

vision channels 2 to 6 and multiplication by 24 covers channels 7 to 13.

In practice, the initial adjustment of the discriminator can be performed very simply when it is in the transmitter with which it is to be used. With the exciter unit under control, the transmitter frequency is automatically adjusted to the value—which makes the dc output of the discriminator substantially zero. The discriminator can then be adjusted by observing the frequency indicated by the direct-reading frequency monitor with which the transmitter is normally equipped. Inductor $L1$ (Fig. 9) is tuned so that the frequency is a maximum; capacitor $C1$ is adjusted so that there is no frequency change when 100 per cent sinusoidal modulation is applied; and $R1$ is adjusted so that the center frequency has the assigned value.

PERFORMANCE

The circuit comprising the oscillator, discriminator, and reactance tube is essentially a system with inverse feedback, wherein the inherent frequency stability of the oscillator is improved by the addition of a feedback loop. A practical figure for the inherent frequency stability of an FM oscillator is 0.1 per cent, and measurements on the exciter unit gave a figure somewhat better than this for normal ambient temperature change, including the change during the warm-up period. With frequency control, the oscillator stability is increased to $0.1/1+A$ per cent, where A is the over-all gain of the feedback loop. It is readily possible to make A so large that frequency variations due to oscillator instability are small compared with the maximum permissible. The measured value of A for the exciter unit described herein was approximately 250, thus making the maximum frequency error due to oscillator instability less than 0.0004 per cent.

The short-period stability of frequency measurement

by the discriminator is determined largely by ambient temperature variation. An average frequency-temperature coefficient of -1.2 parts in 10^7 per $^{\circ}\text{C}$ was measured for the complete discriminator unit in the ambient temperature range 20°C to 70°C . For a normal ambient temperature change of 20°C during warm-up of the transmitter, the change in center frequency is thus 0.00024 per cent.

Several of these FM exciter units have been in service for periods of more than a year and have shown excellent long-period stability. There has been no noticeable frequency drift due to aging or deterioration of components, and the units have not generally required any readjustment during normal operation.

CONCLUSION

It can be concluded that it is quite practical to stabilize the center frequency of a television broadcast aural transmitter by means of a crystal discriminator in which the center frequency is measured by comparing the impedance of a quartz crystal with a reference impedance. The performance of the discriminator is readily amenable to calculation in terms of the circuit parameters, and experimental measurements have confirmed the calculated results. The unit is very simple to build on a production basis, and requires no critical adjustments during testing operation or maintenance.

Use of this crystal discriminator could readily be extended to other applications where an accurate measure of the center frequency of a frequency-modulated voltage is required. One such application for which the discriminator is particularly suited would be the maintenance of a close tolerance on the frequency separation between the visual and aural carriers of a uhf television transmitter, as necessitated by the requirements of intercarrier television receivers.

Nickel Alloys for Oxide-Coated Cathodes*

A. M. BOUNDS† AND T. H. BRIGGS‡, SENIOR MEMBER, IRE

Summary—A survey is presented covering the metallurgical problems and manufacturing methods used in the refining and melting of nickel, and its fabrication into indirectly heated cathode sleeves for electron tubes.

The important role of minor constituent alloys is discussed from both the metallurgical and electronic points of view.

Four of the most important cathode performance characteristics

are defined and the effect of base-metal composition on each one is discussed. The influences of each important element present in cathode nickel alloys are enumerated.

Suggestions are made concerning present and future developmental cathode materials to meet new and more severe demands being placed upon electron tubes.

I. INTRODUCTION

ELECTRON TUBES are notorious for the complexity of their manufacturing operations. The present demand for tube efficiency and reliability makes it desirable to analyze the factors important to achieving these goals. Thus, we can better understand and employ the requisite controls.

* Decimal classification: R331. Original manuscript received by the Institute, August 11, 1950; revised manuscript received, March 2, 1951. The substance of this paper was delivered before Section A of Committee B4-VIII, American Society for Testing Materials, February and June, 1950, meetings.

† Superior Tube Company, Norristown, Pa.

‡ Formerly, Superior Tube Company, Norristown, Pa.; now, Burroughs Adding Machine Company, Philadelphia, Pa.

Few technical products other than electron tubes have ever received as widespread development and use with as little clear understanding of basic theory. A great deal of basic research must still be completed before the mechanism of thermionic emission is explained satisfactorily. One reason for this situation is that many highly specialized skills enter into every part and process of tube manufacture. Another reason is that concise and critical tests on material or process changes are difficult because of the masking effect of the large number of uncontrolled variables.

The oxide-coated cathode assembly is the greatest unknown in the electron tube. It is an aggregate of chemical and metallurgical specialties. The shape and size of the carbonate crystals, the method of coating application, and the exhaust and seasoning schedules are of paramount importance in producing satisfactory results. The cathode base metal plays a secondary role, but it must not be underrated in view of the new and more severe demands now placed upon the electron tubes and ultimately upon the cathode.

A properly chosen base metal of uniform high quality goes a long way in providing greater latitude for cathode spraying and tube-processing tolerances.

Previously, the cathode sleeve was considered primarily as a support for the oxide coating, as a heat transfer medium, and as a portion of the electrical conducting circuit. Any effect of the metal in chemically reducing the coating oxides was only to be considered during initial activation.

Now it is known that the properties of the cathode base metal are important throughout life. The ways in which they enter the tube action are called "performance characteristics."¹ Specifically, they are classified as follows: rate of free barium evolution, rate of activation, rate of sublimation, and degree of interface impedance. They are discussed in detail in Section IV of this paper.

In order to understand cathode action, it is first necessary to review the metallurgy of nickel and the fabrication of cathode sleeves. Then, through consideration of the action of the nickel alloys in conjunction with the coating, it will become evident how the cathode assembly is affected by tube processing and how it enters into tube applications.

II. NICKEL REFINING AND PROCESSING

Compared with other major metals, economic deposits of nickel are quite scarce. Commercially valuable ores are widely scattered in Europe, on New Caledonia in the Pacific, in Venezuela, and in Canada, but there are only a very few major deposits. As is well known, the Sudbury area in Canada is by far the most important, while the New Caledonian ores belonging to France and the Petsamo Mine, now worked by the U.S.S.R., are smaller but significant. The New Caledonian ores are

oxides and chemically basic, while the others are chiefly sulfides and carry varying amounts of cobalt, copper, iron, platinum, palladium, iridium, gold, and silver.

In the Canadian ores the nickel varies from less than 1 to 4½ per cent, and the copper from as little as 0.10 to 3½ per cent. These are smelted to a matte (impure nickel and copper sulfide) and treated with sodium nitrate. When allowed to cool in thimbles the copper matte separates from the nickel matte rather completely, the copper sulfide floating to the top and the heavier nickel sulfides solidifying at the bottom. This is known as the Orford process and its discovery was the key to the commercialization of the Canadian ores.

The "bottoms" (nickel sulfide matte) are separated, crushed, and leached to remove trapped copper and other impurities. The residue is roasted to an impure black oxide of nickel and for the production of pure nickel it is charged into large open hearth furnaces where the oxide is reduced to metal, cast into anodes, and made ready for electrolytic refining.

The electrolytic refining step is very similar to that used for copper and other metals, where the impure nickel anode is gradually dissolved in a sulfuric acid electrolyte as the pure metal is deposited on a cathode starter sheet. During this step the precious metals are removed as slimes and other impurities remain in solution in the electrolyte from which they must be continuously removed. The analysis of a single random sample of electrolytic nickel obtained in 1947 is shown in Table I.

