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LB-941

A SWITCHED-ZONE FURNACE FOR GERMANIUM PURIFICATION

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A Switched-Zone Furnace for Germanium Purification

Approved

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Introduction

This bulletin describes a simple and improved apparatus for purifying germanium by passing a molten zone along the charge of germanium. In this method the heated zone is caused to travel along the charge without mechanical motion of crucible or heater. This is done by enclosing the charge in a series of separate resistance heating units which are individually turned on and off by a timing switch. To increase the speed, three traveling zones are used at one time.

This method is more compact than one using mechanically moved heaters or crucibles and is more economical than r-f induction heating. The entire unit, including power supply, occupies about 8 square feet, expends 4 kilowatts and produces 500 to 800 grams of intrinsic germanium overnight. The switching circuit provides for repeated passes of the molten zone, as many as desired, with no re-setting or other attention.

The Zone-Melting Process

The general principle of zone-melting has been developed and applied to germanium by Pfann.[1] The segregation effect utilized is the same as the gradient freezing described in *LB-890*.[2] The method of segregation differs from gradient freezing in that a short hot zone passes along a boat-shaped crucible, melting only a portion of the charge at any one time. In the usual method there is mechanical motion of the boat or of the heater relative to the other.

In the method described here this mechanical motion is replaced by the application of power to a succession of several heaters lying along the boat. This is done in sequence so that one or more molten zones in the germanium progress along the length of the charge.

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

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

Construction of the Furnace

Fig. 1 shows the external appearance of the furnace. It consists of 34 cells, of which one is sketched in detail in Fig. 2. Each cell is one inch long. The charge is melted in the graphite boat, 40 inches long. This is kept in an inert or reducing atmosphere in the silica tube, extending through all the cells.

The cells are separated by ¼-inch thick firebrick, in order to prevent the heat of one cell from melting the load in other cells at wrong times. These separators also prevent the silica tube from sagging. A hot zone occupies two cells, as described below under "Electrical Connections".

Each cell contains a set of Globar resistance heaters. The Globars are supported by the side brick. Along the top of this lies a nichrome strip, from which spacer tabs extend down to hold the separators in place.

The brick furnace floor rests upon two transite sheets, separated by an air space and having their facing surfaces lined with aluminum

