

24. ELECTRONIC MATERIALS

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This title covers such a wide field that it seems necessary to introduce some restrictions concerning the subjects to be discussed. This chapter is intended to cover only applications of vacuum metallurgical processes to materials used in the construction of electronic devices and, in particular, electron tubes. These applications can be divided into several categories:

(1) Processing of metals at high temperatures in a vacuum to drive out adsorbed and dissolved gases and thus prepare the metals for service in high-vacuum devices.

(2) Vacuum annealing processes designed to remove metal-working stresses without oxidation or other gas-metal reactions.

(3) Joining of metals to metals and of metals to ceramics by vacuum brazing.

(4) Vacuum evaporation of metals to create a metallic deposit.

(5) Preparation of alloys by melting in a vacuum.

High-Temperature Processing. The metallic materials used in the construction of electron tubes generally form the main part of the internal structure. The gas content of these materials ranges from approximately 100 μl per g for clear metals like commercial nickel to about 1000 μl per g for certain types of carbon-coated materials in strip form used for tube plates. A miniature receiving tube, such as type 6CG7, having a volume of approximately 12 cu cm contains almost 2.5 g of carbonized plate material and about 1 g of clear metal for the cathode, leads, grids, and getter. The gas contained in these parts could produce a pressure of the order of 200 mm Hg in the 12-cu cm volume of the envelope. Such a pressure would be about seven orders of magnitude higher than the maximum limit for vacuum-tube operation.

Because tubes usually contain metal parts in a proportion similar to that in the above example, it is necessary to "outgas" these parts before they are suitable for operation in a vacuum. Gases are removed by high-frequency induction heating of the parts to approximately 900°C during the tube exhaust cycle (Figure 1). Adsorbed as well as dissolved gases are pumped off while the parts are at high temperature. The rate of gas development goes through a maximum during this cycle. When, subsequently, the temperature is dropped, this rate is reduced to a negligible value. With

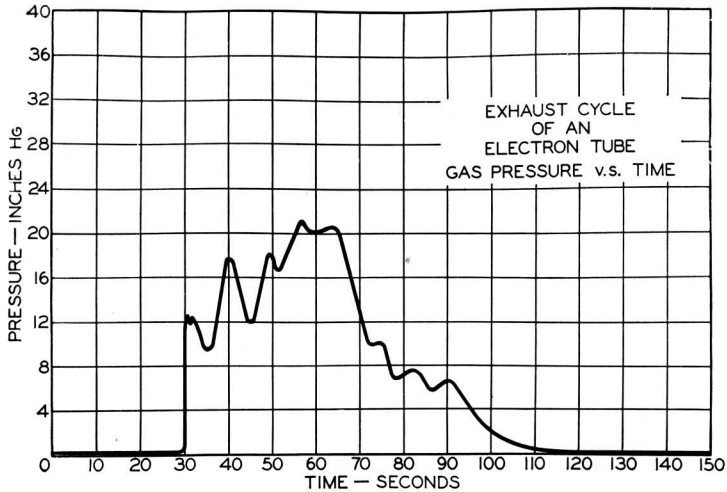


Figure 1. Exhaust cycle of an electron tube gas pressure *vs.* time.

the use of a chemical "pump" called the getter, therefore, a vacuum of 10^{-5} mm Hg can be maintained without difficulty over the normal life of the tube.

This method of vacuum degassing tube parts after assembly is appropriate for small tubes and for moderate production rates. Two factors, however, will tend to revise this practice. The first is the increasing trend toward higher production speeds which reduce the available outgassing time during exhaust. The second is the steadily increasing demand for quality improvement and prolongation of tube life, both of which are based on an even more complete removal of gas from the tube. These two factors have caused a considerable amount of experimentation in the field of vacuum outgassing of tube parts prior to assembly. A variety of vacuum furnaces have been developed for such purposes.

Some of these vacuum furnaces are of the batch type and have containers for parts which can be moved between a hot zone and a cooling chamber without breaking the vacuum. These furnaces process a large number of parts at one time. Other furnaces are of the horizontal semi-continuous type and have vacuum locks at each end and a hot zone in series with a cooling zone so that boats containing parts can be moved through the furnace in the same way as in conventional hydrogen-firing furnaces. The pumping systems are generally equipped with mechanically backed booster-type diffusion pumps which allow operating pressures as high as 1000μ . This feature is advantageous in connection with the initial gas surges which occur when parts to be outgassed are first introduced in the furnace. At the end of the outgassing cycle, the pumps should be able

to reduce the pressure to the range of 0.5 to 0.01 μ of mercury. Furnace temperatures center around 1000°C.

