium pressures of the high-pressure scale were used; however Jeffery *et al.*¹⁰ conclude that the initiation pressures as typically measured in solid-media apparatus are not equilibrium pressures. In order to place pressure calibration on a consistent basis, they recommend a higher pressure value, e. g., 26.2 kbar for bismuth I-II, be used to calibrate the forward transition on increasing pressure in solid-media pressure systems. Zeto and Vanfleet¹³ subsequently demonstrated the existence of a bismuth I-II nucleation barrier, and reported I-II initiation as close as 0.17 kbar above the equilibrium pressure. The nature of initiation-pressure hysteresis phenomena was interpreted according to the theory of nucleation in condensed systems, and they inferred that the equilibrium pressure of 25.5 kbar provides a

more accurate calibration of the initiation of this transition in solid-media systems.

The present investigation was undertaken for the purpose of simultaneously comparing the initiation and equilibrium characteristics of the bismuth I-II and II-I transitions for specimens encapsulated in solids with those directly exposed to a hydrostatic pressure-transmitting medium. The investigation was made possible by the development of a large-volume hydrostatic pressure cell, with a capability of 10 electrical leads exiting directly from the pressure chamber. Experiments were designed in which two identical bismuth specimens, one unencapsulated and the other encapsulated in a solid pressure-transmitting material, were simultaneously examined and compared by means of electrical resistance measurements in a hydrostatic pressure system.

EXPERIMENTAL

Identical samples of bismuth 99.999% pure, with dimensions 0.1 cm diam by 1.5 cm length from the Fitzpatrick Electric Supply Co., were used. Two experiments were conducted, each one utilizing a different solid medium to encapsulate a bismuth specimen for comparison of its transformation behavior with that of the sample exposed directly to the hydrostatic pressure medium. In the first experiment, the bismuth specimen was encapsulated in a cylinder of Epoxy resin 0.32 cm diam and 2 cm

length. In the second experiment, the bismuth specimen was encapsulated in a cylinder of AgCl of about the same dimensions. Copper leads were soldered to the bismuth and protruded from the Epoxy and AgCl encapsulating material. Pressures were obtained from the resistance change of a well-seasoned manganin coil. The resistance of the coil was measured with a Leeds and Northrup G-2 Mueller Bridge having a sensitivity of 0.1 m Ω , which corresponds to a pressure sensitivity of the order of 1 bar. Four-lead resistance measurements were made on each sample and on the manganin coil. In each experiment, the samples and manganin-coil pressure gauge were placed in a stainless-steel cell that contained an equivolume mixture of normal- and isopentane as the pressure-transmitting medium. The pressure cell was inserted in a pyrophyllite cube, and hydrostatic pressures were generated by compression in a 2000-ton hexahedral press. The system is described elsewhere.¹⁴

For any applied pressure, the hydrostatic pressure experienced by the unencapsulated sample was always the same pressure applied to the exterior surface of the solid encapsulant material. The enclosed bismuth specimen experienced only the pressure transmitted by the Epoxy resin or AgCl. The bismuth phase transitions in the unencapsulated and encapsulated specimens were detected independent of each other and irrespective of the manganin pressure gauge. The relative resistance (potential difference at constant current) of each sample was continuously and simultaneously recorded together with the pressure on a Brush Mark 240 four-channel recorder. In this manner, a direct comparison was obtained for the bismuth I-II and II-I transition pressures and transition rates between a specimen subjected to hydrostatic pressure and another subjected to a solid pressure-transmitting medium.

