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THE THALLIUM-INDIUM PHASE DIAGRAM AS A
FUNCTION OF COMPOSITION, TEMPERATURE, AND PRESSURE* †

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ABSTRACT

The thallium-rich region of the thallium-indium phase diagram was determined from atmospheric pressure to 5.5 kbars primarily from electrical resistivity data obtained as a function of composition, temperature, and pressure. Corroborative x-ray diffraction data were taken at atmospheric pressure. Extrapolation of the results of this investigation to high pressures indicates that a triple point occurs between three solid allotropes of thallium at 162°C and 35.8 kbars. The high pressure phase was found to be continuous with the f.c.c. phase observed at atmospheric pressure for thallium containing 40-77 at.% indium. This result indicates that the crystal structure of the high pressure allotrope of

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thallium is f.c.c. The remaining two phases in equilibrium at the triple point are continuous with the h.c.p. low temperature phase and the b.c.c. high temperature phase observed for pure thallium at atmospheric pressure. A revised phase diagram for the thallium-indium system at atmospheric pressure is also proposed.

INTRODUCTION

Crystalline thallium is known to exhibit a phase transformation⁽¹⁾ from h.c.p. to b.c.c. at $\sim 234^{\circ}\text{C}$ at atmospheric pressure. Bridgman⁽²⁾ has investigated the allotropic behavior of thallium as a function of pressure as well as temperature and has found that an additional allotrope of unknown structure occurs at pressures in excess of 40 kbars. Bridgman's more recent work⁽³⁾ on thallium-indium alloys suggests that arguments based upon the continuity of phase fields in the temperature-composition-pressure diagram of the thallium-indium system might be used to deduce the structure of the high pressure allotrope of thallium. Indeed, Bridgman's results combined with the tentative temperature-composition diagram⁽⁴⁾ for atmospheric pressure indicate that the high pressure allotrope is probably f.c.c. This conclusion is, however,

uncertain because details of the phase relationships in the thallium-rich portion of the temperature-composition diagram are incompletely known and because the inherent hysteresis in Bridgman's measurements makes it difficult to determine the degree of compatibility between Bridgman's data and the temperature-composition diagram. On this basis the present investigation was undertaken to examine the temperature-composition-pressure diagram of the thallium-indium system.

EXPERIMENTAL PROCEDURE

Alloys were prepared from thallium and indium which were obtained respectively from the American Smelting and Refining Company and from Consolidated Mining and Smelting Company of Canada. The majority of the measurements were made on material which was specified by the manufacturers to exceed 99.999% purity. A few preliminary measurements were made, however, on thallium with a lower purity of 99.9%. The only significant difference which was observed was that the h.c.p.-b.c.c. transformation occurred in the 99.9% thallium approximately 2°C lower than in the 99.999% thallium.

Alloys were cast either under helium or under vacuum in Pyrex crucibles which had been coated with colloidal graphite

(Aquadag) to facilitate removal of the alloy. Molten alloys were agitated to ensure mixing and then quenched. Further homogenization was achieved by fabricating the cast alloys into rods which were subsequently cut into small segments; these segments were then mixed and recast. Chemical analyses of several alloys indicated that the average compositions of the castings were within 0.02 wt.% of the nominal compositions. However, chemical analyses of sections of wires, which were produced for electrical measurements by swaging of the castings, indicated that random deviations of ± 0.1 wt.% from the nominal compositions occurred along the length of the wires.

Electrical resistivity measurements were used in combination with x-ray diffraction techniques to examine the phase relationships in the temperature-composition diagram at atmospheric pressure. Diffraction patterns for the determination of precision lattice parameters were obtained with a symmetrical back-reflection focusing camera. Precision lattice constants of the cubic phases were determined by extrapolating the lattice constant calculated from each reflection against the Nelson-Riley⁽⁵⁾ function while precision lattice constants for the hexagonal and tetragonal phases were computed with Cohen's least squares technique⁽⁶⁾. Lattice constants from

several patterns of the same alloy were reproducible to within $0.0005\overset{0}{\text{\AA}}$, and the lattice constants in the results section are average values. The samples were in all cases well annealed, and in the eutectoid region, where the transformations are somewhat sluggish, samples were equilibrated for several weeks at room temperature before being used for the x-ray measurements. Diffraction patterns for the identification of phases at elevated temperatures were taken with a modified diffractometer⁽⁷⁾.

Relative electrical resistivity measurements were made by standard D.C. techniques. Wire specimens approximately one millimeter in diameter and one meter long were employed. Temperature was controlled by an electrically heated silicone oil bath. Temperatures were measured with a calibrated mercury thermometer. Thermal gradients were minimized by continually stirring the oil. The positions of the phase boundaries were determined from the temperatures at which changes in slopes and/or discontinuities occurred in plots of resistance versus temperature.