Although the present trend toward pre-outgassing of receiving tube parts may be expected to gain in importance, this practice has already been adopted for several other types of electron tubes, including the larger tubes, known as power tubes, and magnetrons, which contain large masses of solid metal. For many of these, all parts are vacuum-fired prior to assembly. The practice has also been established in the manufacture of some recently developed ceramic and metal tubes. It has been reported¹ in this case that all tube parts are outgassed in a vacuum at 1200°C prior to assembly. The traveling-wave tube is another type for which all parts are frequently vacuum-treated for $\frac{1}{2}$ to 1 hr at temperatures ranging from 700°C for copper to 1800°C for tantalum. It can be expected that for receiving tubes a combination of pre-outgassing and automatic parts handling will ultimately lead to the fulfillment of these requirements.

Vacuum-Annealing. Vacuum-annealing is applied in those cases where it is important that no contamination of the metal occur during removal of the stresses of work hardening. In some cases, for instance, oxidation of minor elements or loss of carbon caused by reaction with a prepared protective atmosphere is to be avoided. Although it is not known whether this technique is standard in production, it has reportedly been used successfully for the intermediate anneals applied during drawing of seamless nickel tubing for electron-tube cathode sleeves. Because of the extreme sensitivity of cathode material to impurities and contamination, it is believed that this technique is ideal for this case.

A point of caution should be made in regard to cleanliness of the material to be vacuum-annealed. Some carbonaceous-drawing lubricants which might be removed by a slightly oxidizing protective atmosphere may behave differently in a vacuum and diffuse into the metal resulting in contamination.

Vacuum-Brazing. The joining of metals to metals and of metals to ceramics by vacuum-brazing does not apply to conventional receiving tubes but it does apply to several of the other classes of tubes mentioned in connection with pre-outgassing. Although many power tubes are still brazed in a protective atmosphere and subsequently exhausted, there is an increasing trend to braze sub-assemblies in a vacuum. In modern ceramic-and-metal-tube manufacture, exhaust and sealing cycles are combined into two successive steps of one and the same process. During this process, the metal and ceramic parts are assembled with a brazing material in the proper locations and placed in a vacuum furnace. Because the tube envelope in the unbrazed condition is still open, a vacuum is created inside as well as around the tube. The temperature is then gradually raised and, after some

cathode processing, brought to the point where the brazing metal melts and seals the tube envelope. It is reported¹ that the whole process can be accomplished within 10 minutes. If the tubes are small, many may be exhausted simultaneously.

The nature of the ceramic-to-metal brazing materials, such as the titanium-copper eutectic alloy, requires a high vacuum if reproducible results are to be obtained. The active ingredient in these alloys has such an affinity for oxygen that it will compete for oxygen with the oxides present in the ceramic and, as a consequence, wet and react with the surface layer of the ceramic part. If gaseous oxygen is present in sufficient amounts, it may react preferentially and prevent a good braze. A pressure in the order of 10^{-5} mm Hg is desirable in such operations.

Vacuum Evaporation. Vacuum evaporation of metals has several applications in the electronics field. First, it is applied in the well-known process of aluminizing the phosphor screens of television picture tubes to provide increased contrast. A stranded tungsten-wire filament having small pieces of aluminum attached to it is inserted in the neck of the picture tube, which is subsequently evacuated to a pressure of the order of 10^{-5} mm Hg. The tungsten filament is then heated to approximately 1400°C by passage of a current, and the aluminum is evaporated onto the screen to a thickness of about 1000 \AA . This process has become highly mechanized and is automatic except for the insertion of the filament.

A second example of vacuum evaporation applicable to electron tubes is the evaporation of barium metal on the envelope by the flashing of a getter. The barium deposit in a glass tube is visible as a bright metallic mirror in the dome of the envelope. It serves, by virtue of its very great affinity for atmospheric gases, as a chemical pump to remove any gas that may have remained in the tube after exhaust or that may be developed from tube parts during operation. The evaporation of the barium is effected during the last phase of the exhaust process by high-frequency induction heating of a small closed metal loop containing a capsule filled with either pure barium or a high-barium alloy. The flashing temperature is about 850°C and the flashing lasts about 1 second.

