METHOD FOR MEASURING THE THERMOELECTRIC CHARACTERISTICS OF SEMICONDUCTORS IN THE SOLID AND LIQUID PHASES AT HIGH TEMPERATURES

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Existing apparatus [1,2] for investigating thermoelectric characteristics of materials in the liquid phase suffers from a number of shortcomings: measurements are conducted in the open, pickup occurs from the electromagnetic fields of the heaters, measurement of temperature and difference potentials are insufficiently reliable, stray thermal emf’s are present, etc. We have designed and adjusted a device which possesses substantial advantages as compared with previous models.

The apparatus whose cross-section schematic is shown in Fig. 1 comprises a high-temperature, rectangular, 240 x 240 x 600-mm vacuum furnace.

The casing of the device is welded and made of stainless steel. Twelve lead-in terminals 3 with vacuum packing, used for supplying power to the heaters and for the potential and current lead-out conductors, are mounted on lower plate 2. The apparatus is evacuated and filled with inert gas through connecting pipe 4. Flanged branch pipe 5 carries thermocouple lead-out wires. The casing and lower plate of the equipment are cooled by running water.

Main heater 6, intended to provide the required temperature level, consists of a quartz tube which has an internal diameter of 55 mm and is wound with a 300-mm long bifilar wire made of alloy Kh25Yu5 or molybdenum. The heater has a system of quartz and stainless steel screens.

A small boat for the sample, shown in Fig. 2, is placed inside the main heater, in its middle part. The boat, 100 mm in length, is filled with the tested substance. Along the edges of the boat molybdenum sleeves are inserted into the tested substance through a ceramic plate. The surface of the sleeves (with the exception of the end faces) is coated with a thin layer of alundum. To prevent molybdenum interaction with the semiconductor, sleeves can be made of another high-melting-point metal, or the end faces given a thin coating of platinum, graphite, carbide, nitride, or molybdenum disilicide. The junctions of the graduated thermocouples are spot-welded to the bottom of each sleeve. The boat and the ceramic bearing plate are enclosed in a band made of sheet niobium or zirconium 0.5-0.7 mm thick. The band serves simultaneously as a getter.

For the purpose of creating a temperature gradient along the boat with the substance, there are two additional bifilar 0.5-mm molybdenum wire heaters at its ends. Each heater has its own supply from an autotransformer with a stabilizer through a step-down transformer, which ensures smooth regulation of the heaters’ operating conditions. The molybdenum sleeves serve simultaneously as leadouts for measuring the thermal emf. The electrical circuit for measuring the thermal emf is made entirely of molybdenum, including the vacuum lead-in conductors and the nuts, making it possible to exclude the effect of stray thermal emf’s.
The emf's of the thermocouple and the semiconductor are registered by means of semiautomatic potentiometer R2/1. For the express method of measurements, the thermal emf's between the sleeves is read on millivoltmeter N-373-1.

For simultaneous measurements of the thermal emf coefficient and conductivity, two thin molybdenum potential probes are inserted in addition to the two extreme sleeves. The extreme sleeves serve to pass the current through the substance, the thin middle probes to measure the voltage drop on the sample. The generally accepted measuring circuit is used with reversible direct current read on potentiometer R2/1 or high-resistance millivoltmeter N-373-1 (the express method). The maximum measurement error was evaluated at ±6% for the thermal-emf coefficient and ±5% for the specific resistance. It is possible to raise the precision of measuring the thermal-emf coefficient by using platinum thermocouples calibrated with reference thermocouples.

The above apparatus serves to measure the thermoelectric characteristics of semiconductors in the solid and liquid phases up to temperatures of 1200°C. The upper temperature level can be raised to 1500°C by using for the heater an alundum Former and molybdenum wire. The quartz boat should then be replaced by a boat made of spec-trally pure aluminum oxide.

Measurements of the thermal-emf coefficient and specific conductivity are carried out in steady-state operating conditions. The temperature drop at the boat ends which is obtained in measuring the thermal-emf coefficient, amounts to 100°C. Calculations show that convectional movement does not arise in the liquid semiconductor with a layer thickness of 4-5 mm. Control experiments with the liquid phase and temperature drops of 40, 80, and 120°C produced identical values of the thermal emf coefficient within the limits of the experimental error.

During the experiment, the "zero" thermal emf is periodically determined in the solid and liquid phases. For this purpose, the temperature along the sample is equalized in such a way that the thermal emf at the extreme potential sleeves in a steady-state condition is equal to zero (within the limits of the potentiometer's maximum error), and at that moment the thermocouple readings in the potential sleeves are registered. Usually, the value of the thermal emf of thermocouples measured in such conditions corresponded approximately to 3-4, i.e., did not exceed double the thermocouple error. A considerable "zero" thermal emf (≈20)° was observed in the case when the thermocouple junctions were not welded to the sleeves.

Control experiments in studying the temperature field along the length of the investigated example showed that the temperature gradient is close to linear. The temperature field was studied with the help of a number of fine potential probes placed along the sample. By measuring the thermal-emf distribution along the sample length, and taking into account the known relation of the thermal-emf coefficient to temperature, it is possible to calculate the temperature distribution along the sample.

The following characteristic was revealed by measurements of the thermal-emf coefficient of semiconductors with hole-type conductivity: at high temperatures there is a discrepancy between the data obtained for alundum boats and those for quartz boats. Figure 3, which gives the thermal-emf coefficient relationship to temperature for the Cu–Te–S alloy ("r" type), shows that the use of a quartz boat at temperatures above 930°C results in a higher value for the thermal-emf coefficient (curve 1) compared with the data obtained for the alundum boat (curve 2). The reason for this discrepancy is that alundum boats manufactured by our industry contain an admixture of a few percent of titanium dioxide, which is itself an electronic semiconductor.

At high temperatures, titanium dioxide produces a certain thermal emf of the opposite sign and, as a consequence of the perceptible conductivity of alundum, shunting occurs of the tested substance's thermal emf.