For pressure measurements, the resistivity samples were placed in a beryllium-copper pressure cell. In this case temperature was measured with a calibrated thermocouple which was in direct contact with the sample. Pressure was supplied by means of an intensifier which was purchased from the Harwood Engineering Company, and pressure was measured with a manganin pressure gauge which had previously been checked against a Heise gauge. The precision of the pressure determinations was approximately ± 10 bars.

Since partial melting of a sample occurs at the solidus temperature, a special sample holder was constructed so that the same sample could be used to determine the solidus temperature at several different pressures. This holder consisted of a grooved Teflon form upon which the sample wire was wound. This Teflon form was coated with Wards Bio-Plastic and then placed in a close-fitting Teflon sleeve. This sample holder maintained the sample geometry sufficiently well so that an open circuit did not develop during partial melting.

TEMPERATURE-COMPOSITION DIAGRAM AT ATMOSPHERIC PRESSURE

The measured lattice constants and c/a ratios of alloys in the face-centered tetragonal (f.c.t.) indium-rich phase

are shown in Fig. 1 together with values found by Guttman⁽⁸⁾ and by Raynor and Graham⁽⁹⁾. The results of this investigation agree with the latter two investigations in that a discontinuous transition between the f.c.t. and f.c.c. phases was observed. This statement is based on the fact that the plot of $\underline{c}/\underline{a}$ versus composition in Fig. 1 shows that the ratio still exceeds unity at the terminus of the f.c.t. phase. The position of the terminus was established by resistance measurements and its position is in agreement with the results of previous investigations^(8,9,10).

The lattice constants of the f.c.c. intermediate phase for alloys in both the f.c.c. region and the f.c.c.-b.c.c. two-phase region are shown in Fig. 2. The present results indicate 59.9 at.% thallium as the position of the f.c.c./(f.c.c.+ b.c.c.) boundary at room temperature. This agrees well with the value of 59.2 at.% thallium reported by Guttman.

The values of $\underline{a}$, $\underline{c}$ and $\underline{c}/\underline{a}$ found at room temperature for pure h.c.p. thallium were respectively 3.4573 Å, 5.5266 Å, and 1.5985. For these three quantities Lipson and Stokes⁽¹¹⁾ obtained 3.4566 Å, 5.5248 Å, and 1.5984. Values of $\underline{a}$ and of $\underline{c}/\underline{a}$ as a function of indium concentration are shown in Fig. 3. The $\underline{c}$ parameter of the h.c.p. phase was found to be relatively

insensitive to indium concentration with additions of up to 11.4 at.% indium decreasing the value by only 0.0008 Å. Thus as indium is added to thallium, both the decrease in volume and the increase in the c/a ratio are due almost entirely to the decrease in the a parameter.

Values of the volume per atom as a function of composition were calculated from the measured lattice parameters. These values are plotted together with other available data in Fig. 4. The solid line in Fig. 4 represents the volume per atom that should be expected if ΔV of mixing were identically zero. Bridgman⁽³⁾ has determined the densities of 15 thallium-indium alloys and while his data are inadequate to yield precise values for ΔV of mixing, nonetheless they do give an upper limit for ΔV comparable to the values indicated in Fig. 4. Thus thallium-indium solid solutions are very nearly ideal with respect to volume at room temperature.

The proposed temperature-composition diagram is shown in Fig. 5. The construction of the diagram considers the results of Valentiner⁽¹²⁾, Guttman⁽⁸⁾, and Moore et al.⁽¹⁰⁾ along with the present measurements. The general features of the present diagram agree with the tentative diagram proposed by Hansen⁽⁴⁾

but the uncertainty in the delineation of the phase boundaries in the thallium-rich portion of the diagram is considerably reduced. A major shift from 24.0 to 17.5 at.% indium is indicated for the eutectoid composition while less pronounced shifts from 14.5 to 12.5 at.% and from 43 to 47 at.% are indicated for the thallium-rich termini, respectively, of the lines which show the eutectoid reaction and the peritectic reaction.