A third example is the production of capacitor paper for so-called "self-healing" capacitors by the evaporation of metal onto paper. A continuous jet of metal vapor is directed against a varnished paper strip as it moves past the evaporation source, and a continuous metal film about 1000 \AA thick is deposited. Zinc is frequently used for this purpose. The paper moves at a speed of about 20 ft per second. A vacuum of not more than 10^{-2} mm Hg is sufficient because the dense metal vapor jet prevents intruding gas molecules from penetrating its periphery and thus keeps them from getting between the jet and the paper. This process, which has evap-

oration-rate control and the feature of high-speed motion in a vacuum, is an example of the progress made in vacuum technology in recent years. A detailed description of this process is found in an article by H. G. Wehe.²

A fourth example is the evaporation of a copper pattern onto a phenolic resin sheet to form the basis for a printed circuit. The copper pattern is too thin to be used as deposited and is built up to approximately 0.015 in. by electroplating. In the case of a deposit on plastic, it is often favorable to outgas the surface by preheating, and to drive off the last traces of adsorbed water vapor and gases by means of electron or ion bombardment. A voltage of 2500 volts and a current in the milliamperage range are used for this purpose. Further examples are the manufacture of selenium rectifiers and the application of gold to quartz crystals for frequency-control devices.

Vacuum Melting. The preparation of alloys by melting in a vacuum is in its infancy in the electronics industry, but it is growing in importance. It is a well-known fact that experimental work with vacuum melting of magnetic alloys has been going on for many years. In addition, there is a small group of alloys like chrome-copper, titanium-copper, titanium-nickel, zirconium-silver, magnesium-silver, and magnesium-nickel, which contain relatively large amounts of highly reactive metal additions. Although some of these alloys are still made by conventional air melting, experimental evidence shows that vacuum melting would provide many advantages. Chromium, for instance is difficult to alloy with copper because of its strong tendency to form an adherent oxide skin. The copper has to be heated almost to the melting point of chromium before the latter goes into solution. When melted in vacuum, the chromium addition goes in solution without difficulty as soon as the copper becomes liquid. Some difficulties have been encountered because some high-titanium alloys wet the ceramic crucible and tend to penetrate the walls and run out. A recent advancement has been reported,³ however, to the effect that crucibles made from zirconium oxide mixed with metallic titanium are suitable for such alloys and are not wetted by them.

Cathode-Sleeve Materials

Alloys used for electron-tube cathode sleeves are of an intricate nature and affect the operational properties of the tube as it is manufactured, as well as during operation. Their main ingredient is nickel, with the addition of cobalt, silicon, magnesium, manganese, carbon, tungsten, aluminum, titanium or other elements in various amounts and combinations, most of them in quantities not larger than $\frac{1}{10}$ to $\frac{1}{100}$ of 1 per cent. Because the cathode performance is dependent upon a reduction reaction between these alloying agents and the electron-emissive alkaline-earth oxide coating

which is applied to the cathode sleeve, the amount of these reducing agents and their state of availability in the nickel are important. The commercial nickel alloys which are largely used for this purpose have the serious drawback that their composition is insufficiently controlled for the delicate function they serve in the electron tube. Minute amounts of impurities or a small excess of normal constituents are not significant in stainless steel or other high-nickel alloys for which most nickel is being used. However, these same slight quantities may adversely affect electron tube production. Vacuum melting was initiated to obtain the needed composition control.

At RCA, the production of directly heated filamentary-type cathode alloys has continued successfully for a number of years. Figures 2 and 3 show the vacuum furnace used for this work. Because most cathodes, however, are of the indirectly heated type (which comprises the use of a cathode sleeve over a heater), it can be expected that this field will be attacked next. Experimentation in that direction is going on.

Crucible Materials

Because every crucible melting operation is essentially an act of contamination, and because strict composition control is the prime objective, it is mandatory to obtain crucible materials having sufficient inertness to reduce contamination to a harmless level. Among the available materials