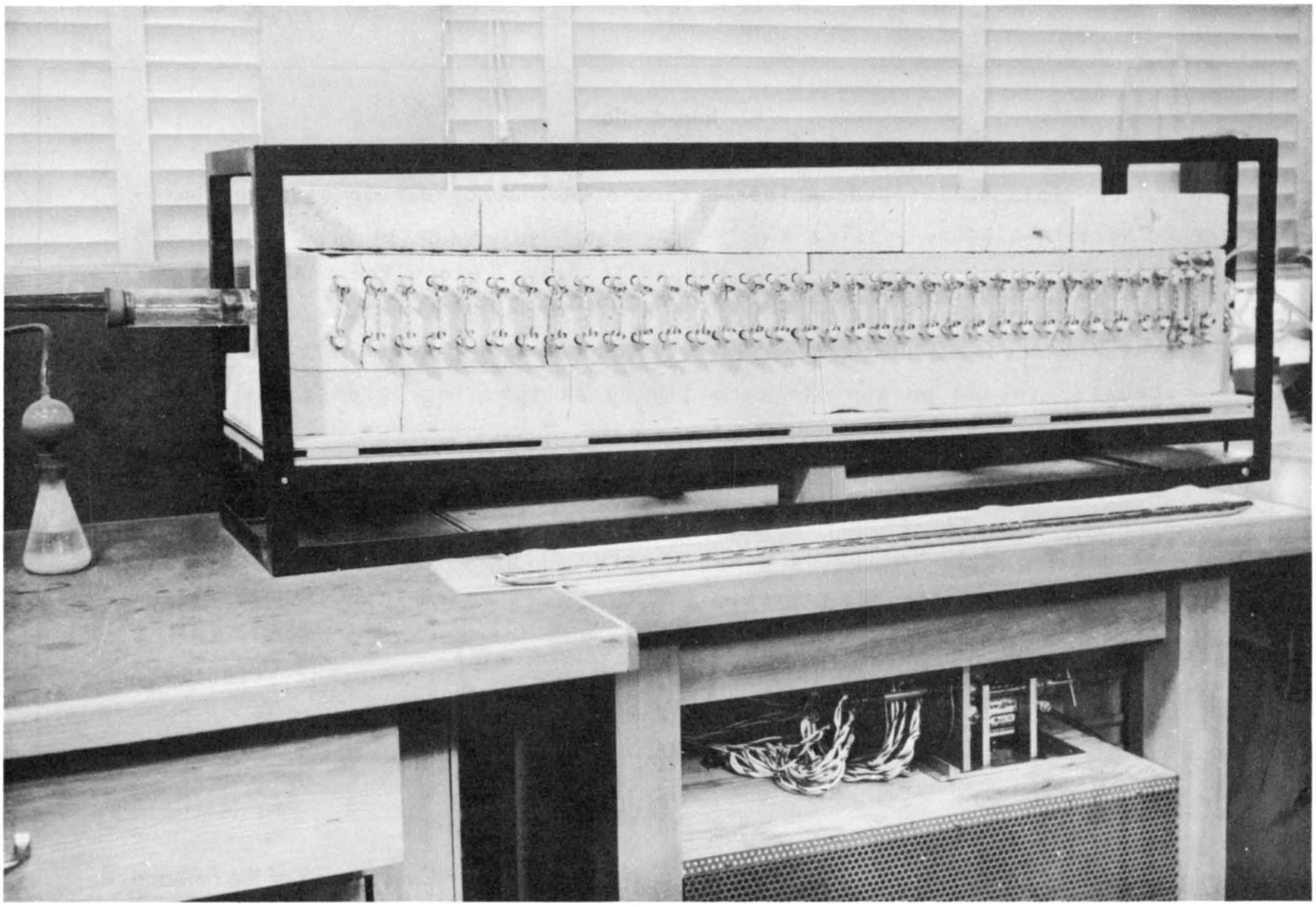

Fig. 1 - Front view of furnace showing a refined ingot on table in front of it.

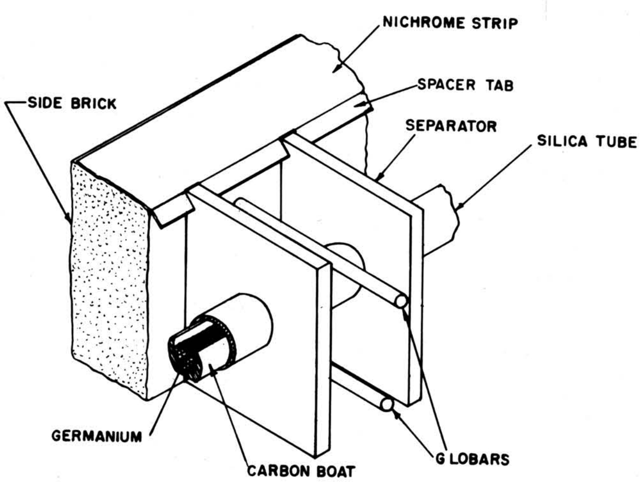

Fig. 2 - Typical cell.

sheets to reduce radiation. The covering bricks leave an open slit directly above the boat, serving three purposes: (a) to provide a view of the molten material when necessary; (b) to hasten heat loss and freezing of germanium in cells not being heated; (c) to provide corrective heat loss so that the middle cells do not overheat. The opening is about $\frac{1}{2}$-inch wide near the middle of the furnace, tapering to $\frac{1}{4}$-inch near the ends.

The furnace is supported in an angle iron frame and pivoted at one end to allow an adjustable slope. This is necessary because the expansion of germanium on freezing tends to push material ahead with the traveling zone. Tilting the forward end of the crucible about 2 degrees above the horizontal counteracts this effect and maintains a uniform cross-section in the ingot.

Electrical Connections

Rotating tap switcnes provide the means for heating the cells in succession, and thu advancing the molten zone. The first two cells have two Globar pairs each instead of one, so that the 34 cells utilize 36 Globar pairs and 36 tap connections. It is necessary to supply this extra heat for initial fusion of the molten zone and to correct for heat losses at the starting end of the furnace.

The 34 cells are arranged in three groups of 10, 12 and 12 each, connected correspondingly and operated simultaneously. This forms three separate molten zones moving in step. In a typical group the taps are connected to Globar pairs in the following order, "0" standing for "On" and "-" for "Off":

Tap No.	Globar pair No. 1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	-	-	-	-	-	-	-	-	-	-
2	-	0	0	-	-	-	-	-	-	-	-	-
3	-	-	0	0	-	-	-	-	-	-	-	-
4	-	-	-	0	0	-	-	-	-	-	-	-
5	-	-	-	-	0	0	-	-	-	-	-	-
6	-	-	-	-	-	0	0	-	-	-	-	-
7	-	-	-	-	-	-	0	0	-	-	-	-
8	-	-	-	-	-	-	-	0	0	-	-	-
9	-	-	-	-	-	-	-	-	0	0	-	-
10	-	-	-	-	-	-	-	-	-	0	0	-
11	-	-	-	-	-	-	-	-	-	-	0	0
12	0	-	-	-	-	-	-	-	-	-	-	0

It is necessary to heat two cells for each position of the molten zone to give overlap, so that the zone does not freeze before each new cell has heated to the melting point.

