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Measurement of the Melting Temperature of Aluminum and Copper at Pressures up to 18000 kg/cm^2

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Until recently our information on the effect of superhigh pressure on the melting temperature of metals was limited to the data of Bridgman /1, 2/ who studied the melting of certain low-melting metals (potassium, sodium, lithium, rubidium and cesium, lead and gallium) at pressures up to 12000 kg/cm^2 and of bismuth at pressures up to 17000 kg/cm^2.

Since 1953 investigations of phase transformations of metals under conditions of superhigh pressure have been conducted in the Institute for Crystallography of the Academy of Sciences SSSR. The procedure worked out for obtaining and measuring a high temperature inside the channel of a high-pressure vessel has made it possible to widen the temperature interval in studies of the melting of metals under superhigh pressure /3/. Measurements have been made of the melting temperature of tin and lead up to a pressure of 34000 kg/cm^2 /4/, of antimony, cadmium, zinc, and tallium at a pressure up to 30000 kg/cm^2 /5/, and of bismuth up to a pressure of 30000 kg/cm^2 /6/. The measurements indicated were made with specimens of metals placed in a heated crucible in a medium of isopentane in the channel of the high-pressure multiplier. The melting temperatures of the metals enumerated above, with the exception of bismuth, gallium, and antimony, rise with an increase of pressure. In the case of bismuth and gallium the melting temperatures drop only to the ternary point: α-phase - β-phase - melt. In the case of antimony the reduction of the melting temperature was observed over the entire interval of pressures studied.

In 1955 were published measurements of the melting temperature of germanium at pressures up to 180000 kg/cm^2 which were ~~conducted~~ evidently made in an apparatus for the synthesis of ~~diamond~~ diamonds /7/. The germanium specimen was placed in a graphite cylinder which ~~was at the same time~~ at the same time served as the heating element. The pressure was determined by means of a calibrated curve constructed on the basis of points of polymorphous transformations of bismuth, tallium, cesium, and barium. The temperature was measured by a platinum-platinorhodium thermocouple. It was found that the melting temperature of germanium decreased over the entire pressure interval.

Experimental Part

In the present work are presented the results of the measurement of melting temperatures of aluminum and copper at pressures up to 18000 kg/cm^2. It is difficult to obtain a temperature above 600° in the channel of the multiplier in a medium of isopentane, since cracking of the isopentane occurs and the carbon hereby evolved closes the coils of the heating spiral. Therefore, in conducting experiments involving superhigh pressure and high temperature it is expedient to use gas as the medium trasmitting the pressure.

During the development of the multipler design described earlier /8/ in the Institute for Crystallography two types of units were designed which made it possible to create superhigh gas pressures in conjunction with high temperature. In the first of these the medium transmitting the pressure was carbon dioxide. In it was conducted a study of the dependence of the polymorphous transformation of black phosphorous on pressure and temperature /9/. In the second type of apparatus the medium transmitting the pressure is nitrogen or argon. The conical vessel for superhigh pressure in this apparatus is provided with a unit making it possible to feed gas compressed to 2000 kg/cm^2 to it and then to cut off the channel of the cone from ~~gas transmission~~ the gas feed.

The determination of the dependence of the melting temperatures of aluminum and copper on pressure was conducted in an apparatus of the second type. Pure aluminum (99.99%) and copper (99.995%) were used in the investigations.

The scheme of assembly in the channel of the multiplier is shown in Figure 1.

Melting of the aluminum specimen was conducted in a graphite crucible 1 10 mm in diameter and 14 mm high placed inside the heating element 2 made of Nichrome wire. In order that the graphite should not close the coils of the Nichrome spiral, the crucible was isolated from it by a thin layer of mica. The melting temperature of aluminum under pressure was measured by a differential platinum-platinorhodium thermocouple 3. To prevent the "hot" junction of the thermocouple ~~ex~~ from dissolving in the molten aluminum, it was placed in a thin quartz jacket 4 fastened in the graphite lid of the crucible. The "cold" junction of the thermocouple was placed deep in the electric lead-in 5. Its temperature was measured by another thermocouple 6 ~~in~~ introduced into the ~~housing~~ casing of the electric lead-in from the outside; the distance of the junction of this thermocouple from the "cold" junction of thermocouple 3 did not exceed 6 mm.