TABLE I

	Electrolytic Nickel	Carbonyl Nickel
	<i>per cent</i>	<i>per cent</i>
Carbon	—	0.07
Copper	0.007	0.001
Iron	0.03	0.013
Manganese	0.0005	0.0005
Sulfur	0.001	0.003
Silicon	0.015	0.016
Magnesium	0.006	0.003
Cobalt	0.44	0.001
Lead	0.003	<0.001

In other countries the nickel may be purified by the Mond process in which carbonyl nickel of the formula Ni(CO)₄ is produced by first reducing roasted (oxidized) matte to metallic form by treatment in producer gas and then retreating in the same gas. Nickel carbonyl is volatile as low as 50°C. When heated above 200°C it decomposes to yield metallic nickel in the form of shot. Since cobalt is not similarly affected by carbon monoxide, carbonyl nickel is free of this sister element. A single analysis of European carbonyl nickel, made in 1947, is shown in Table I.

It is evident that by either method there is available a very pure nickel for melting and processing into cathodes. Up to this point the procedure is not a great deal different from that for other nonferrous metals,

¹ Reports #926 from Electronics Laboratory, Superior Tube Company, December, 1948 to May, 1951.

nor is it a great deal more difficult. However, until 1870 nickel was not considered to be a malleable metal. It readily cracked under small amounts of either hot or cold work. It was the discovery of the magnesium deoxidation process in that year which permitted the melting and casting of nickel and high nickel alloys that could be hot and cold worked. Simple deoxidation with magnesium was not the entire answer since metal produced by this process was still "tender" or "short" (cracked easily during working) below 1,600°F (870°C), and did not permit hot piercing to seamless tubes and similar severe hot working.

In the United States nickel is melted in acid (silica) brick-lined open hearth furnaces of 6- to 20-ton capacity, in carbon arc electric furnaces lined with basic (magnesia) brick of 7- to 20-ton capacity, or in basic refractory-lined high-frequency furnaces holding from 400 to 10,000 pounds. In Europe the melting of such alloys is on a much smaller scale and induction melting is chiefly used. Vacuum melting of nickel containing aluminum for filamentary type cathodes is practiced to a small extent in Europe and such alloys are deoxidized by a small addition of calcium silicide only. Obviously nickel alloys containing magnesium cannot be vacuum-melted because of the volatility of that metal.

According to Mudge,² "The process of malleabilization includes four essentials: (1) deoxidation to remove harmful oxides; (2) degasification to remove carbon monoxide, nitrogen, or hydrogen; (3) fixing of harmful elements; [i.e., sulphur] and (4) no injurious effect from the malleabilizing materials added.

"As far as is known, no single addition element satisfied all four of these requirements. Aluminum will deoxidize, but will not fix harmful elements; calcium will deoxidize and fix sulphur, but an excess of it [even a trace] causes brittleness; phosphorous will convert a harmful element, such as calcium, to a harmless constituent, but will not remove gases; titanium will not provide adequate deoxidation; and magnesium although sufficient for deoxidation and fixation of sulphur will not always provide for adequate degasification, nor will it fix selenium or tellurium completely.

"The treatment for optimum malleability, therefore, requires the use of two or more addition elements . . .

"Treatment of molten nickel with only magnesium gives a sound material that can be hot worked satisfactorily over the temperature range of approximately 1,600 to 2,250°F (870 to 1,235°C). The preferred treatment with small amounts of magnesium, titanium and boron gives a product that can be hot worked at all temperatures from approximately 1,100 to 2,350°F (600 to 1,290°C)."

Since the elements magnesium, titanium, and boron are added specifically for their scavenging effect, the difficulty of control of residual amounts of these ele-

ments must be self-evident.

And yet, present theory of the reducing action of nickel cathode on oxide coatings indicates that the control of residual amounts of these elements and the control of their state of combination with gases, impurities, and each other is the key to control of the "reducing potential" of the cathode alloy. If these functions are not mutually exclusive, they at least present an extremely difficult metallurgical problem and one which cannot be solved by an arbitrary rearrangement of composition limits whenever it is desired to slightly modify the activation characteristics of a cathode nickel. It is truly remarkable that such a degree of uniformity has been attained in the melting and processing of cathode nickel alloys.

But what of the other impurities in cathode nickel? Manganese, iron, copper, and silicon are all present in significant amounts and subject to specification. Manganese appears to enhance considerably the hot-working characteristics of nickel, particularly large masses of coarsely crystalline metal. For this reason manganese is purposely added to nickel when it is to be cast into large ingots, and a compromise must be arranged between the requirements of the metal producer and those of the electronic engineer with respect to this element. As with most compromises, neither can be completely satisfied.

Economic considerations require the reworking of a certain amount of scrap nickel into each new heat and some iron may be derived from this source. In addition, the manganese and other alloy additions carry small amounts of iron, so there is a practical lower limit below which iron cannot be reduced economically. Similarly, copper is derived from the original electrolytic nickel and from scrap, but little if any comes from the alloy additions. Nickel may be melted to closer limits and greater purity in 600- to 12,00-pound heats than in larger quantities, but such small heats would preclude the cathode melt approval method of production tube testing which is presently used by the electron tube manufacturers.

Whenever metal having an affinity for silicon is melted in siliceous refractories or under siliceous slags, chemical laws indicate a small amount of reduction of silicon to the metal. Given fixed furnace practices, it is evident that a relatively constant silicon residual will be present and it is not even necessary to try to control it. On the other hand, controlled additions of silicon to a nickel melt present a different problem, and this is a reason that small contents of silicon of the order of 0.02 per cent in nickel remain constant from heat to heat while larger quantities show variability.

Wise has reported the analyses of alloy additions for small experimental melts of nickel to be approximately as follows in Table II.³

² W. A. Mudge, "Non-ferrous melting practice," Institute of Metals Division, Symposium Series, American Institute of Mechanical Engineers, New York, N. Y.; 1946.

³ E. M. Wise and R. H. Schaefer, "The Properties of Pure Nickel," Reinhold Publishing Corp., New York, N. Y., September to December, 1942.

TABLE II

Element	Form of Addition	Analysis
Mg	Ni Mg	68.3 per cent Mg, 31.5 per cent Ni, 0.16 per cent Fe
Si	Ni Si	24 per cent Si, 74.3 per cent Ni, 0.80 per cent Fe
Mn*	Electrolytic Mn	97.3 per cent Mn, 0.74 per cent Si, 1.5 per cent Fe

* (Note: Electrolytic manganese of 99.9 per cent purity is now available.)

These addition alloys are about as pure as can be commercially obtained, but it is evident that they do carry very small amounts of unwanted impurities.

The processing of cathode nickel ingots into fine tubing and strip is lengthy and in general believed to be without great effect on cathode characteristics providing the methods remain constant. However, they will be very briefly reviewed:

Seamless Tubing

Nickel ingots are mechanically overhauled to remove approximately $\frac{1}{4}$ inch from each surface, heated to approximately 2,250°F (1,135°C) and hot forged to billets. These are again machined, cut into short lengths, and reheated for extrusion. Extruded tubes, approximately $3\frac{1}{4}$ inches outside diameter (see Fig. 1), are annealed in a reducing atmosphere produced from natural gas,

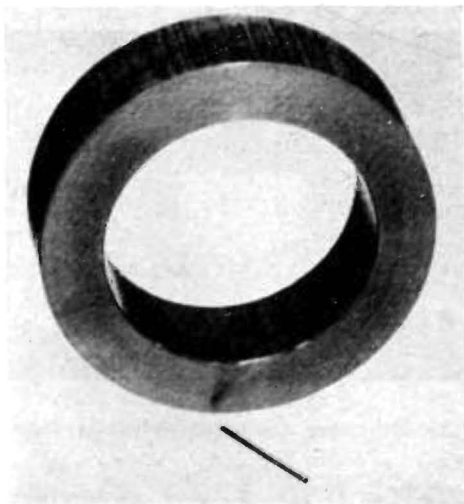


Fig. 1—A hot-finished seamless cathode nickel alloy tube, and seamless cathode drawn from it.

pickled, and again ground to remove defects. From this point onward they are cold reduced in tube-reducing machines and by bench drawing with intermediate annealing in controlled atmosphere. For the larger tubes the atmosphere is that produced from the partial burning of natural gas which is free of sulphur, while smaller tubing is annealed in cracked ammonia.

