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LABORATORY EQUIPMENT FOR GERMANIUM PURIFICATION

RADIO CORPORATION OF AMERICA

RCA LABORATORIES DIVISION

INDUSTRY SERVICE LABORATORY

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Approved

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Introduction

This bulletin describes flexible laboratory equipment for purifying germanium by passing a moving heat source along a fixed container. When the heat source is around the container, the germanium is melted in one or more zones; as the heat source passes on, the germanium is preferentially frozen so as to purify at the moving liquid-solid interface. The apparatus uses a 1/8-inch pitch drive screw, rotated by a motor and gear train, to move a 6-inch by 14-inch platform on which the heat source can be mounted, for a traverse of 21 inches. A Vycor tube surrounds the germanium container; a helium atmosphere is used to prevent oxidation. Operation can be either horizontal or vertical and any type of heat source may be used.

As herein described, the apparatus is used vertically with a single long cylindrical electric furnace. Automatic temperature control and automatic shutoff is provided to allow long operating cycles with no attention by an operator.

General Discussion

It is known that germanium can be purified by passing a molten sample through one or more thermal gradients which causes it to freeze preferentially.[1] Preferential freezing can be accomplished in several ways, each involving relative motion between the container of germanium and the heat source. In one method, the sample is moved away from the heat source. In a second method, both the sample and the furnace are kept stationary while the furnace is caused to cool from one end to another. In a third method, with which this report is concerned, theheat source is moved with respect to a stationary sample. If the heat source consists of a multiplicity of separate short heating zones, a cascade process of purification results.[2]

The apparatus discussed in this bulletin has been designed for use in a research laboratory and will operate either vertically or horizontally; it is shown in the photograph Fig. 1, using the vertical plane of operation and with a single long heat source. As shown, the apparatus consists of a Vycor muffle tube, a tubular type electric furnace, a mechanism for moving the furnace, an inert gas supply, and a temperature regulator. Both the furnace power and inert gas atmosphere can be shut off automatically at the end of the processing cycle.

The apparatus is flexible enough to permit wide variations in heat source and operating conditions, as needed in research. It will here be described in the form shown in Fig. 1.

[1] LB-890, *Purification of Germanium by Gradient Freezing.*

[2] W. G. Pfann, "Principles of Zone Melting", *Journal of Metals*, Vol. 4, p. 151, 1952.

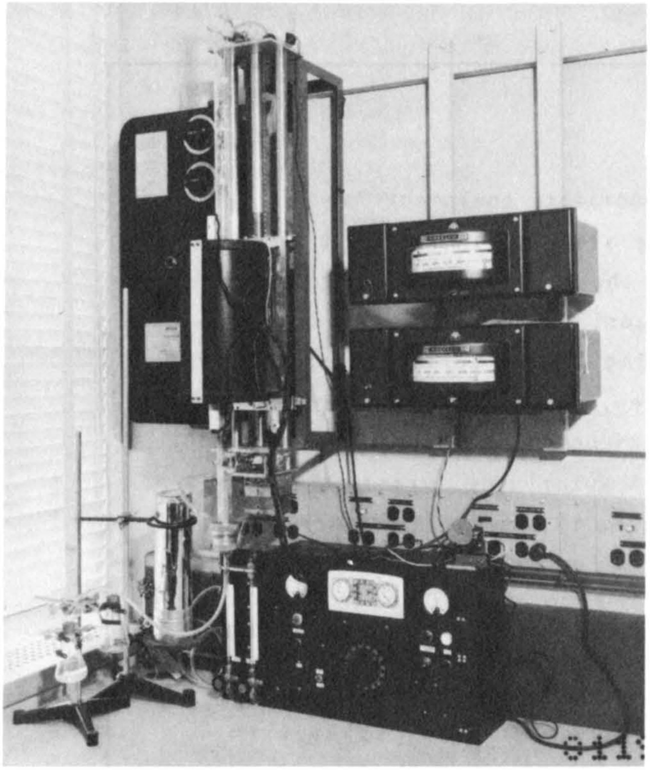

Fig. 1 - Photograph of germanium purification apparatus.

