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Materials and Techniques for electron tubes

by

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lefunken Laboratories in Germany developed the "Ceto" getter orld War II which contains the metals cerium and thorium; it is from a mixture of thorium powder and a cerium-aluminum alloy ith thorium comprising at least 80 per cent of the mixture. Espe[43] a detailed description of its preparation as practiced in Germany oduction of microwave tubes. After being degassed at 800°C, such atings exhibit marked getter action already near 100°C and have tion maximum at several hundred degrees centigrade.

the past few years, extensive development of Ceto-type getters carried out by Wyman and Kuhnapfel[44] at the Reliable Tube Bendix Aviation Corporation and by Briggs Associates[27] under ip of New Process Metals, Inc.,* from which company Ceto-type e commercially available under the tradename "CerAlloy 400." ly approach, following that practiced by Telefunken, was to powder onto metal flags which were attached to electrodes of tructure in such positions that the getter was raised to a suitable re in operation. Direct coating of electrodes, such as anodes, was ced. The sintered powder is black and thus has a high thermal ; it can be applied to iron, steel, "Kovar," nickel, nickel-plated bdenum, Monel, and copper.

cently, work at Bendix[45] has culminated in the production of llets contained in nickel cups which are strategically located tube. The over-all effectiveness of the getter is thereby increased ıbt also the ease of handling.

ess of manufacture is described as follows:[45]

thorium powder is produced by reducing ThO_2 with calcium rucible (50 pts ThO_2 + 30 pts Ca (b.wt.)). The mixture is heated a vacuum of $< 10^{-4}$ Torr and then fired at 950°C in a dry argon at a pressure of 20 Torr, or more. After cooling, the resultant is washed in water and acetic acid until pure thorium remains; ng in methanol, the thorium powder is vacuum dried.

lloy of cerium and aluminum is made by mixing fine shavings which have been degreased in acetone, with aluminum granules ratio of 72 Ce:28 Al and heating in a BeO crucible at 800°C 10^{-4} Torr. An exothermic reaction occurs, and much gas is that pumps with adequate speed (~ 100 l/sec in the micron t be used. The resulting alloy is shiny and brittle; it is ground s of 240 mesh and stored in an argon atmosphere.

Ce-Al alloy powder and thorium powder are mixed in a weight nd 50 gm of the mixed powder is compacted at high pressure ng rods and sintered at 1000°C in a vacuum furnace at a pres-

nufacturers Place, Newark 5, N.J.

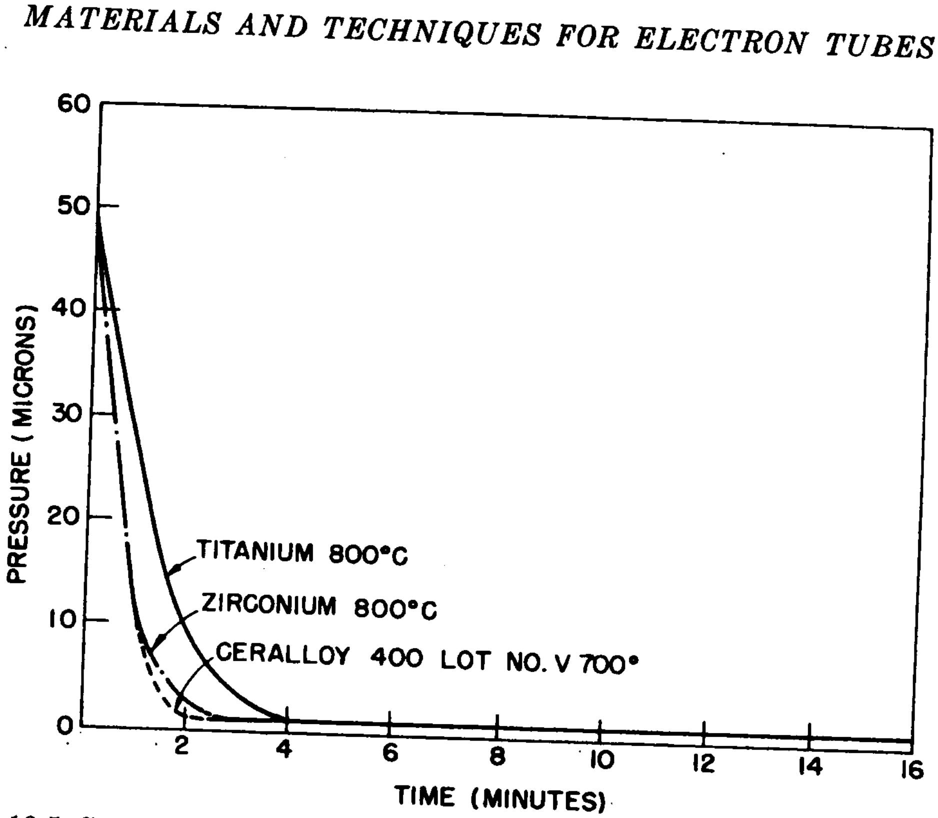

Figure 16.5. Sorption rate of various getters for carbon dioxide. After Wyman an Kuhnapfel.[44] (*Courtesy Bendix Aviation Corporation.*)

sure of 5×10^{-5} Torr, or less, for 1 hr. Melting must be avoided, as th getter properties of the sintered alloy are by far superior to those of th cast material and also because the cast material is ductile and cannot easil be pulverized.[43]

(4) The sintered compacts are ground to granules and screened to 34 mesh size under acetone. Small nickel cups are filled with the granule and pressed into pellet form, ready for mounting in the tube.