In cold drawing, tubing is drawn through tungsten carbide dies and over hardened and polished steel mandrel rods or fixed tungsten carbide plug mandrels. Lubricants vary from heavy viscous oils to light petroleum products, and care must be exercised constantly to prevent their contamination by sulphur or chlorine.

In "rod drawing" an expanding operation between hardened steel rolls follows each draw in order to free the tube from the mandrel rod. After degreasing in stabilized trichlorethylene the tubing is annealed continuously through muffle furnaces in a cracked ammonia atmosphere from which residual ammonia has been carefully removed. The temperature may vary from 1,450 to 1,600°F (790 to 870°C) depending upon tube size, prior cold reduction, and other detail fabricating requirements.

After as many as fifteen or more redrawing and annealing operations the tubing is finished in the hard temper, straightened, inspected, and gaged. It is then

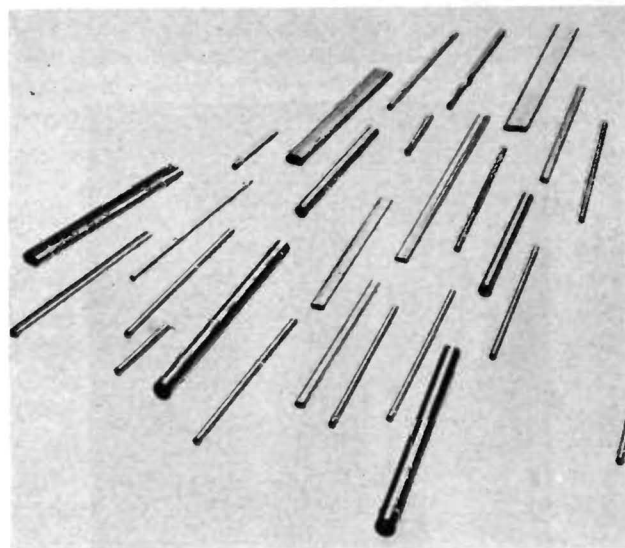


Fig. 2—Variety of seamless and lockseam special nickel-alloy cathodes.

ready for shipment in random lengths or for cutting and embossing as a finished part. The final operation is always a thorough degreasing treatment in trichlorethylene, and sometimes other solvents as well. (See Fig. 2.)

Strip for Seamed Cathodes

Ingots must be carefully prepared for strip as for tubing, and approximately $\frac{1}{4}$ inch is removed from all surfaces before the nickel ingots are heated to 2,250°F (1,232°C) and forged to square blooms. (Figs. 3 and 4.) These blooms are again chipped and ground, reheated to about 2,150°F (1,176°C) and hot rolled to billets. There follows another overhauling operation and a further reheating for hot rolling to coiled strip approximately $\frac{1}{8}$ inch thick. (See Figs. 5 and 6.)

The coiled strip is annealed in a reducing atmosphere, pickled and cold rolled to approximately 1/16 inch thickness. Such strip may be annealed and slit for conversion into welded tubing which, after welding by the inert arc process, is processed exactly the same as seamless tubing. For seamed cathodes, the strip is rerolled many times and reannealed in cracked ammonia atmospheres until reduced to a thickness of approximately



Fig. 3—Ingot of cathode nickel (499 alloy) being lathe-turned before hot rolling (Courtesy of Driver-Harris Company).

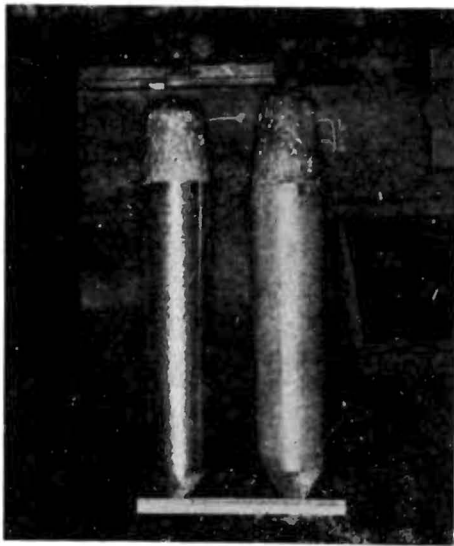


Fig. 4—300-pound ingots of cathode nickel (499 alloy) as cast, and after lathe turning to remove surface imperfections (Courtesy of Driver-Harris Company).

0.002 inch and in just the right temper for forming into cathodes. (See Fig. 7.)

Effects of Processing

In the working of nickel to cathode form, by whatever process, there are several possibilities of slightly changing the original composition or state of oxidation of the reducing elements. Contamination with sulphur would render the nickel unfit for further working, so there is little likelihood that such contamination could ever reach the cathode user. There is a slight and measurable increase in surface-iron content because of the many contacts with steel tools. This can be and is removed by acid pickling close to finish. Some oxidation of such components as magnesium, silicon, titanium, and the like inevitably occurs at the surfaces of the nickel tube or strip even though highly reducing furnace atmospheres are used. Care must be used to keep such atmospheres to dew points in the neighborhood of -40°C or lower, but even so, small air infiltrations into the furnaces raise the dew point of the actual

furnace atmosphere sufficiently to cause some oxidation of surface silicon and magnesium. This is one reason why electropolishing and similar surface stripping methods applied to cathodes often improve their speed of activation.

Carbon content is also slightly changed. The original carbon content of most of the cathode alloys will run from 0.05 to 0.12 per cent with some of the special passive alloys going as high as 0.25 per cent. The many

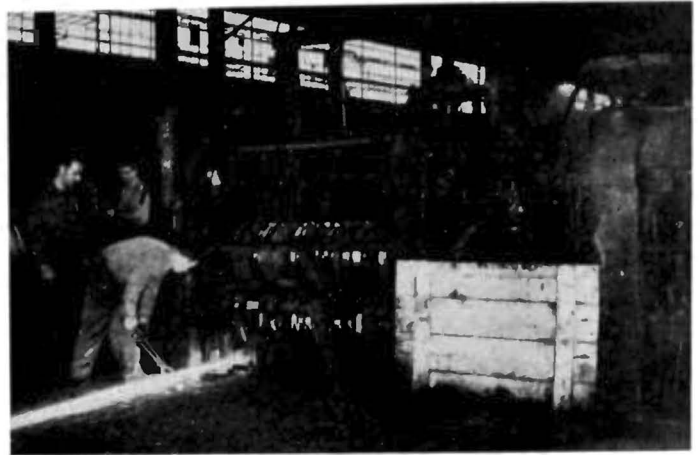


Fig. 5—Hot rolling of nickel alloy rods for strip as used for lockseam cathodes.