Since the sole purpose of the two experiments was to determine the influence of a solid pressure-transmitting medium on the bismuth phase transitions, the usual two-point pressure calibration of the manganin coil was unnecessary. The manganin coil was utilized for relative pressures only, and the absence of pressure hysteresis of the manganin resistance is well known. For the pressure scales in Figs. 1 and 2, the manganin coil in each experiment was calibrated at the center of the region of indifference of the unencapsulated sample using the values¹⁵ 25.499 kbar for the equilibrium pressure at 25 °C with $dP/dT = -54.5$ bar/°C. The first experiment was run at 19 °C, and the second at 23.5 °C. This expediency has no bearing on our conclusions since they are based on relative pressures and on an independent and simultaneous comparison of identical samples simultaneously exposed

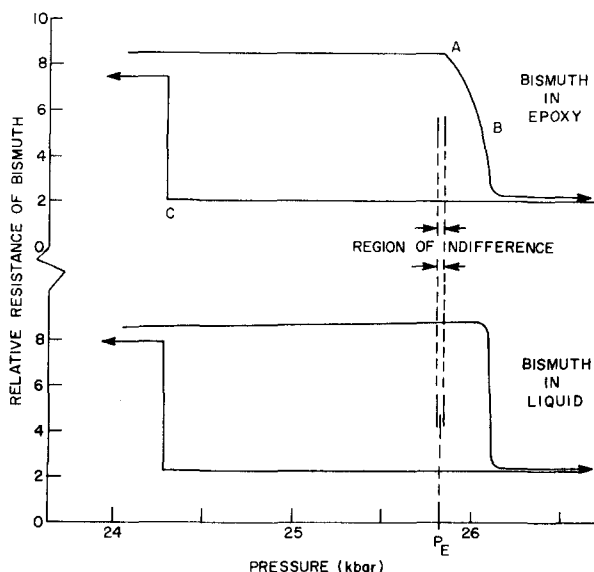


FIG. 1. Simultaneous tracings of the initiation-pressure hysteresis of the bismuth I-II point at 19 °C for Epoxy encapsulated (top) and unencapsulated (bottom) samples in a hydrostatic pressure-transmitting medium. The pressure axis is based on the resistance change of manganin calibrated with the equilibrium pressure P_E of the unencapsulated sample. The equilibrium pressure of each sample was independently detected by the reversal of electrical resistance across the region of indifference, which occurred at the same manganin values for each sample.

to different pressure media at the same conditions of pressure and temperature.

The samples were pressure cycled several times at a constant pressurization rate to determine the initiation pressures of the bismuth I-II and II-I transitions, i. e., the sample hysteresis. The pressurization rate varied only in the range 5-25 bar/min from cycle to cycle. No attempt was made to study the transformation behavior with respect to the pressurization rate. In pressure cycling, the pressure was increased well beyond the II-III transition and was decreased to ~ 5 kbar below the I-II equilibrium pressure. This procedure was followed to insure that only a single-phase component was present in the sample at the initiation of the I-II and II-I transitions. The initiation pressures were taken as the pressure at which the resistance of the sample showed the first change toward lower or higher values, respectively. The region of indifference was measured on each sample after the manner of Bridgman.¹⁶ Pressure was first adjusted so that no rate of transformation between phase I and phase II was detected when nearly equal amounts of the two phases were present in a sample. From this starting point, the region of indifference was measured as the pressure interval necessary to

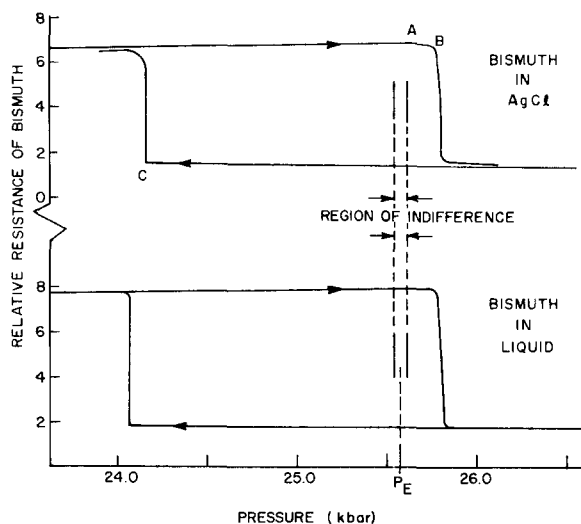


FIG. 2. Simultaneous tracings of the initiation-pressure hysteresis of the bismuth I-II point at 23.5°C for AgCl encapsulated (top) and unencapsulated (bottom) samples in a hydrostatic pressure-transmitting medium. The pressure axis is based on the resistance change of manganin calibrated with the equilibrium pressure P_E of the unencapsulated sample. The equilibrium pressure of each sample was independently detected by the reversal of electrical resistance across the region of indifference, which occurred at the same manganin values for each sample.