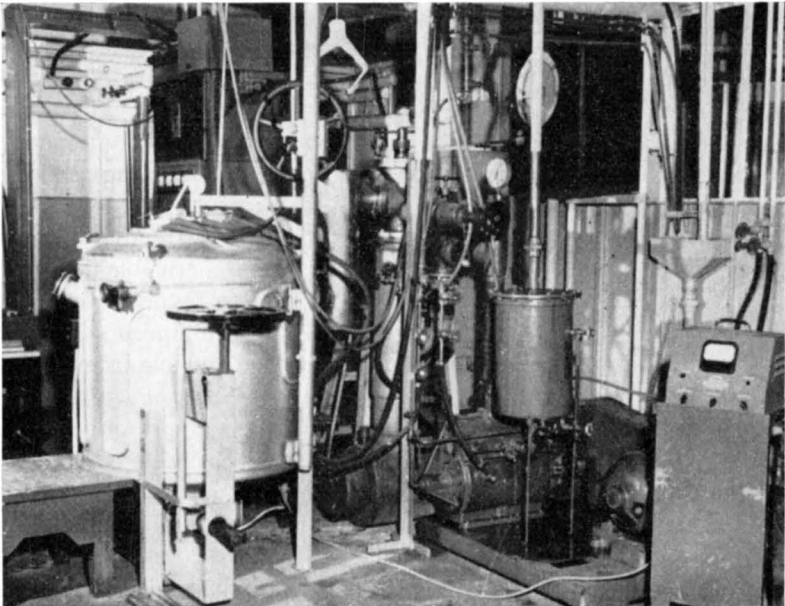


Figure 2. Vacuum induction furnace installation.

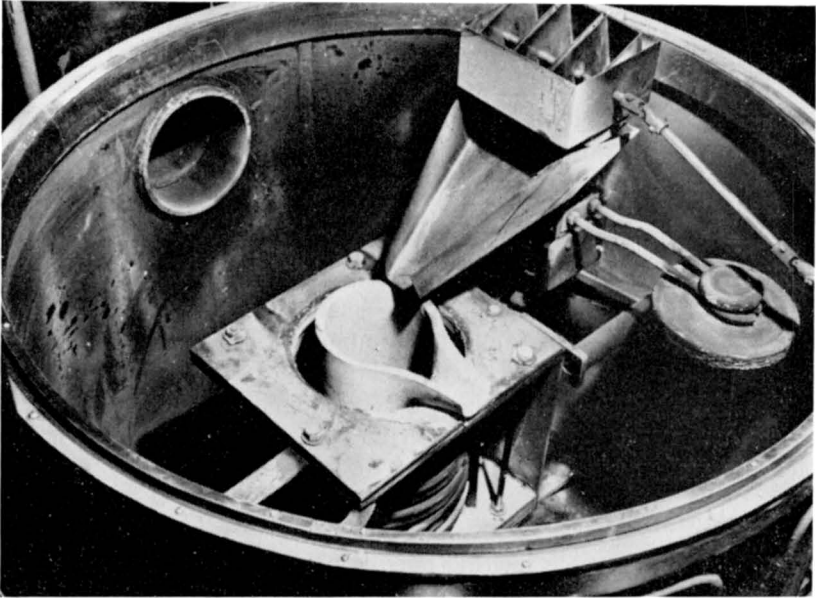


Figure 3. Close-up view of crucible and charging device.

investigated were beryllium oxide, stabilized zirconia, zirconium silicate, aluminum oxide, and magnesium oxide. The first four materials were found to be satisfactory from the point of view of contamination, but magnesium oxide caused magnesium contamination of the order of a few hundredths of a per cent if carbon was added to the melt. It was found that the electrically fused variety of magnesium oxide does not produce this contamination. All materials, however, showed unsatisfactory mechanical properties and crucible life after repeated use.

This problem caused considerable initial trouble and material damage. The first improvements resulted from a change in the crucible design from a flat to a half-spherical bottom, which has a more favorable expansion-contraction pattern. It also appeared necessary to minimize shrinkage of the insulation material which directly supports the crucible from below by a proper choice of materials. Sinter shrinkage of the bottom support causes loss of contact between the crucible bottom and the support and eventually results in failure of the bottom with its various undesirable consequences.

Satisfactory crucible life was obtained by using a lined crucible. It is believed that this method is not too well known because crucible life still seems to be an industry-wide problem. A life of 10 to 20 melts per crucible was recently referred to as a good record in industrial vacuum melting. With a lined crucible, this number can be multiplied tenfold. This

technique involves the use of an ordinary ceramic melting crucible which is installed in the conventional manner by ramming insulating material between it and the high-frequency coil. However, a ceramic lining approximately $\frac{1}{2}$ in. thick is applied to the inside of the crucible in paste form and baked in place by the local application of a high temperature. This lining can easily be removed when it starts to show physical damage and can be replaced without removing the crucible itself, which is a major operation. Relining is also faster and simpler than making a rammed crucible and, because very little material is used, it is simpler and faster to outgas. This procedure also permits the choice of a material which is compatible with the alloy composition even if the crucible is not.

One point concerning crucibles which is of interest in connection with the pumping system is the fact that ceramics generally contain considerable quantities of water. It is not always possible to remove this water by prebaking, particularly when a lining is used. The water will escape under heat in a vacuum and pass through the pumping system. For this reason, it is recommended that a gas ballast control be supplied on the mechanical pump to prevent reduced pumping capacity and oil changes.