Vycor Muffle Tube

The furnace muffle is made of 96 per cent silica glass which is sold under the trade name of Vycor. It is four feet long with a 30mm outside diameter and 26mm bore. The muffle tube is held in place by two tube clamps which are fastened to the fixed end plates of the furnace-moving device. The clamps allow the muffle tube to be easily aligned with the furnace tube in spite of the irregularities that seem to be present in almost every piece of this type of glass tubing. The Vycor tube is necked down at one end and is fitted with a small diameter tube to take a ¼-inch hose for the inert atmosphere. The other end of the muffle is left straight and is fitted with a gas outlet cap.

The gas outlet cap is made of two pieces of brass which screw together. It contains a Teflon gasket which provides for a gas tight seal when the two halves of the cap are screwed together. The gas outlet cap serves a double purpose. It not only prevents air from entering the system but, when the apparatus is used in the vertical position, the brass gas outlet is at the bottom and supports the carbon crucible containing the germanium within the tube. A quartz rod is used to support the crucible at the proper height and it in turn rests on the gas outlet cap.

The Heat Source

As used in Fig. 1, the charge is heated by a commercially available tubular type Hoskins electric furnace. The furnace tube is 13 inches long with a 1 3/8-inch bore. The furnace encircles the muffle tube. The furnace is attached to a movable platform which causes it to move along the muffle. The temperature profile at the operating temperature of such a furnace is shown in Fig. 2.

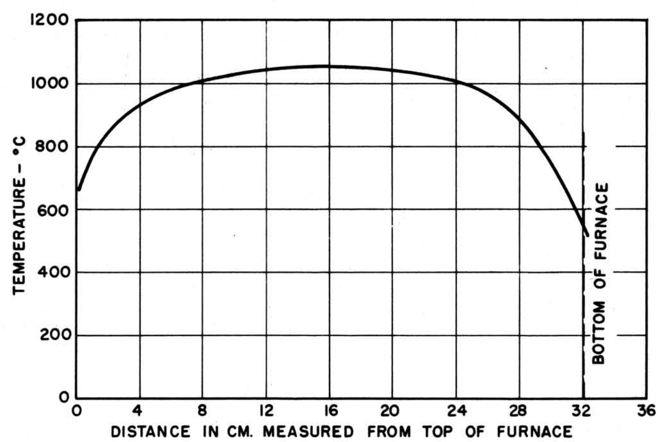

Fig. 2 - Temperature profile of a Hoskins type FD303A tubular electric furnace.

Furnace Atmosphere

An inert atmosphere is necessary to prevent oxidation of the germanium; in this case dry helium is used. Before the gas is allowed to come in contact with the germanium, it is freed of oxygen, dried, and passed through a liquid-air trap. The gas is admitted at the necked-down end of the muffle tube at a pressure slightly above atmospheric (3 to 5 psi gauge).

Oxygen and water vapor are removed by a Deoxo Puridryer, which is a catalytic type purifier and dryer in which hydrogen (10%) is added to the incoming helium to combine with the oxygen; this is followed by the liquid-air trap to assure freedom from water vapor and condensible impurities. The volume of gas is controlled and measured by passing the gas through a flowmeter which indicates the volume of gas passing into the furnace per unit time. The helium-hydrogen mixture is admitted at a flow rate of one cu. ft./hr. and is conducted round the system by means of Tygon hose having a ¼-inch bore. Rubber hose was not used for fear of introducing impurities such as sulfur into the system. After passing through the furnace, the gas is vented to the room.

Mechanism for Moving the Furnace

The mechanism that is used for moving the heat source consists essentially of a platform on which the heat source can be mounted and a means for guiding and driving the platform. The platform is made of a ¼-inch steel plate and is 6 inches wide by 14 inches long. It is fitted with bronze bearings which slide on two 1-inch diameter drill-rod guides that are 36 inches long. The guide rods are fastened to two ¼-inch steel end plates, approximately 4 by 6 inches in size. In addition to supporting the guide rods, the end plates support the clamps which hold the muffle tube, bearings for the drive screw, the drive motor and its gears, a switch used for automatic operation of the entire unit, and a pulley used in counterweighting the furnace during vertical operation.