The data points which are shown in Fig. 5 show that the construction of the phase diagram was quite straightforward. However, the delineation of the boundaries of the h.c.p.-b.c.c. two-phase field does merit some discussion. Equilibration in the h.c.p.-b.c.c. two-phase region is precluded at normal heating and cooling rates because the diffusion rate at the temperatures in question is quite small. Thus it should be expected that the h.c.p. phase would persist during heating until the upper boundary of the two-phase region was crossed and conversely the b.c.c. phase would persist during cooling until the lower boundary of the two-phase region was crossed. Experimentally it was observed that in the alloys only a single, nearly isothermal transformation occurred during either heating or cooling with the transition temperature

being invariably higher during heating than during cooling. The amount of deviation from isothermal behavior is explicable on the basis of the previously noted ± 0.1 wt.% inhomogeneities and subsequent measurements on shorter and more homogeneous wire samples have shown that the transitions are indeed isothermal. Thus the observed behavior is such that the transitions during heating can be taken to represent the upper boundary of the two-phase region while the transitions during cooling can be taken to represent the lower boundary.

The transitions in this region were examined with heating and cooling rates varying between 0.01 and 40°C/min., and in no case was the transition temperature found to be rate dependent during heating. The transition temperature during cooling was also found to be independent of rate for the thallium-rich alloys but some supercooling at higher cooling rates was observed in alloys with higher indium content. The severity of the supercooling increased both with increasing indium content and with increasing cooling rate. Only those points which were reproducible at more than one cooling rate were used for delineating the position of the lower boundary of the h.c.p.-b.c.c. two-phase region in Fig. 5.

Additional justification and corroboration for drawing

the boundaries of the h.c.p.-b.c.c. two-phase region as shown in Fig. 5 can be made by calculating the enthalpy associated with the solid state transition in pure thallium from the relationship for dilute solutions⁽¹³⁾,

$$\Delta H_t = \frac{RT_t^2 (N_{\text{In}}^{\text{BCC}} - N_{\text{In}}^{\text{HCP}})}{T_t - T} \quad (1)$$

where R is the gas constant, T_t is the transition temperature of pure thallium, and $N_{\text{In}}^{\text{HCP}}$ and $N_{\text{In}}^{\text{BCC}}$ are respectively the mole fractions of indium in the h.c.p. and b.c.c. phases in the two-phase region at the temperature T . In the limiting region where $N_{\text{In}}^{\text{HCP}}$ and $N_{\text{In}}^{\text{BCC}}$ are both linear functions of temperature, the calculated value is 95 cal/mole which is in excellent agreement with the currently accepted value^(14,15) of 90 cal/mole. A similar calculation for the enthalpy of fusion from the limiting slopes of the liquidus and solidus lines gives 820 cal/mole for pure thallium which compares well with the tabulated value^(14,15) of 1020 cal/mole.

THE EFFECT OF PRESSURE ON THE THALLIUM-INDIUM PHASE DIAGRAM

The complete temperature-composition-pressure diagram was not determined. Rather measurements were made of the effect of pressure on those features of the temperature-

composition diagram which were relevant to deducing the crystallographic structure of the high-pressure allotrope of pure thallium, and as a result a temperature-composition-pressure diagram for the thallium-rich portion of the thallium-indium system is proposed. Experimental data were measured in 5.5 kbars to determine electrical resistivity as a function of temperature and pressure at fixed composition.

The temperature, T_U , of the upper boundary of the h.c.p.-b.c.c. two-phase region was determined with alloys containing 3.32, 6.37, 8.74, and 11.36 at.% indium. Statistical interpretation of the data by the method of least squares with linear relationships leads to the following expression,

$$dT_U/dP = - (2.03 \pm 0.04) - (17.1 \pm 0.5) N_{In}, \quad (2)$$

where T_U is in $^{\circ}\text{C}$, P is in kbars, and N_{In} is the mole fraction of indium. The intercept of equation (2) lies between the values for pure thallium of $-1.96^{\circ}\text{C}/\text{kbar}$ found by Bridgman⁽²⁾ and $-2.11^{\circ}\text{C}/\text{kbar}$ found by Werner⁽¹⁶⁾; thus measurements on alloys extrapolate to a value for pure thallium which is consistent with independently determined values. Integration of equation (2), with the temperature-composition data at atmospheric pressure serving to define the constants of

integration, gives an expression,

$$T_U = 234 - (1.2 \times 10^3) N_{In} - (2.03 + 17.1 N_{In}) P, \quad (3)$$

which defines the surface representing the upper boundary of the h.c.p.-b.c.c. two-phase region.