cause the transformations to run in opposite directions. The observation of a transformation corresponded to the detection of a transformation rate of $10^{-4}\%$ /sec with the sensitivity employed. The midpoint of the region of indifference was taken as the equilibrium pressure.

RESULTS AND DISCUSSIONS

Figure 1 shows the comparison of the initiation and equilibrium pressures between a sample encapsulated in the Epoxy-resin solid pressure-transmitting medium, and an unencapsulated sample subjected to the hydrostatic pentane medium. The results of the second run, Fig. 2, show the similar comparison for the bismuth I-II and II-I transitions between the sample encapsulated in AgCl and the sample subjected to the pentane mixture. In the vicinity of the forward and reverse transitions, the samples were pressurized at a constant rate of about 15 bar/min. For Fig. 1, the region of indifference was about 30 bar wide for the unencapsulated sample, and about 40 bar wide for the sample encapsulated in Epoxy resin. A less precise determination of about 80 bar was made for the region of indifference of each sample in the second run. The center of the region of indifference was the same within 10 bar

between the encapsulated and unencapsulated samples in each experiment. The initiation of the I-II transition in Epoxy resin was detected near the upper boundary of the region of indifference, i. e., about 20 bar above the equilibrium pressure. The initiation of the I-II transition in AgCl was detected about 60 bar above the equilibrium pressure. For the unencapsulated samples under hydrostatic pressure, initiation of the bismuth I-II transition was observed between 150–300 bar above the equilibrium pressure. Several pressure cycles were made in each experiment, and the simultaneous strip-chart recordings unequivocally evidence the fact that the I-II transition initiated first in the samples encapsulated in the solid pressure media.

The encapsulated samples were closely examined under magnifications ranging from 7 \times to 30 \times after removal from the press. The Epoxy encapsulated sample showed what appeared to be several very fine fault lines along the length of the cylindrical surface. These fault lines were not open cracks nor did they appear to have impaired the encapsulation in any way. It is assumed that these lines were caused by rapid compression of the Epoxy resulting from the large volume changes at the bismuth phase transitions. No visible sign of deformation was observed for the AgCl encapsulated specimen. The possibility of the pentane mixture leaking in and around the bismuth in the encapsulated specimens was ruled out, for had this been the case the transformation characteristics would correspond to those of the unencapsulated specimens. Furthermore, if partial leakage occurred around the encapsulated specimens initially, one would expect severe deterioration of the leakage condition due to pressure cycling and a resulting change in the bismuth phase-transition characteristics from cycle to cycle. This was not observed as the characteristics of the bismuth I-II transition were very consistent over three pressure cycles.

The data represented in Figs. 1 and 2 reveal that the bismuth I-II transition on increasing pressure initiated in the encapsulated samples at or near the region of indifference. This behavior provides experimental justification for the practice of assigning the equilibrium pressure to the initiation of the I-II transformation in solid-media systems. Conversely, the data are not in agreement with the conclusion of Jeffery *et al.*¹⁰ who state that the I-II transition takes place at a significantly higher pressure than the equilibrium pressure in solid-media systems. Accordingly, the procedure of using 26.2 kbar to calibrate the initiation of the bismuth I-II transformation is not correct. The asymmetrical location of the equilibrium pressure between the initiation pressures is also in direct contrast to the practice of assigning the equilib-

rium pressure to the center of the initiation pressure hysteresis. For the unencapsulated samples, the equilibrium pressure was about 15–20% from the high-pressure side of the initiation-pressure interval. For the encapsulated samples, the equilibrium pressure was even closer to the bismuth I-II transformation. With solid-media systems in which the region of indifference cannot be measured in the usual manner over a small pressure interval, the initiation of the bismuth I-II transition provides the best representation of the equilibrium pressure.