Nickel Deoxidation

Because carbon was used for deoxidation of the base nickel in the air-melting procedure, it was also tried first in a vacuum. However, it was found to be too troublesome because spitting and boiling are accentuated by the vacuum and because of the uncertainty of carbon retention.

The problem of deoxidation of the molten nickel has been solved by allowing the nickel to react with hydrogen. Cathode-alloy melts are presently deoxidized by holding the molten nickel at a temperature of approximately 100°C above its melting point in hydrogen, at a pressure of 20 mm Hg for 10 minutes. Figure 4 shows graphically the pressure, temperature, and power-input record of a melting cycle, including the deoxidation process. The mole ratio of hydrogen to nickel in the furnace volume is about 1 to 10, which is a large excess compared to the oxygen content of the nickel. This mole ratio is probably the reason why deoxidation is so complete that, after removal of the hydrogen, solid carbon can be introduced into the melt without the slightest development of gas. If carbon is introduced in a vacuum melt which has already been well deoxidized, boiling and spitting may still occur if the carbon has not been previously outgassed. The carbon may be outgassed by heating in a vacuum to a temperature of approximately 1500°C in a graphite crucible until gas development ceases. The hydrogen-deoxidation procedure is effective and simpler than the method in which hydrogen is pumped through the furnace by continuous introduction and removal. The oxygen content of the result-

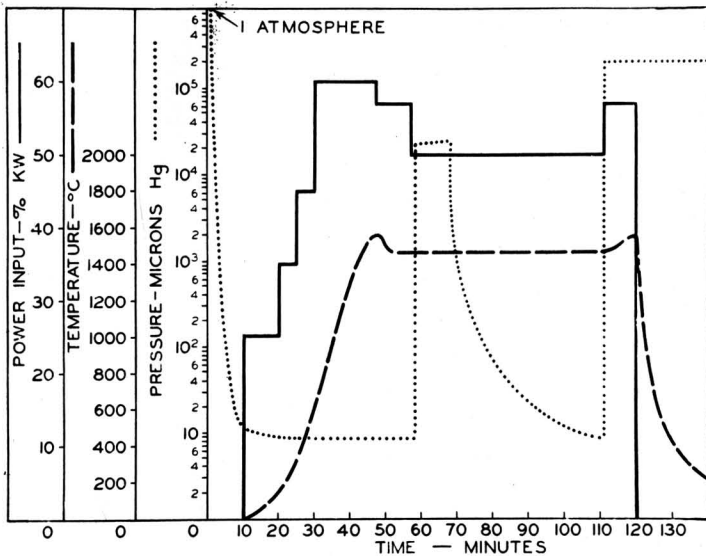


Figure 4. Pressure, temperature and power input record of a melting cycle.

ing cathode material is between one and two orders of magnitude lower than that produced by conventional air melting

Retention of Alloying Additions

As indicated before, the additions for cathode nickel consist mainly of silicon, carbon, manganese, magnesium, tungsten, or cobalt. Because no oxidation losses occur, retention depends mainly on vapor pressure of the addition metal, time between addition and pouring of the melt, temperature during that period, and chemical interaction between alloying constituents. When hydrogen deoxidation was carried out effectively, it was found that silicon, carbon, and manganese can be expected to be retained almost completely if added in quantities up to 0.2 per cent. Tungsten and cobalt show no losses because their vapor pressures are too low. However, magnesium exhibits a considerable loss by evaporation. If added, for instance, in an amount of 0.2 per cent, it will be retained, under a given set of standard conditions, in the amount of 0.04 ± 0.01 per cent. Although it has not been proven conclusively, there is evidence to show that magnesium evaporation is retarded by the presence of carbon in the melt. A similar condition reported in the literature⁴ for manganese has been attributed to association of the two dissolved elements in the molten state.

In addition to improved composition control, another advantage was realized for alloys which are drawn to extremely fine wire sizes, such as the filament alloy used in miniature tubes of the "instant warm-up" type.

These wires have a diameter of 0.001 inch. Drawing them from air-melted material used to be a problem because of the presence of nonmetallic inclusions which caused breakage and high die wear. The change to vacuum melting has resulted in greatly improved wire-drawing conditions and reduced the problem to insignificant proportions.

Conclusions

In conclusion, it can be said that vacuum metallurgy in its relatively short existence has already found numerous applications in the realm of electronic materials. It is to be expected that its usefulness in this field will increase considerably in years to come.

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