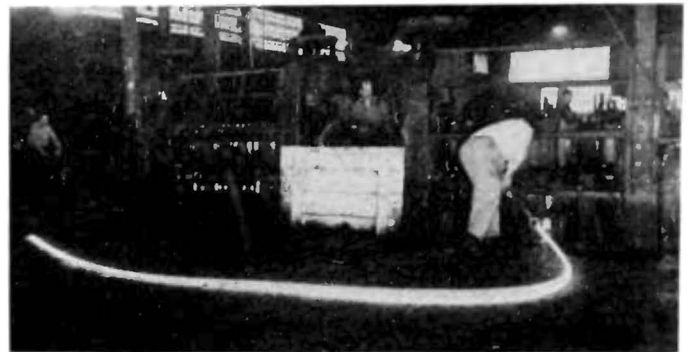


Fig. 6—Further hot rolling of nickel-alloy rod as shown in Fig. 5.

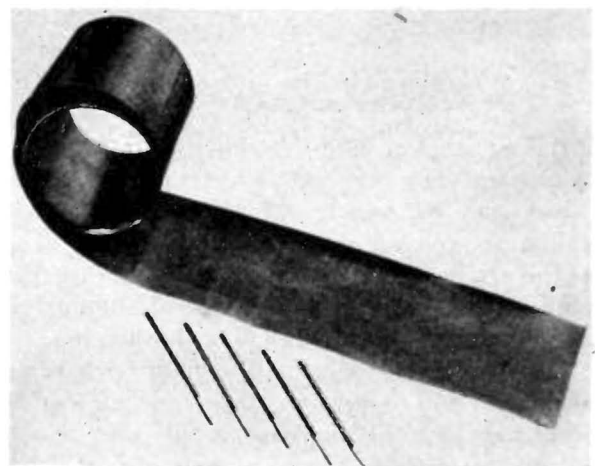


Fig. 7—0.002-inch thick cathode nickel-alloy strip and integral tab lockseam cathodes made from it.

successive anneals in highly reducing hydrogen atmospheres and the purposely applied decarburizing treatments in the case of "passive" alloys reduces carbon content to the neighborhood of 0.03 per cent to 0.05 per cent in the finished product. Little, if any, changes in cathode characteristics have been definitely shown to be caused by a small change in carbon content.

The Role of Reducing Elements from the Metallurgical Standpoint

The primary metallurgical reasons for the inclusion of various reducing or deoxidizing elements in nickel have been briefly explained. The metallurgist no doubt approaches the rôle of these elements in cathode activation from a somewhat different standpoint than does the physicist or electronic engineer.

There is a widespread opinion both in the United States and abroad that magnesium, silicon, and similar elements which can reduce the coatings are the primary source of emissive activity. Practically all of the recent work in this country has been on the basis of this hypothesis, and there is a long list of research papers which might be cited in support of the theory.

There are good reasons for separating the effects of reducing elements upon the initial activation of the cathode from their effects on emission properties during life. One investigator⁴ believes that "active" nickel and "pure" nickel approach each other but do not actually coincide in efficiency as a base metal for an oxide cathode during life. If this is true, the effects of reducing elements would be chiefly in the direction of rapid activation which is of great commercial interest. Of course they also have an effect on interface impedance and evaporation rate. Consideration of the reducing elements as initial activators only would also explain the successful use of "passive" alloys in commercial electron tubes by some producers, while others deem the use of more active alloys to be essential for the proper operation of the same tube.

Assuming that the reducing elements contained in the immediate surface of the metal cathode are converted to their oxides during the activation cycle, the supply of these elements to the surface becomes dependent upon the rates of their diffusion in nickel. These diffusion rates for the different elements are dependent upon temperature, concentration, the melting point of the solute element, atomic size compared with interatomic distance in the solvent lattice, degree of solubility and by the peculiar and often anomalous effects of the presence of other elements. Knowledge of diffusion rates of the various constituents in complex alloys is still somewhat meager. A fundamental discussion of the subject may be found in the literature.⁵

Whether, under all of the conditions for diffusion noted above, a continuous supply of reducing elements

is available at the surface of the cathode after initial activation is being investigated. In this connection it is interesting to note that a German patent indicates that plating of the inside surface of a cylindrical cathode with pure nickel effectively reduces emission in the direction of the heater, thus increasing heater-cathode resistance. Although the nickel deposit is extremely thin, it would appear that the reducing elements do not diffuse through the coating sufficiently during life to re-establish the normal emission level of the inside surface of the unplated cathode. If this be true, then the concentration of activating elements on and near the surface of the metal is the only consideration of significance. However, this concept is complicated by the known fact, mentioned above, that the highly reactive elements near the surface of the cathode are often already combined with oxygen, nitrogen, or other elements when the cathode is put into service. The concept is supported, however, by a German investigation⁴ which showed no detectable loss of magnesium in the cathode base metal during life. This same investigator showed a very considerable diffusion of barium into the base metal, approaching the limit of solubility of that element in nickel. (More recent research in this country has indicated magnesium loss of upwards of 30 per cent from the cathode during life.)

There have been many reports of electrical leakage and other troubles which presumably were caused by evaporation of such elements as copper, iron, manganese, and magnesium from the cathode under the conditions of operation of a vacuum tube. It would appear that after initial evaporation of these elements from the surface (assuming that they are not oxidized or otherwise chemically combined) their evaporation is directly dependent upon their rates of diffusion, which, in turn, are dependent upon the number of factors enumerated above. Two chemical laws are of interest in this respect: The vapor pressure of an alloy will be governed *in part* by a law analogous to Dalton's law of partial pressures,⁶ thus: "*The total vapor pressure of an alloy is equal to the sum of the partial vapor pressures of its constituents, but the partial pressure of each component of the alloy is lower than the normal vapor pressure which the element would exert if it were not contained in an alloy.*" According to Raoult's law, as applied to dilute solutions, the vapor pressure of the solution is lower than that of the pure solvent by an amount which is proportional to the concentration of the solute.

That the cathode nickel alloys do not rigidly conform with these laws has been indicated by a number of experiments which are still in progress in the authors' laboratories. For instance, the rate of evaporation of nickel from a very pure cathode seems to be less than the rate from a cathode containing more of the alloying elements.

⁴ Unpublished data.

⁵ R. F. Mehl, "Diffusion in solid metals," *Trans. AIEE*, vol. 122, pp. 19-27; 1936.

⁶ Allison Butts, "A Textbook of Metallurgical Problems," McGraw-Hill Book Co., Inc., New York, N. Y.; 1932.

If one ignores diffusion constants, which is evidently unwarranted, and also any chemical combination of the alloying elements with nickel and with each other, which is just as unwarranted, one can rather easily calculate the vapor pressures of a series of elements commonly found in cathode nickel from vapor pressure data found in the literature. The difficulty lies with the credibility of the vapor pressure data in the temperature range in which we are interested. Based on vapor pressure data published by Espe and Knoll,⁷ Kelley,⁸ and Dushman,⁹ such calculations have been made for a heat of #220 (normal alloy) cathode nickel which has been used for the past five years as a reference standard by Section A of Sub-Committee VIII, Committee B-4 of the ASTM. That is Superior Tube Company melt #66, International Nickel Company heat #N-6564A. These calculations appear in Tables III and IV, and may form a useful reference in checking the casual and sometimes uninformed statements which have been made concerning evaporation from vacuum-tube cathodes. Variations in cathode-operating temperatures in commercial vacuum tubes appear to be larger than suspected, and may be the cause of much of the evaporation trouble reported.