Extreme precautions are necessary in all the processing steps becaus thorium and the alloy powders are not only pyrophoric but also emi α-radiation. Any attempt to duplicate these procedures should be undertaken only after reading the much more detailed original references[43, 4] and consultation with those already experienced in handling these materials.*

The results reported on the merits of Ceto-type getters evidently warrant the considerable effort involved in their production. Wargo and Shepherd[46] made brief reference to these getters and report that a mixture of 80% Th + 5% Al + 15% Mischmetal sintered onto a molybdenum ribbon and outgassed at 1100°C at 10^{-7} Torr did thereafter getter all gases except helium when operated in the range from 350 to 500°C. Wyman and Kuhnapfel[44] and Briggs[27] have given more detailed accounts of results obtained. Figure 16.5 shows the pressure drop *vs.* time observed in a 2-liter volume

* N— R — M — —

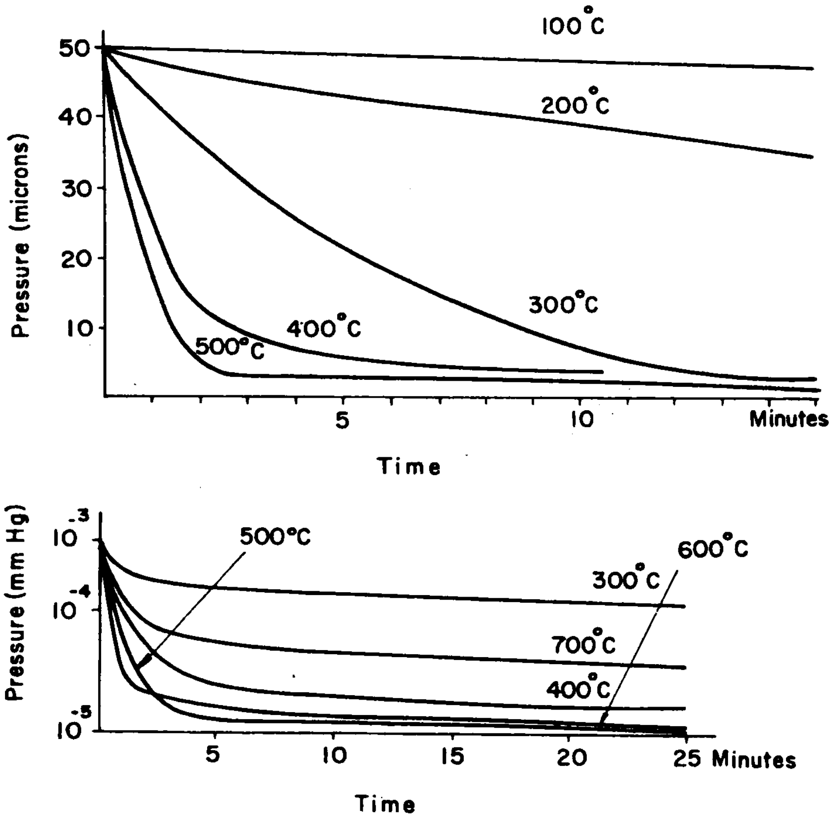

Figure 16.6. Sorption rate for CerAlloy 400 getters in carbon dioxide at different temperatures. After Wyman and Kuhnapfel.[44] (*Courtesy Bendix Aviation Corporation.*)

after CO_2 was admitted at $p = 5 \times 10^{-2}$ Torr and the different getters were heated to the temperatures indicated on the curves. Figure 16.6 gives the sorption rate for CO_2 at various getter temperatures, as read by a Pirani gauge. The CerAlloy 400 getter was heated by induction and temperatures read by a thermocouple. Briggs[27] has reported improved emission evels, greater uniformity of emission, low values of heater-cathode leakage, ow grid leakage, and low contact potential on controlled tests with Standrd Diodes and receiving tubes. Bendix reports that no desorption of gas vas noticeable after baking some of their tubes on life test at 400°C for 6 hrs, a condition under which all conventional getters had caused failure wing to excessive gas currents.

Tantalum, zirconium, and thorium have been used as coating getters in ower tubes for many years. Powders of these metals are usually sintered nto the anode surfaces to which they can be applied by spraying a suspenion of the powder in a binder solution, or by cataphoresis.