In order to thermally insulate the furnace from the walls of the channel of the cone the entire free space in the channel of the multiplier was filled with fine powder of aluminum oxide with the exception of the upper part in which the piston is situated. The ~~ef~~ emf of both thermocouples was measured by two potentiometers type PP-1. To determine the pressure in the channel of the multiplier the coil of a manganinin manometer 7 was mounted on the electric lead-in. Measurement of the resistance of the manganin coil was accomplished by a MVL-47 resistance bridge. The accuracy of measurements of the pressure and temperature was ± 100 kg/cm^2 and $\pm 2^o$ respectively.

Figure 1. Schematic cross section of the measuring device in the channel of the vessel for superhigh pressure

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Figure 2. Dependence of the melting ~~temperatures~~ temperature of aluminum on pressure: 1) in an argon medium; 2) in a nitrogen medium

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Experiments with the melting of aluminum under pressure were conducted in a medium of nitrogen and argon (because of the possibility of the reaction of aluminum with nitrogen to form a nitride). The results of the measurements are shown in Figure 2. As is evident from Figure 2, the melting temperature of aluminum rises to the same extent when pressure is increased in the argon and nitrogen media.

When determining the dependence of the melting temperature of copper on pressure in order to obtain a higher temperature the Nichrome spiral was replaced by a tungsten spiral, and the quartz jacket protecting the "hot" junction of the thermocouple was replaced by a steel "pocket" with a wall thickness of 0.4 mm. The arrangement and procedure of the measurements was as before. In these experiments nitrogen was used as the medium transmitting the pressure. The results of the measurements are shown in Figure 3. The accuracy of the temperature measurements in the interval $1050-1250^{\circ}$ we estimate to be $\pm 5^{\circ}$.

Within the limits of accuracy of the measurements the melting temperatures of aluminum and copper increase linearly with pressure. For aluminum the quantity dT/dP is 6.3×10^{-3} deg$\cdot$cm^2/kg and for copper 4.6×10^{-3} deg$\cdot$cm^2/kg.

Discussion of the Results

Simon and coworkers /10/ proposed the following equation expressing the dependence of the melting temperature of substances on pressure:

(1)

where P is the pressure, T and T_0 are the melting temperatures in $^{\circ}$K at the pressure P and at atmospheric pressure respectively, and α and c are constants. For non-polar substances the quantity α turned out to be closely related to the so-called internal pressure defined on the basis of the energy of vaporization of the substance (λ)

(2)

where V is the fluid volume. For these substances the quantity c was found to lie between 1 and 2. Thus, c for argon is equal to 1.16 /11/, for helium 1.554 /12/, and for nitrogen 1.775 /11/. At c = 1 the melting temperature should rise linearly with pressure. As c increases the melting curves T - P deviate more and more from a straight line in the direction of the pressure axis. Simon /13/ attempted to apply equation (1) to the melting of alkaline metals, making use of the data of Bridgman /1/. It turned out that for these metals the quantity c is from 3.8 to 4.8. Moreover, all attempts to compute the magnitude of c on the basis of various equations of state of liquids and solid bodies (cf. /14-16/) led to $1 < c < 1.5$. Apparently, Simon's equation may only be considered empirical for the case of the melting of metals.

Figure 3. The dependence of the melting temperature of copper on pressure. The points represent the results of individual tests

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A computation indicates that in the case of the melting of lead and tin /4/ the values of c are approximately equal to 2.5 and 4.0 respectively; it must be noted, however, that the quantities α and c are extremely sensitive to the smallest variations in the melting curve, and therefore the accuracy of determining these quantities from melting curves is not very great. The melting curve for tallium also bends toward the pressure axis /5/. In the case of of copper and aluminum, and also cadmium and zinc /5/, the dependence of the melting temperature on pressure is expressed by a straight line within the accuracy of the measurements.

It may be hoped that further accumulation of experimental data on the melting of metals under pressure will make it possible to give a theoretical explanation of the observed regularities and relate them to the structural characterisitics of the metals.

CONCLUSIONS

1. The melting temperatures of aluminum and copper have been determined in a medium of inert gas up to pressures of 18000 kg/cm^2. It has been found that within the limits of accuracy of the measurements the melting temperatures of these metals increases linearly with increase in pressure.

2. The question of the applicability of Simon's equation to the melting of metals at high pressures has been considered.

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