The effect of pressure on the eutectoid temperature, T_E , was determined from measurements made on an alloy containing 28.16 at.% indium. A linear representation of the results is

$$T_E = 30 + 3.69 P. \quad (4)$$

Equations (3) and (4) show that as pressure increases the eutectoid temperature increases while the temperature of the upper boundary of the h.c.p.-b.c.c. two-phase region decreases with a concomitant decrease of the indium content at the eutectoid point. Extrapolation of these results to higher pressure indicates that a triple point might be expected in pure thallium at 162°C and 35.8 kbars. While this is a large range for extrapolation, the agreement with the triple point at 153°C and 38.3 kbars reported by Bridgman⁽²⁾ is excellent, and the discrepancy could easily be eliminated with a very minor amount of curvature in the extrapolation. Thus it may be concluded that these phase boundaries are not interrupted nor discontinuous with pressure.

Further, the variation of the temperature of the solid

/(liquid + solid) phase boundary with pressure was determined for alloys containing 43.16, 44.59, 57.24, 61.72, and 64.96 at.% indium. Within the precision of these data an elevation of 4.9°C/kbar occurs for both the line representing the peritectic reaction and the adjacent portions of the solidus line. While these data are inadequate for precise evaluation of the peritectic composition and the composition of the thallium-rich terminus of the peritectic reaction as functions of pressure, the constant slope found for all of the alloys indicates that these compositions are relatively insensitive to pressure.

The foregoing data, together with linear extrapolations to the triple point of the termini of the line representing the eutectoid reaction at atmospheric pressure and with the melting point data as a function of pressure for pure thallium determined by Butuzow et al.⁽¹⁷⁾, were used to construct a temperature-composition-pressure diagram for the thallium-rich portion of the thallium-indium system. Representative isobaric sections are shown in Fig. 6. Corroboration of this proposed diagram is shown in Fig. 7 where the experimental transition points at room temperature reported by Bridgman⁽³⁾ for thallium-indium alloys and by Kennedy and LaMori⁽¹⁸⁾ and by Boyd and England⁽¹⁹⁾ for pure thallium are shown in an isothermal section

together with a projection of the proposed eutectoid surface. It is evident from Figs. 6 and 7 that the f.c.c. phase which occurs between 40 and 77 at.% indium at room temperature and atmospheric pressure is continuous with the high pressure phase of pure thallium. Thus it may be concluded that the crystal structure of the high pressure allotrope of pure thallium is f.c.c.

DISCUSSION

Lumsden⁽²⁰⁾ has used available thermodynamic data to derive expressions for the differences in free energy at atmospheric pressure among h.c.p., b.c.c., and f.c.c. thallium. His expressions indicate that the free energy balance among the three allotropes is delicate, and the reports of the appearance of the f.c.c. allotrope at atmospheric pressure by Sekito⁽²¹⁾ and Schneider and Heymer⁽²²⁾ substantiate this. It is probable that these two observations occurred because of stabilization by minor amounts of contaminants. However, quenching, even at extreme rates of up to $8100^{\circ}\text{C}/\text{sec}$, is reported⁽²³⁾ not to affect the normal allotropic behavior of high purity thallium at atmospheric pressure.

Kaufman⁽²⁴⁾ has used Lumsden's relationships together with additional approximations in a calculation of the effect of pressure on the phase transformations in thallium. His calculation gives the right order of magnitude for the pressure associated with the allotropic transition at room temperature. Further, the calculation is in agreement with the present results in that the high pressure allotrope is indicated to be f.c.c.

Subsequent to the completion of the present experimental investigation Piermarini and Weir⁽²⁵⁾ have published, in agreement with the present results, that x-ray powder patterns of thallium at 60 kbars were indexed on the basis of a f.c.c. unit cell.

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- Figure 1. Lattice constants and c/a ratio of f.c.t. indium versus thallium concentration.
- Figure 2. Lattice constants of the thallium-indium intermediate f.c.c. phase versus thallium concentration.
- Figure 3. a lattice constant and c/a ratio of h.c.p. thallium-indium alloys versus thallium concentration.
- Figure 4. Volume per atom of thallium-indium alloys versus thallium concentration.
- Figure 5. Proposed thallium-indium phase diagram at atmospheric pressure.
- Figure 6. Isobaric sections of the thallium-rich region of the proposed thallium-indium phase diagram. The sections shown for atmospheric pressure and 5 kbars are based on experimental results while the sections shown for 30 and 40 kbars were obtained by extrapolation of the observed pressure dependence.
- Figure 7. Room temperature isothermal section of the proposed thallium-indium phase diagram. The symbols denoting the transformation pressures observed by Bridgman have the following meanings: 0-pressure-volume measurements made with increasing pressure, x-resistivity measurements made with increasing pressure, Δ -pressure-volume measurements made with decreasing pressure, $\dagger$ -resistivity measurements made with decreasing pressure.

Figure 1. Lattice constants and $\underline{c}/\underline{a}$ ratio of f.c.t. indium versus thallium concentration.

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Figure 7

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