In this discussion we have ignored the effects of intermetallic compounds formed between the various elements present in cathode nickel alloys. That such compounds exist, and that they have a real effect upon "reducing potential" and evaporation characteristics is not to be doubted. Silicon combines with nickel to form the intermetallic compound Ni_3Si which is stable at room temperature. Similarly, nickel forms compounds with manganese, magnesium, boron, aluminum, and titanium to mention only a few. The reducing elements of chief interest in cathode nickels, magnesium and silicon, form a compound Mg_2Si which in the pure form is liquid just slightly above the operating temperature of a cathode. Copper forms numerous compounds with silicon and magnesium and the possible intermetallic compounds between all of the elements present are exceedingly numerous. Each such compound displays a free energy different from the elements which compose it; each displays its own peculiar melting point and vapor pressure characteristics; each displays its own characteristic diffusion rate. A really thorough study of the "performance characteristics" of cathode nickel alloys will include all of the diverse properties which have been mentioned, and probably others yet to be isolated.

III. OXIDE-COATED CATHODES

Cathode sleeves are conventionally spray-coated with mixed crystals of $Ba \cdot Sr \cdot CO_3$.¹⁰ Frequently, a

⁷ W. Espe and M. Knoll, "Werkstoffkunde der Hochvakuumtechnik," Verlag von Julius Springer, Berlin, Germany; 1936.

⁸ K. K. Kelley, Bureau of Mines Bulletin #383; 1935.

⁹ S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y.; 1948.

¹⁰ E. G. Widell and R. A. Hellar, "Effect of coating composition of oxide-coated cathodes on electron emission," *Jour. Appl. Phys.*, vol. 21, p. 1194; November, 1950.

small percentage of $CaCO_3$ is added. During exhaust the coating is decomposed to the corresponding oxides, and mixed $Ba \cdot Sr \cdot Ca \cdot O$ crystals are slowly formed during activation or "seasoning." The cathode assembly is then ready to deliver copious amounts of free electrons when operated at about $825^\circ C$.

The cathode structure is generally conceived as consisting of several strata (Fig. 8)¹¹ The estimated potential gradients are graphed below the respective layers.

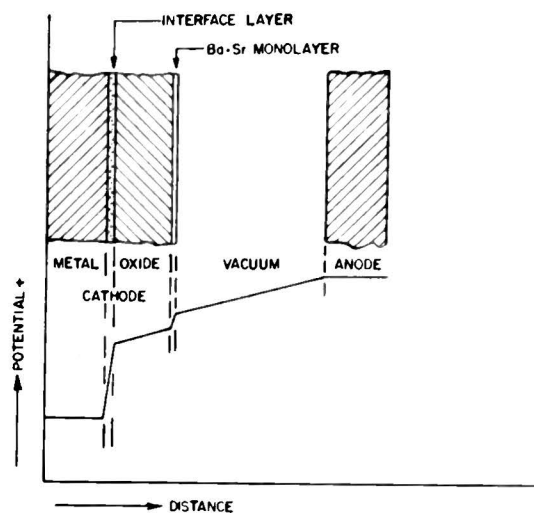


Fig. 8—Schematic view through a diode tube with potential distribution approximation.

The free $Ba \cdot Sr$ layer on the surface of the coating is constantly being depleted by evaporation and by chemical recombination. It must constantly be reformed to provide a low work function which, in turn, allows ready liberation of free electrons.

Ba evaporates from this monolayer more readily than Sr at operating temperatures. It deposits upon the grid wires to cause grid emission. The evaporation energy or temperature of Sr on SrO is lower than that for Ba on BaO . However, for the Ba, Sr layer in $BaO \cdot SrO$ mixed crystals the Ba apparently boils off more easily.

The energy of the electron beam is believed capable of decomposing films on positive electrodes.¹² These are fundamentally $Ba \cdot O$ compounds evolved during coating decomposition and activation. When the SrO^{--} negative ions are liberated by the electron beam energy they react easily to form compounds with the nearby layer of $Ba^{++} \cdot Sr^{++}$, reducing the activity of the cathode surface layer. Any other chemically active gases present in the tube also can be "gettered" by free Ba . These are the most serious causes for fluctuating and slumping tube characteristics.

The depletion of free Ba through evaporation and

¹¹ R. Loosjes and H. J. Vink, "Distribution of potential in the coating of an oxide during a pulse of great current density," *Le Vide*, vol. 5, p. 731; January, 1950.

¹² J. Cardell, et al., "Fundamental Research on Raw Materials Used for Electron Emissivity on Indirectly Heated Cathodes," Reports for ONR Contract N7 onr-389.

gettering action must be balanced by reactivation. This is partially controlled through correct selection of the base alloy. For long and reliable tube operation there is a premium upon the best possible vacuum and the cleanest metal mount parts. Unless these conditions are observed, there is a large uncontrolled variable present.

Obviously, means for regenerating the surface Ba layer of the coating must be provided during tube life. This is accomplished in part by the reducing action of certain elements in the cathode base metal.

The ASTM cathode committee¹² has classified cath-

¹² A.S.T.M. Specification B239-49T.

TABLE III

MAXIMUM VAPOR PRESSURES OF METAL COMPONENTS OF MELT 66, INCO #220 ALLOY, AT 800, 900, AND 1,000° BY 3 DATA SOURCES: DUSHMAN,⁹ ESPE AND KNOLL,⁷ AND KELLEY⁸

Melt 66	at %	Dushman	Espe & Knoll	Kelley
800°C				
		<i>mm Hg</i>	<i>mm Hg</i>	<i>mm Hg</i>
Mg	0.09	40,000. × 10 ⁻⁶	30,000. × 10 ⁻⁶	20,000. × 10 ⁻⁶
Ca	0.0004	3. × 10 ⁻⁶	3. × 10 ⁻⁶	3. × 10 ⁻⁶
Mn	0.11	0.14 × 10 ⁻⁶	0.1 × 10 ⁻⁶	0.17 × 10 ⁻⁶
Al	0.01	0.0002 × 10 ⁻⁶	0.00003 × 10 ⁻⁶	0.007 × 10 ⁻⁶
Ni	98.54	0.00008 × 10 ⁻⁶	0.008 × 10 ⁻⁶	0.001 × 10 ⁻⁶
Cu	0.02	0.00002 × 10 ⁻⁶	0.00001 × 10 ⁻⁶	0.00004 × 10 ⁻⁶
Si	0.06	4. × 10 ⁻¹²	4. × 10 ⁻¹²	0.003 × 10 ⁻¹²
Cr	0.0009	3. × 10 ⁻¹²	0.01 × 10 ⁻⁶	0.8 × 10 ⁻¹²
Fe	0.07	0.7 × 10 ⁻¹²	7. × 10 ⁻¹²	3. × 10 ⁻¹²
Ti	0.04	0.3 × 10 ⁻¹²	no data	no data
B	0.02	0.3 × 10 ⁻¹²	no data	no data
Co	0.74	0.078 × 10 ⁻¹²	no data	no data
C	0.29	500. × 10 ⁻²⁰	16. × 10 ⁻²⁰	0.0004 × 10 ⁻²⁰
900°C				
Mg		200,000. × 10 ⁻⁶	90,000. × 10 ⁻⁶	80,000. × 10 ⁻⁶
Ca		15. × 10 ⁻⁶	15. × 10 ⁻⁶	14. × 10 ⁻⁶
Mn		1.9 × 10 ⁻⁶	1.4 × 10 ⁻⁶	1.8 × 10 ⁻⁶
Al		0.003 × 10 ⁻⁶	0.0007 × 10 ⁻⁶	.08 × 10 ⁻⁶
Ni		0.005 × 10 ⁻⁶	0.2 × 10 ⁻⁶	.05 × 10 ⁻⁶
Cu		0.0005 × 10 ⁻⁶	0.0004 × 10 ⁻⁶	.0008 × 10 ⁻⁶
Si		0.0002 × 10 ⁻⁶	0.0002 × 10 ⁻⁶	.3 × 10 ⁻¹²
Cr		0.00008 × 10 ⁻⁶	0.06 × 10 ⁻⁶	.00002 × 10 ⁻⁶
Fe		0.00003 × 10 ⁻⁶	0.0001 × 10 ⁻⁶	.00009 × 10 ⁻³
Ti		9. × 10 ⁻¹²	no data	no data
B		10. × 10 ⁻¹²	no data	no data
Co		4. × 10 ⁻¹²	no data	no data
C		500. × 10 ⁻²⁷	200. × 10 ⁻²⁷	1,800. × 10 ⁻²⁷
1,000°C				
Mg		500,000. × 10 ⁻⁶	300,000. × 10 ⁻⁶	300,000. × 10 ⁻⁶
Ca		60. × 10 ⁻⁶	50. × 10 ⁻⁶	50. × 10 ⁻⁶
Mn		10. × 10 ⁻⁶	10. × 10 ⁻⁶	10. × 10 ⁻⁶
Al		0.03 × 10 ⁻⁶	0.01 × 10 ⁻⁶	.6 × 10 ⁻⁶
Ni		0.1 × 10 ⁻⁶	3. × 10 ⁻⁶	1. × 10 ⁻⁶
Cu		0.008 × 10 ⁻⁶	0.006 × 10 ⁻⁶	0.01 × 10 ⁻⁶
Si		0.003 × 10 ⁻⁶	0.004 × 10 ⁻⁶	0.00002 × 10 ⁻⁶
Cr		0.001 × 10 ⁻⁶	0.3 × 10 ⁻⁶	0.0003 × 10 ⁻⁶
Fe		0.0006 × 10 ⁻⁶	0.003 × 10 ⁻⁶	0.002 × 10 ⁻⁶
Ti		0.0002 × 10 ⁻⁶	no data	no data
B		0.0004 × 10 ⁻⁶	no data	no data
Co		0.0001 × 10 ⁻⁶	no data	no data
C		200. × 10 ⁻²¹	300. × 10 ⁻²¹	0.002 × 10 ⁻²¹