The platform is moved by means of a drive screw to which it is coupled by means of a split-nut arrangement. The split nut allows one to move the furnace manually to any position along its travel and then engage the screw drive. Rotation of the drive screw is accomplished by using a Barber-Coleman synchronous reduction motor.[3] The motor chosen rotates at one rpm and is capable of delivering 100 lb.-in. of torque. Between the motor and the 1/8-inch-pitch drive screw a gear train can be introduced which allows furnace speeds of 1/8 inch, 1/16 inch, 1/32 inch and 1/64 inch per minute using 1:1, 2:1, 4:1 and 8:1 reductions respectively. Alternatively, the gear train can be left fixed and speed reduction accomplished by a periodic interruption of the motor circuit to vary its duty time.

The drive screw gives the proper furnace excursion, 21 inches, and also contains a safety feature. The threads were so machined that after the furnace reaches the end of its travel the split nut is caused to ride in a groove. The motor and screw can continue to rotate but the furnace ceases to move just before it reaches the end plate. The screw is mounted in ball bearings and is made with square threads in order to reduce frictional losses as much as possible.

By counterweighting the furnace and its platform, for vertical operation, accidental dropping of the furnace has been eliminated. In addition, the counterweight reduces the torque requirements of the drive motor.

Temperature Regulation

It has been found that satisfactory ingots of germanium can be obtained by operating the furnace at 1000 ± 5 degrees Centigrade. This can easily be accomplished by using a differential system for heating the furnace and a Wheelco Proportional Regulator[4]: A chromel-alumel thermocouple is used as the temperature sensing element. The thermocouple is placed at the midpoint of the furnace between the Vycor muffle and the furnace tube. In Fig. 3 is shown a simplified wiring diagram of the temperature control circuit.

Below the normal operating temperature the relay contacts across R_1 are closed. The input power to the furnace is then at a level to cause the furnace temperature to be slightly greater than the operating temperature with the heat losses present. As the temperature swings past the operating temperature the relay contacts open and R_1 is inserted, thus reducing the input power. The lower limit is

[3] Model PYAZ 929-J-2.

[4] Model No. 252-P.

slightly below the operating temperature of the furnace. No values have been given here for the upper and lower limits of input power, for the settings must be arrived at by trial and error. For a detailed account of the operation of the Wheelco Regulator the reader is referred to the Wheelco publication entitled "Automatic Temperature Control Systems, *Educational Bulletin No. 5*".

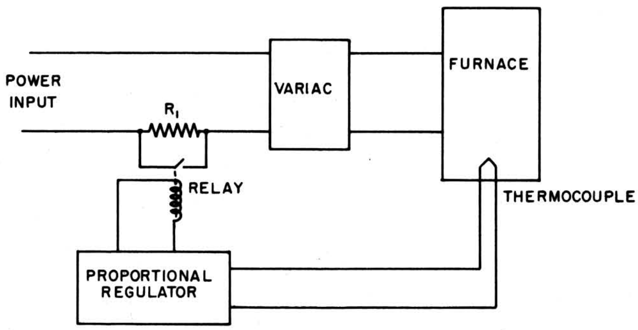

Fig. 3 - Differential temperature control circuit.

Automatic Operation

The time necessary to complete a processing cycle often takes longer than eight hours. In order to operate the equipment unattended, beyond the working day, automatic features were incorporated in the design. They involve shutting off the furnace power and the inert gas supply.

The usual sequence of operations followed using the automatic features are as follows.

The inert gas supply is turned on electrically by energizing a solenoid type valve. After the gas has flowed long enough to flush the air from the system the furnace power is turned on. After the furnace has been brought up to temperature and the sample to be purified is molten, the furnace drive motor is energized. The furnace then starts to move. At a 1/32 inch per minute travel, the furnace takes approximately 11.2 hrs. to move the entire length. Upon reaching the end, a switch is closed. This switch causes the furnace power to be shut off and it begins to cool down. When the sample within the furnace has cooled sufficiently so that oxidation cannot take place, the gas supply is shut off by means of a time switch.

Performance

Under laboratory conditions the entire system has proven to be both rugged and dependable. It has been operating continuously for several months with a minimum of attention. Its automatic features have helped increase the production of purified germanium ingots, for, once an operating cycle is started, the unit will continue to operate unattended until the entire process is completed. The unit will then shut itself off and await the next insertion of a charge to be processed. The design is also flexible enough to allow use of other heat sources and operating conditions than those here described.

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