Tantalum is capable of absorbing several hundred times its own volume f gas (740× for H_2) when it has been properly outgassed near 2000°C (see

p. 347) and is then operated at a red heat, anywhere between 700 and 1200°C. The relatively high cost of Ta mitigates against its use as a bulk anode material, except in special-purpose tubes, so that coating with powders offers an economic advantage provided the processing cost is not excessive.

Tantalum is also a very effective flash getter when placed in the form of a wire loop in a separate bulb connected with the tube under study. Becker[47] was able to produce and maintain ultra-high vacua of the order of 10^{-14} Torr in a field emission microscope by repeatedly laying down a film of Ta.*

Zirconium[48-54] is an effective getter for O_2, N_2, CO, CO_2, and H_2O; it does not react with mercury and can thus be used in mercury vapor rectifiers. According to Fast,[52] 40 atomic per cent of oxygen and 20 atomic per cent of nitrogen are taken up by zirconium without compound formation, the gases dissolving in the metal and being retained up to 1650°C. Both gases are rapidly sorbed at 800°C, and so are CO and CO_2.[53] Hydrogen is sorbed most copiously at 300°C, desorbed at higher temperatures but taken up in a narrow temperature range near 870°C. As suggested above, several Zr getters may thus be operated at different temperatures in one tube.

The form of the Zr getter may be a coating on an electrode, a tab attached to the heater leg, a separate wire wound on a higher-melting support wire which can be externally heated, or a component made from Zr in bulk. Zirconium hydride, rather than pure Zr powder, may be used as a coating material which decomposes on heating during processing of the tube. These materials are highly flammable in finely dispersed form and will ignite on exposure to shock or abrasion. Extreme precautions must be taken in handling them.

Thorium falls into the same category. It is not only useful as a constituent of Ceto-type getters, as described above, but may also be used as a coating or flash getter by itself.[32, 33] Wagener[33] found that thorium powder electrolytically deposited on cathode nickel sleeves exhibited a higher sorption rate for oxygen than it did for hydrogen. The rate of sorption for O_2 is also higher than it is for H_2, and the decay of the sorption rate is smaller for O_2. The sorption rate for H_2 increases with temperature to a maximum at 750°K.

By heating the Th powder to 1150°K for about 5 minutes, sorbed hydrogen is completely released. Oxygen is released by heating to this temperature only when the sorbed quantity has been small. It is suggested on

* It is of passing interest to note that the endpoint of life for a Ta filament was found to be reached after a 6-percent reduction of the wire diameter; this agrees with the most recent findings for tungsten filaments (see p. 273).

the basis of these observations that oxygen is sorbed by chemisorption in which a stable oxide, probably ThO_2, is formed; the activation energy for this process is 0.75 Kcal/mole. Hydrogen, on the other hand, reaches an equilibrium of solution in Th and can be injected or removed at will; the heat of solution of H_2 in Th is 13 Kcal/mole.

As thorium is a constituent of Ceto-type getters, desorption of hydrogen and of oxygen in part must be expected above 850°C, as stated above.

Titanium has a very high reactivity with gases, especially at elevated temperatures, as shown by Gulbransen and Andrew,[55-57] and other investigators. Stout and Gibbons have studied the sorption properties of Ti for various gases and vapors and found that O_2, N_2, and CO_2 are gettered above 700°C while H_2 is absorbed in the temperature range of 25 to 400°C. The sorption rates for the various gases are markedly different at any given temperature, oxygen being sorbed at a much greater rate than nitrogen or carbon dioxide throughout the temperature range from 700 to 1100°C. Rare gases and mercury do not interfere with the gettering action of Ti.

Carbon, oxygen, and nitrogen form stable compounds with Ti and are not released when the metal is heated to elevated temperatures. The presence of a surface film of oxide will prevent sorption of hydrogen at room temperature.[58, 59]

Champion concluded from his studies on the suitability of Ti as a grid material for the suppression of primary and secondary emission that Ti should not be operated above 900°C when in the proximity of an oxide-coated cathode (see Chapter 8, p. 251). Recent investigations in several laboratories suggest that the outgassing temperature of Ti should be held in the range of 1030 to 1050°C.

The gettering properties of titanium-zirconium alloys have been described by Stout and Gibbons.[57] An alloy containing 87 atomic per cent Zr was found most suited for gettering, as it will dissolve its surface oxide film below 200°C and thus be active in sorbing hydrogen in addition to oxygen, nitrogen, and carbon dioxide.

Getter-ion Pumps

The degree of vacuum that is attainable by commercially available pumps has been steadily advanced in recent years; the term "ultra-high vacuum" has thus been introduced for pressures below 10^{-8} Torr.[60] Pressures as low as 10^{-13} Torr have been reached in special systems in the laboratory. Initial advances were principally due to the utilization of ion gauge pumping coupled with the use of all-metal valves, according to Alpert,[8] which permitted separation of the tube under exhaust from the oil diffusion pump after it had done its duty by reducing the pressure to the level of 10^{-7} Torr.