TABLE IV

SATURATED VAPOR PRESSURE AT 800°C OF ELEMENTS COMMONLY USED IN CATHODE NICKEL ALLOYS, ACCORDING TO DATA PUBLISHED BY DUSHMAN, KELLEY, AND ESPE AND KNOLL

Element	Dushman	Kelley	Espe & Knoll
	<i>mm Hg</i>	<i>mm Hg</i>	<i>mm Hg</i>
Mg	410,000. × 10 ⁻⁴	240,000. × 10 ⁻⁴	280,000. × 10 ⁻⁴
Ca	7,400. × 10 ⁻⁴	7,200. × 10 ⁻⁴	7,000. × 10 ⁻⁴
Mn	1.3 × 10 ⁻⁴	1.6 × 10 ⁻⁴	*1.1 × 10 ⁻⁴
Cr	0.0035 × 10 ⁻⁴	0.00086 × 10 ⁻⁴	*13. × 10 ⁻⁴
Al	0.027 × 10 ⁻⁴	1.2 × 10 ⁻⁴	0.0056 × 10 ⁻⁴
Cu	0.001 × 10 ⁻⁴	0.0024 × 10 ⁻⁴	0.0006 × 10 ⁻⁴
Fe	0.001 × 10 ⁻⁴	0.0038 × 10 ⁻⁴	0.01 × 10 ⁻⁶
Si	0.0066 × 10 ⁻⁶	0.000004 × 10 ⁻⁶	*0.0071 × 10 ⁻⁶
Ni	0.000085 × 10 ⁻⁶	0.0015 × 10 ⁻⁶	0.0080 × 10 ⁻⁶

Dushman's values were obtained by calculation from his recommended constants. Kelley's values were mathematically extrapolated from range 0.076 to 760 mm. Hg. Espe and Knoll values were taken from a plotted curve except for mathematical extrapolation for starred values.

ode alloys as "passive," "normal," or "active," depending upon the rate at which the reducing agents of the base metal react with the oxide coating. Table I summarizes the composition of the presently available commercial cathode alloys.

To obtain the designed level of electron emission with long life and without grid emission requires a careful balance between the reducing activity of the cathode, and the evolution of "poisons" from other tube parts.

The important alloy reducing agents presently used are Mg, Al, Si, W and C. In reacting with BaO they produce compounds at the core-coating interface.^{1,12,14,16}

White¹⁶ has reported a thermodynamical analysis of some oxide cathode reactions. He shows that at 1,273°K the rate of BaO loss by dissociation to gaseous products ($Ba^{++}(g) + O^{--}(g)$) is negligible compared to the loss of BaO molecules by evaporation. Consequently, to obtain Ba^{++} ions requires the BaO to be broken down by chemical reduction. SrO and CaO can thermally decompose theoretically to a slight extent. However, in practice, traces of oxygen inhibit this reaction. Therefore, they too must be chemically reduced.

The following tabulation (also from White¹⁶) shows the free energy in Kilocalories which must be added at a given temperature (1,073°K) to obtain the products shown for these typical oxide cathode reactions:

	Kilocalories
$2BaO(s) = 2Ba(g) + O_2$	255
$2SrO(s) = 2Sr(g) + O_2$	254
$2CaO(s) = 2Ca(g) + O_2$	280
$BaO(s) + H_2 = Ba(g) + H_2O$	82
$BaO(s) + CH_4 = Ba(g) + CO + 2H_2$	73
$BaO + Ni(s) = Ba(g) + NiO(s)$	93
$BaO(s) + C(gr) = Ba(g) + CO$	78
$2BaO(s) + Si(s) = 2Ba(g) + SiO_2(l)$	102
$3BaO(s) + Si(s) = 2Ba(g) + BaSiO_3(s)$	77
$BaO + Mg(g) = Ba(g) + MgO(s)$	2

It is generally being found that those compounds remaining at the interface have semi-conductor properties and show an equivalent electrical circuit impedance. The resistance value may be almost zero or build up to hundreds of ohms. The capacity has a value less than a microfarad. These are dependent upon the composition, previous history of the cathode, and circuit application of the tube.¹⁷⁻¹⁹

By X-ray diffraction analysis some of the interface compounds have been identified as MgO, Ba_2SiO_4 ,

TABLE V

COMPOSITION OF U. S. COMMERCIAL CATHODE ALLOYS¹³
(Maximum per cent by weight, unless range is shown)

A.S.T.M. Grade	Cu	Fe	Mn	Mg	Si	Ti
	(Active Alloy Type)					
1	0.20	0.20	0.20	0.01-0.10	0.12-0.20	0.02
2	0.04	0.10	0.05	0.01-0.10	0.12-0.20	0.01
3	0.20	0.20	0.20	NS	0.15-0.25	NS
4	0.04	0.05-0.10	0.10	0.01	0.15-0.25	NS
5	0.04	0.05-0.10	0.10	0.05-0.15	0.05-0.15	NS
6	0.04	0.05	0.02	0.01	0.15-0.25	NS
	(Normal Alloy Type)					
11	0.02	0.02	0.02	0.01-0.10	0.01-0.05	NS
	(Passive Alloy Type)					
21	0.04	0.05	0.02	0.01	0.01	NS

NS = not specified.

Normally: S < .005 per cent.

C = 0.01 per cent per 0.001 inch thickness of nickel sleeve wall.