The transformation curves in Figs. 1 and 2 for the encapsulated samples showed a decrease in resistance initiating at or near the high-pressure side of the region of indifference A. At B, the resistance decreased sharply to completion with increasing pressure. In the interval AB, the pressure coefficient of transformation was about 0.23%/bar for the Epoxy-resin encapsulated sample, $10^{-4}\%$ /bar for the AgCl encapsulated sample, and undetectable for the samples in pentane. At point B for increasing pressure, the coefficient increased to about 2%/bar for all samples to completion. Initiation of the II-I transition did not occur close to the equilibrium pressure in any sample, nor was a two-stage transformation curve observed. An increase in the electrical resistance was not observed in the pressure interval AC on decreasing pressure until point C was reached, and then an extremely abrupt transition was detected. Completion of the bismuth II-I transition was less abrupt for the encapsulated samples, even though this behavior is not discernible from the reduced data in Figs. 1 and 2.

All of the present results can be explained by the interpretation of hysteresis phenomena presented previously in terms of the strain and kinetic dependences of nucleation.¹³ A plausible explanation of the I-II behavior is that the kinetics of nucleation dominated over the pressure interval AB; whereas, at point B, the kinetics of growth became dominant due to overdriving the transitions with pressure. The effect of the solid-media material was to create lower-energy nucleation sites and to accelerate the nucleation kinetics so that the I-II transformation initiated at the upper boundary of the real strain hysteresis. Conditions that increase the number of nucleation sites in the lattice, such as strain, impurity, microstructure, size, shape, etc., increase the nucleation rate at a constant pressure/temperature. The initiation of the II-I transition at pressures appreciably away from the equilibrium pressure is attributed to the nucleus/matrix strain energy that arises from the volume change on nucleation. The data in Figs. 1 and 2 demonstrate that the I-II initia-

tion pressure is governed primarily by the nucleation kinetics, whereas, the II-I initiation pressure is governed primarily by the strain energy associated with the elastic free-energy change of nucleation. The fact that the real initiation-pressure strain hysteresis is virtually one sided shows that the nucleus/matrix strain energy is very small for the I-II transformation. For II-I initiation, it is necessary to lower pressure below equilibrium until the nucleus/matrix strain energy is surmounted by the Gibbs volume free-energy difference. The required underpressurization of about 1.4 kbar is large, so that once nuclei are formed the growth rate becomes very rapid to complete the transformation. The region of indifference is a much smaller pressure interval than the initiation-pressure hysteresis since the former represents transformation reversal with both phases present in the sample, and thus the strain and kinetic barriers associated with nucleation are absent.¹³

The width of the initiation pressure interval was about 1.7 kbar for the unencapsulated samples with a 0.5-kbar variation on the low-pressure side from cycle to cycle. For the encapsulated samples, the width of the initiation hysteresis was about the same in AgCl and was about 0.3 kbar less in Epoxy resin. This behavior is in variance to the suggestion that the width of the initiation hysteresis would be larger for a sample subjected to a nonhydrostatic pressure-transmitting medium vs a sample exposed to hydrostatic pressure.¹⁰ No significance is attached to the absolute value of the initiation-pressure hysteresis. This interval is variable with respect to the nature of the sample, the pressure cycle, the pressurization rate, and the pressure medium. With approximately the same pressurization rate and the same type sample, the width of the initiation hysteresis was only about 0.77 kbar when the II-III transitions were not included in the pressure cycle.¹³ This was probably due to the effect of the pressure treatment on microstructure and nucleation sites. With samples 0.41 cm diam by 0.57 cm length and with approximately the same pressure cycle and pressurization rate, the initiation hysteresis varied between 0.56 and 0.91 kbar.¹² These smaller hysteresis values are attributed to sample size or, more precisely, the larger volume-to-surface ratio which was about 0.75 mm compared to 0.24 mm in the present study. For larger ratios, there is a higher probability of having low-energy nucleation sites due to anisotropic compression and a larger bulk sample. Samples that are otherwise identical would thereby exhibit faster initiation of the transitions and consequently smaller initiation-pressure hysteresis.