Each pair of Globars is connected in series to form a cell resistor. To achieve the desired heating order, these resistors are in turn connected in series to form a ring of resistors as indicated in Fig. 3. The junctions between resistors are attached each to two tap switches as shown. For instance, with the switches in position 2, resistors R_2 and R_3 are heated. One-fifth as much current also flows back through the rest of the ring, losing a negligible 4 per cent of the heating power.

A special switch construction is required. 12-tap Ohmite switches are mounted in tandem, with their stops removed to permit continuous rotation. To provide quick and positive movement of the switch from one position to the next, an auxiliary spring-action detent (Fig. 4) is inserted between the switch and the reduction gear of the driving motor. The switch speed is one revolution in 45 minutes.

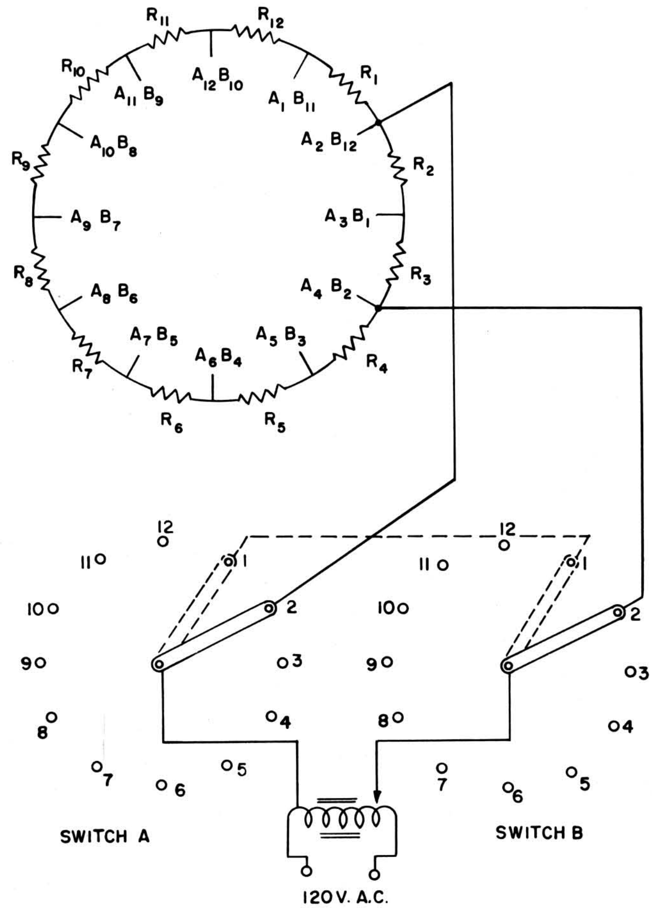

Fig. 3 - Switching circuit.

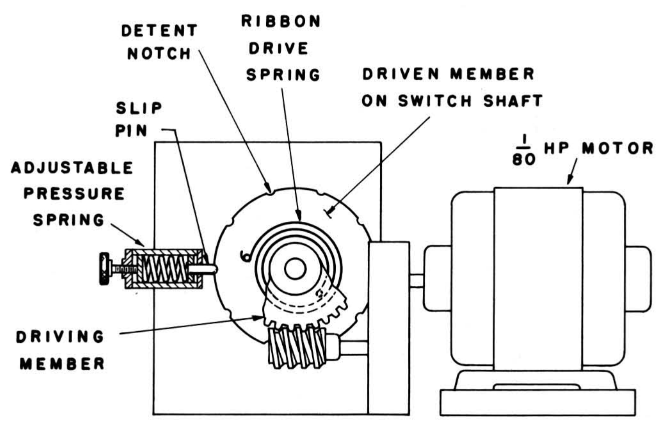

Fig. 4 - Drive for tap switch.

Operation

The boat charged with germanium is placed in the furnace so that the charge begins in the second cell. This pre-heats the end of the crucible and so aids in the initial melting of a zone. If power is applied at a constant level, the germanium may not melt during the first pass of the hot zone. This is permissible, since the furnace operates automatically overnight, making an ample number of effective passes.

On stopping the furnace, provision must be made for the last zone to travel to the impure end while no new zones start. Any unfinished zones would leave impure spots in the ingot, and might form troublesome "sprouts" of expanding germanium where the zones freeze. To prevent this difficulty, two 12-pole knife switches may be inserted in the leads going respectively to the first two groups of resistors. With these the power may be cut off from the first and second groups just in time to avoid starting new zones. Or more simply, the operator may progressively remove bricks from the top of the furnace, keeping the charge frozen behind the last zone.