$BaWO_3$, $BaWO_4$, or even Ba_3WO_6 . The thickness varies widely, but is of the order of 10^{-4} cm. It is possible to measure the interface impedance by pulsed techniques and to construct equivalent RC circuits which can be evaluated.

Through operation of tubes under cutoff conditions, with no cathode current drain, and for several hundred hours, the interface resistance buildup can be accelerated. This characteristic is of particular importance for application in computers and similar devices where there may be long stand-by periods of operation followed by pulse currents. The pulses are distorted or attenuated when the interface impedance is high.

Experience has shown that the silicon interface compounds are most likely to produce a high resistance. Aluminum, if held to relatively low values does not seem to develop a resistance.¹ None at all has been found when Mg, W, C are employed.

Another cathode characteristic is the tendency of nickel alloys to sublime at activation or operating temperatures. Metal ions are released from the cathode which condense upon cooler portions of the tube, resulting in electrical leakage, noise, or shifts in contact potential.^{1,12} It is believed that sublimation occurs into the coating as well as into the vacuum directly from uncoated areas of the sleeve. This is particularly important in the disc cathodes used in television picture tubes, where the coated area is unusually small.

It has been shown that Mg sublimates readily and is the element causing most leakage and tube noise. As pointed out earlier, Mg is also a powerful reducing agent upon the oxide coating. Thus, as it sublimates away from the cathode, it is no longer available to regenerate free Ba, and the cathode emission falls off; the useful tube life may be shortened.

Analysis of the bulb deposits from thermionic cathodes shows that at operating temperatures (825°C) it is predominantly Mg which sublimates in significant quan-

¹⁴ D. A. Wright, "Electrical conductivity of oxide cathode coatings," *Phys. Rev.*, vol. 78, p. 355; May 1, 1950.

¹⁵ A. S. Eisenstein, "Oxide Coated Cathodes," *Advances in Electronics*, Academic Press; 1948.

¹⁶ A. H. White, "Application of thermodynamics to chemical problems involving the oxide cathode," *Jour. Appl. Phys.*, vol. 20, p. 856; September, 1949.

¹⁷ A. S. Eisenstein, "The Leaking-Condenser Oxide Cathode Interface," ONR Technical Report #2, N7 onr-292; September, 1950.

¹⁸ L. S. Nergaard, "Cathode Impedance and Tube Failure," Report of 10th Annual Conference, Physical Electronics, MIT; March, 1950.

¹⁹ J. F. Weymouth, "Deterioration of Oxide Cathodes under Low Duty Factor Operation," Report of 10th Annual Conference, Physical Electronics, MIT; March, 1950.

tity.¹ At somewhat higher temperatures Mn and Cu appear, and then large amounts of Fe, Co, Ni. The Mg, Mn, Cu are present in greater proportions in the deposit than in the original sleeve. The related elements Fe, Co, Ni are in the same proportions as originally. At higher temperatures (about 1,000°C) when the nickel contains very little Mg, Mn, Cu, then Ni and Co do not sublime appreciably. This offers the interesting possibility that presence of impurities provides some sort of mechanism for boiling off the Ni and Co. The process is probably quite complex and a theory has not yet been advanced.

In compensation for the loss of Mg, other reducing agents are available to the cathode coating from other tube parts. This has only recently been shown, and is not yet generally appreciated.^{1,12} Migration occurs primarily from plates and getters, but may involve micas, lead wires, glass, and other parts. Spectrochemical analyses show reduction in Mg, Si, Cu from such tube parts, and a buildup of these elements upon the cathode can best be detected if it is a "passive" (high purity) nickel alloy.

The design and production of tubes requires the proper choice of all materials to obtain control of electron emission over a long life period.

Fig. 9 is a time-temperature relationship for obtaining a given amount of evaporated metal for a very pure and for a commercial grade of cathode nickel ("passive" and "normal"). The normal operating temperature for cathodes is at the knee of this curve, and hence changes in temperature are most critical. A change of 70°C will alter the time for a fixed amount of sublimation by about one order of magnitude. Temperature control is seen to be much more effective than differences between most cathode alloys. This is especially true for uncoated cathode sleeve areas. In cathode ray tubes such sublimation deposits upon ceramic insulators cause loss of grid control, resulting in tube failure.

The following data have been obtained on a wide range of cathode alloys. Comparisons were made between cathodes sleeves removed from standard diodes after 5,000 hours of life and identical sleeves which had not been mounted. Only the central portion of the metal under the oxide coating was exposed to the spectrograph arc.

Element	Per Cent Loss	Valid Over Composition Range—Percentage
Co	0	0.1–0.7 by weight
Ti	0	0.002–0.03
Si	10	0.008–0.042
Mg	0	0.005 (a possible measure of free Mg,
Mg	30	0.04 capable of sublimation)
Cu	70	0.007–0.022
Mn	60	0.005 (probably due to compounds)
Mn	90	0.11
Fe	50 GAIN	0.0–0.02 (migration from getter?)

Each element in the base metal has a migration rate dependent upon the atom size, concentration, solubility, chemical activity, and sleeve temperature. Thus the processes inside the cathode metal are merely those

normal to metallurgy for alloys at elevated temperature. Use is made of these same properties once the elements reach the metal surface. The molecules either react in the desired manner to keep the coating activated and form an interface layer of varying quality; or they continue to sublime through the coating and into the vacuum in a generally undesired manner.

As these agents diffuse to the surface, their concentration, and consequently, their diffusion rate, is reduced. A more constant supply over a longer period of time—for longer life—can only be obtained by increasing the mass of metal (wall thickness) or by receiving the reducing agents through migration from external tube parts (anode, grid, getter).

The base metal reducing agents and the coating react at a rate dependent upon the materials and temperature. The desired rate of activation, free Barium evolution, sublimation, and interface resistance should determine the amount and type of reducing agents in the base metal.

As pointed out in the preceding section on the metallurgy of nickel, some portion of the reducing agents—particularly near the sleeve surface—can be compounded during processing. In general, these are stable compounds, such as MgO. They are larger molecules, have lower mobilities and cannot react to reduce the coating. In processing cathodes, only the uncompounded reducing agents can be considered as active. This requires the hydrogen cleaning treatment to be conducted

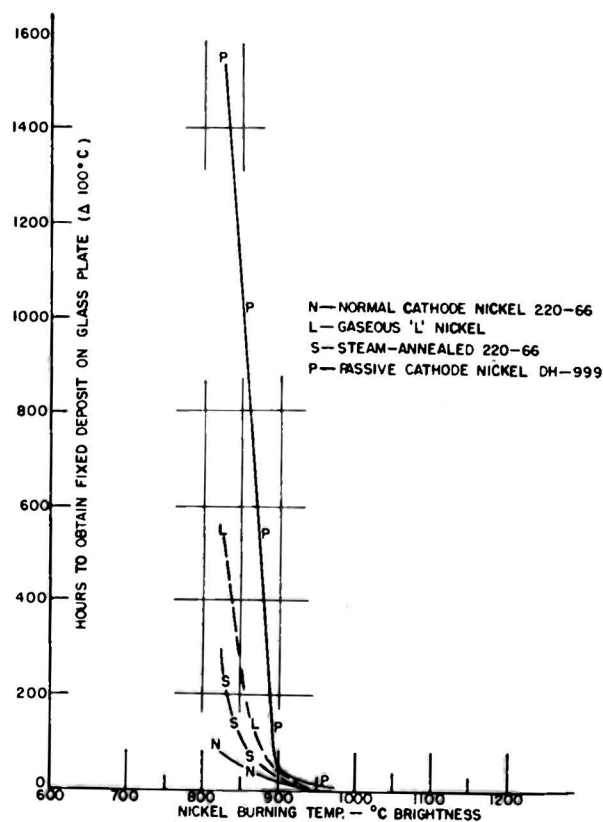


Fig. 9—Bulb deposit absorption time versus burning temperature for four alloys of nickel.

with a low dew point ($< -40^\circ$) in the furnace muffle itself.