A somewhat similar encapsulation experiment was performed by Corll¹⁷ on a polycrystalline material that undergoes a ferroelectric-to-antiferroelectric transformation at about 2.76 kbar. An Epoxy encapsulated sample transformed before an unencapsulated sample on increasing pressure. This behavior was attributed to pressure enhancement within the encapsulated sample after the theoretical treatment presented earlier by Corll and Warren.¹⁸ Pressure enhancement due to encapsulation cannot explain the lower I-II initiation pressures shown in Figs. 1 and 2. For these data the equilibrium pressure serves as the basis for comparing the initiation behavior of encapsulated and unencapsulated samples, and the equilibrium pressure is thermodynamically invariant with respect to the pressure-transmitting medium at constant temperature. Also, at the equilibrium pressure our experimental technique yields an independent measurement and direct comparison of (a) the transmitted pressure on the encapsulated sample and (b) the hydrostatic pressure on the encapsulating medium. The equilibrium pressure in the encapsulated samples is detected by the reversal of electrical resistance of the sample across the region of indifference. The resistance of the manganin gauge is measured simultaneously, and the hydrostatic pressure on the encapsulating medium is obtained from the resistance of the manganin gauge calibrated with the equilibrium pressure of the unencapsulated sample. The experimental results are therefore unambiguous and incontrovertible—the equilibrium pressure was unchanged by the encapsulation, and thus the forward transformation initiated in the encapsulated samples at a lower *sample* pressure than in the unencapsulated samples. Thus for the Epoxy experiment, where bismuth is probably less compressible than the encapsulating medium, any pressure enhancement was immeasurable. For the AgCl experiment, where bismuth is more compressible than the encapsulating medium, a pressure deficiency rather than a pressure intensification should obtain at the encapsulated sample. In this case, the effect of encapsulation is towards causing a higher rather than a lower hydrostatic pressure for initiation of the transformation. Pressure alteration by encapsulation, therefore, cannot explain the present results. Rather, the lower initiation pressures of the bismuth I-II transition in the encapsulated samples are explained satisfactorily by the acceleration of nucleation kinetics by the encapsulating medium. Corll's encapsulation experiment appears inconclusive to us since equilibrium pressures were not measured, initiation of a transformation can be altered by means other than pressure (such as nucleation kinetics or shear stress), the Curie points of polycrystalline materi-

als are very sensitive to shear, and the extremely rapid pumping rate of about 55 bar/sec introduces an effect of temperature due to compression. The experimental technique employed in the present investigation accounts for these factors.

CONCLUSIONS

It is demonstrated that the bismuth I-II transition initiates near the equilibrium pressure in AgCl and Epoxy-resin solid pressure-transmitting media. Encapsulation by each of these solid media lowers the I-II initiation pressure, but does not alter the equilibrium pressure. The region of indifference is about 30 bar wide and is asymmetrically located toward the high-pressure side of the initiation-pressure hysteresis, even in hydrostatic pressure media. The transformation behavior is consistent with a thermally activated nucleation and growth mechanism in which the solid-media material accelerates the nucleation kinetics and induces initiation of the bismuth I-II transition at the boundary of the strain hysteresis of initiation, which for this transition is near the equilibrium pressure. For standard calibration of solid-media systems on increasing pressure, it is concluded that the equilibrium pressure should be employed to calibrate the initiation of the bismuth I-II transition. For accurate pressure calibration in this manner, it is concluded that the initiation pressure should be defined as the pressure at which the resistance of the sample first shows a change in slope toward lower resistance, and that small loading increments and pressurization rates should be utilized.

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