PREPARATION OF ELECTRONICS GRADE BISMUTH, ANTIMONY, TELLURIUM, CADMIUM AND ZINC BY VACUUM DISTILLATION AND ZONE REFINING (*)

A.J.Singh, B.S. Mathur,
P.Suryanarayana & S.N.Tripathi,
Bhabha Atomic Research Centre,
Trombay, Bombay.

Bismuth, antimony, tellurium, cadmium and zinc, in their ultra-high purity forms (99.99 to 99.999%), have recently acquired special significance in the electronics industry. Several methods such as precipitation, crystallization, electrolysis, distillation, ion-exchange, solvent extraction, zone melting, etc. are available for the preparation of such high purity and electronics grades materials.

On the basis of the annual requirements of the electronics grade materials in India by 1975, vacuum distillation and zone melting techniques have been developed to prepare bismuth, antimony, tellurium, cadmium and zinc of the appropriate grades. Starting with the best commercially available materials(purity 98 to 99.9%), the methods were, in the initial stage, worked out for 250 g to 1 kg per batch scale operations and were subsequently stepped upto 3 kg to 10 kg scale. A purity of 99.999% and better has been achieved for these materials, as far as we know, for the first time in the country. Plans are already underway to prepare these materials in quantities indicated above and for this purpose a Special Materials Plant is being set up at Hyderabad.

Vacuum Distillation:

During the distillation of metals, non-attainment of equilibrium leads to a steady rate of evaporation of metal atoms from the surface of the melt. This rate is dependent on vapour pressure, residual gas pressure and pressure gradient of the metal atoms between the metal surface and the condensate. Vacuum distillation has the following advantages over distillation under normal conditions:

(*) Paper for presentation at the Symposium on "Recent Developments in Non-Ferrous Metals' Technology" - 4th to 7th December, 1968, Jamshedpur.

i) the rate of evaporation increases with decrease in residual pressure,

ii) better separation of volatile constituents may be achieved at lower pressure,

iii) the possibility of inter action of metal atoms with ambient gas is reduced or eliminated,

and iv) working at a lower temperature is an asset because of negligible chances of metal to container interaction and the low running cost of the process.

Zone Refining

Purification of a substance by zone melting depends on the difference in solubility of an impurity in the molten and the frozen phases in equilibrium. In practice, liquid-solid interfaces are obtained by causing a narrow molten zone to traverse the length of an ingot of the charge. Depending on whether an impurity lowers or raises the melting point of a material, passage of a molten zone through the charge will concentrate the impurity in the molten or frozen phase respectively. Conditions such as narrow molten zone length, low rate of zone traverse and more number of passes, make the separation efficient.

Zone refining was carried out using boats made of pyrex glass for bismuth, quartz for tellurium and graphite for antimony and cadmium. Small ring resistance heaters, made out of sillimanite tube, were employed to produce narrow molten zones. The entire equipment was fabricated in the Division's workshop.

System Description:

The apparatus for vacuum distillation was made of stainless steel with two graphite crucibles inverted one over the other for containing the metal. The lower crucible acts as container for the charge while the upper, with a hole, serves as substrate for the deposit. The vacuum system consists of a rotary pump and a liquid air trap to give pressures of the order of 3 to 0.3 x 10^{-1} torr.

...3.

The automatic zone refining unit, fabricated in the Chemistry Division Workshop, comprises: (a) a slow drive mechanism to have a final steady molten zone speed varying from 0.5 cm/hr. to 20 cm/hr; (b) reversing motor with clutch arrangement; and (C) a moveable carriage for resistance heaters. The tube containing the charge is fixed horizontally. At the end of each pass, the movement of the heaters is reversed quickly to bring them back to their original starting positions.

The melting points of the metals under consideration are: Bi, 270°C; Sb, 630.5°C; Te, 449.5°C; Cd, 319.6°C and Zn, 419.5°C.

Bismuth

The best commercially available bismuth metal (99.95%) was charged in two capsules (total charge, 7 kg) fixed parallel on the zone refining unit. 15 passes at 4 cm/hr under a pressure of 3×10^{-2} torr gave an ingot containing 80% by weight of the metal in 99.999% purity.

Antimony

Distillation of commercial grade antimony (charge 6 - 7 kg of 98% Sb) at 900°C and 3×10^{-1} torr, yielded about 60% of the charge as 99.97 + % pure metal with arsenic content of 100 p.p.m. This was suitable for producing Sb-124 (for Sb-Be neutron sources).

Zone refining a charge of 650 - 700 g of chemically purified antimony metal (arsenic free) in a graphite boat 30 x3x 2 cm, with 20 passes at 3.5 cm/hr. in an atmosphere of nitrogen gas, yielded 75% of the ingot having purity 99.999%.

Tellurium

250 g of chemically purified tellurium powder was taken in a 25 x 3 x 1.5 cm quartz boat. A step, involving the hydrogen treatment of the tallurium powder at 500°C prior to zone refining, was found essential. 20 molten zones were made at a rate of 7.5 cm/hr in an atmosphere of hydrogen gas gave a refined ingot of 99.999% purity (yield 80% by weight).

...4.

Cadmium

A charge of 5 kg metal (99.95%) distilled in a graphite crucible, at 450°C and 7 x 10^{-2} torr gave 80% of the condensate as 99.999% cadmium.

The same grade of metal (99.95%) zone refined in graphite boats, with 20 passes at 7.5 cm/hr, in an atmosphere of nitrogen or hydrogen gave an ingot 80% of whose length had a purity 99.999%.

Zinc

The apparatus and experimental conditions were similar to those for the distillation of cadmium metal except that the working temperature was 500°C. Spectrographic analysis and comparison of different samples with imported standard material, showed that 75% of the charge was collected as condensate with purity 99.999%.

/Ahmed