The power supply is a large adjustable autotransformer. By adjusting the voltage of this source, the length of the molten zone is controllable within limits. About 35 amperes at 110 volts maintain proper zone-length. This may vary between 3 and 4 inches, depending on changes of line voltage and of heat loss.

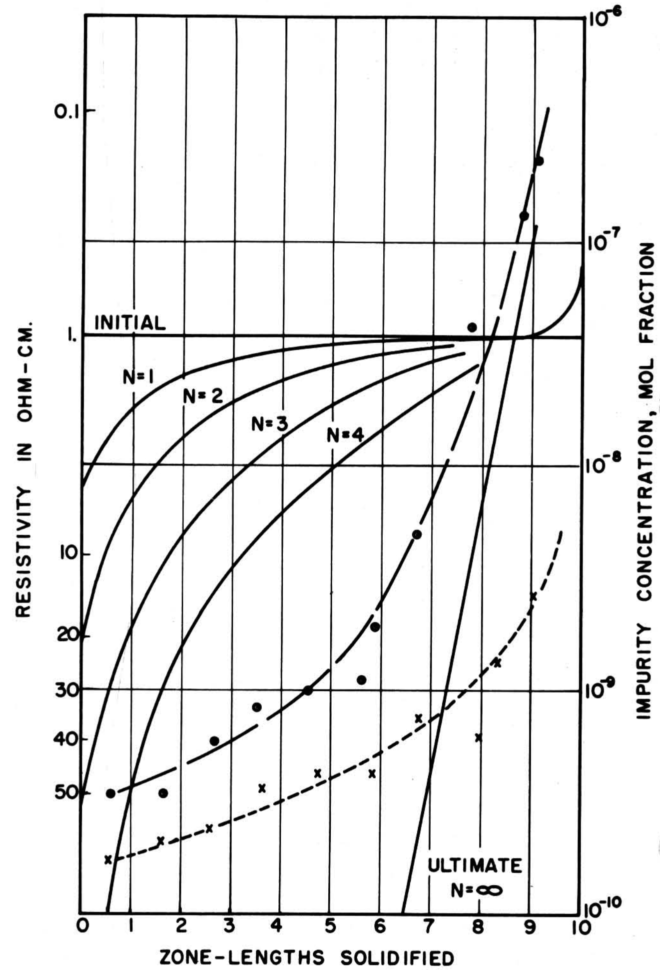

Fig. 5 - Resistivity of two refined ingots. x, initial charge about 10 ohm-cm. ⊙, initial charge about 1 ohm-cm. Solid lines show theoretical impurity distribution for this case.

Discussion

Mathematical analysis of zone refining[1,3] shows that the impurity concentration should vary along an ingot approximately as shown by the solid lines in Fig. 5. The present crucible length is about 10 zone lengths, and the effective distribution coefficient for native germanium impurities is about 0.2. The parameter N is the number of zone passes. The plotted points show measured resistivity values on typical ingots after 18 passes in an overnight run of the furnace.

The ingot represented by circles was produced from a 1000-gram load of rejected ingot tails with resistivity about 1 ohm-cm. The impurity concentration is related to the resistivity as discussed in *LB-899*.[4] As the data indicate, about half of the charge is purified practically to the intrinsic range. A better charge yields about 75 per cent of intrinsic germanium.

The purity obtained is quite satisfactory for most purposes, so that more elaborate development of the furnace was not worthwhile. For higher purity: (a) the cell-length may be shortened to give zones down to about 2 inches; (b) the furnace may be operated for a longe time, though there is small advantage in more than 18 passes; (c) for the greatest improvement, the furnace may be re-loaded with a charge of higher purity. Even with an infinite

[3] N. W. Lord, "Analysis of Molten-Zone Refining", *Journal of Metals*, Vol. 5, p. 1531 (1953).

[4] LB-899, *Theoretical Resistivity and Hall Coefficient of Impure Germanium Near Room Temperature.*

number of passes, there is a finite impurity concentration at every part of the ingot, because not all of the impurity can be restricted to the final zone to freeze. This ultimate impurity concentration is proportional to the total impurity in the charge.

The efficiency of each pass is somewhat low, probably because of the intermittent motion of the zones. Eighteen passes are more than are necessary for usual purposes, but are a convenient number for an overnight run.

Thus the switched-zone furnace is simple in construction and automatic in operation. It is shorter than systems using a moving crucible, and eliminates some problems involved in mechanical motion at high temperature. It is much smaller and less costly to build or operate than an induction-heated furnace of the same capacity. It has produced high-purity germanium with trouble-free operation over a period of many months.

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