Until now, there has been no accurate means for determining what portions of the cathode sleeve reducing agents are still uncombined and able to react with the coating. Solution of this testing problem is the greatest obstacle to forecasting the emission behavior of a given melt of cathode base metal. When this information does become available it will be possible to rate alloys and their melts for any desired type of service. At present, only the inaccurate, expensive, time consuming prove-in method of actually making production tube tests is possible.

IV. CHARACTERISTICS OF CATHODE ALLOYING ELEMENTS

With the previous background concerning the mechanism of thermionic emission, it is now possible to consider the effects of each common additive to nickel base cathode alloys. This data is summarized in Table VI and discussed in the following paragraphs.

TABLE VI

TENTATIVE RATING OF CATHODE ALLOYS FOR PERFORMANCE CHARACTERISTICS. LOWEST FIGURE IS BEST, HIGHEST FIGURE IS POOREST. * = VERY POOR

A.S.T.M. Grade	Activation	Sublimation	DC Emission Level (ohrs)	Interface Impedance	Gm Life
(Active)					
1	3	3	3	3	High Silicon Alloy Probably Poorest
2	3	3	3	3	
3	2	3	2	5*	
4	4	2	4	4*	
5	1	4*	1	?	
6	5	2	4	4*	
(Normal)					
11	6	3	5	2	
(Passive)					
21	7*	1	6*	1	

A. Reducing Agents

Magnesium is the most active of the reducing agents employed. Cathodes activate rapidly to a high emission level. However, Mg is readily oxidized or compounded, so that some of it, as reported by chemical analysis, is not available for coating reaction. Due to high vapor pressure it rapidly migrates from the cathode, giving short emission life. The interface resistance of MgO is negligible. The sublimation rate is high, and bad electrical leakage effects occur when Mg exceeds about 0.07 per cent.

Aluminum is next to Mg in reducing activity. Filamentary emitters employ 1 to 2 per cent to produce high emission and long life.²⁰ For indirectly heated cathodes the Al must be reduced to 0.05 to 0.10 per cent for similar good results. (Patents are pending for

compositions of this type.) The interface compound is not yet positively identified but may be Al_2O_3 or $BaAlO_3$, having negligible resistance. It does not show any sublimation at operating or activating temperatures. To date, it has only been used experimentally for cathode sleeves, but it appears to be unusually promising.

Silicon is a major variable in cathode alloys for altering emission activity. It is intermediate in speed of cathode activation, and can be present in a wide range of alloy composition (0.02 to 0.25 per cent) with significant effects upon dc emission and related tube characteristics. The emission life with high Si content is long, but there is evidence that it has a depressing effect upon Gm life. The interface compound has been identified as Ba_2SiO_4 . Under certain conditions (cutoff operation) this develops an ohmic resistance of hundreds of ohms! The sublimation rate is low.

Titanium acts as a reducing agent upon the coating, but is not now added for this purpose. Usually Ti content is kept as low as possible, since it forms a heavy black interface of high resistance, which radiates heat so well that the cathode temperature is reduced—even to the extent of effecting heater current. It shows no sign of sublimation or migration.

Tungsten has a slight reducing action upon BaO. It has long been used for directly heated filaments, either alone or in combination with Al in a nickel base alloy. When tested in cathode sleeves (4 per cent W, bal. mainly Ni) it produced a high dc and pulsed emission level and exceptionally long life.¹ The interface compound may be $BaWO_3$, which is found to have little, if any, interface resistance. There is no sign of sublimation.

Carbon has been shown to be a slow reducing agent for BaO,²¹ but it is exceedingly difficult to control in the completed cathode since it reacts to form CO and CO_2 , which are gaseous. Some belief exists that it is effective only in pure nickel cathodes, relatively free from the other reducing agents, known as "passive" grade alloys. Great care must be exercised not to confuse the reducing power of carbon with the action of other agents migrating in from external elements. No visible or measurable interface layer is formed, and there is no sublimation of a metallic leakage film.

Cobalt cathodes have been reported to behave as normal nickel cathodes.^{21,22} However, high Co-Ni alloys seem to have good activity. Meager reports indicate good life, low interface resistance, and low sublimation.

B. Other Elements

Chromium is never intentionally present in significant quantities in cathode alloys. It has been reported as a reducing agent, but it is also harmful, since the heavy black interface reduces the expected operating

²⁰ M. Benjamin, "The influence of impurities in the core metal on the thermionic emission from oxide-coated nickel," *Phil. Mag.*, ser. 7, vol. 20, July, 1935.

²¹ E. G. Widell, "Cathode for Electron Discharge Device,"—U. S. Patents 2,179,110, November 7, 1939, and 2,192,491, March 5, 1940.
²² Confidential Report.

temperature, and sublimation is probably fairly rapid.

Copper and *iron* are harmless to emission if their percentage is confined to low values by usual good metallurgical practices. Surface iron is definitely detrimental to emission. Copper can be harmful since it migrates and sublimes with greater ease than Fe, Ni, and Co. Cu and Fe probably have no effect upon interface resistance, since they do not enter into any of the compounds which have been determined by X-ray diffraction.

Manganese is purposely present due to previously mentioned metallurgical requirements. The amount is dependent upon the size of the ingot cast at melting and practices of the particular melter. The almost universal experience of tube engineers is that Mn is undesirable from an emission standpoint.²² Less than 0.05 per cent should be present, although 0.15 per cent is used when the reducing agent content is increased to offset it.²³ The explanation may lie in the fact that Mn-O compounds, which may be formed during metal processing, have a higher vapor pressure than Mn alone. Chemically indicated Mn migrates from the cathode sleeve at a very high rate. We believe that a Mn-O compound introduces excess oxygen into the coating to the detriment of emission. There seems to be no interface resistance effect due to this element.

Lead, *tin*, and *zinc* are rarely, if ever, found in significant quantities in cathode alloys. If present, they rapidly sublime to create intolerably high levels of electrical leakage on tube insulator surfaces.

V. PRESENT AND FUTURE CATHODE ALLOYS

The strength of cathode sleeves requires improvement to enable tubes to operate under severe mechanical conditions. This can be accomplished by use of recognized hardening agents. Most promising candidates are W, Co and Mo. A certain amount of mechanical processing may be needed to enhance their hardening properties. Future and further investigation are warranted.

At present, there are nine commercial and important cathode alloys in the United States. England and the European countries each have their own favorite and different cathode alloy compositions.²²

From the comments in the previous sections, it is easily seen that most existing U. S. cathode alloys have serious faults. They were developed to meet needs of their times. Current requirements, which are far more severe, demanding tube efficiency, reliability, and new operation conditions, have outmoded these alloys with startling rapidity. Recent advances in the knowledge of cathode behavior have provided information permitting evolution of new and improved alloys.

We believe that four alloys of three grades will fill the needs of the radio receiving-tube industry for some time

to come. They must have uniformly low levels of impurity content: such elements as Cu, Fe, Mn, and Ti. Suggested specifications for the reducing agents are tabulated below.

Alloy & Grade	Aluminum	Magnesium	Silicon	Tungsten
	(per cent composition by weight)			
Active-Premium	0.03 max	0.02-0.07	0.03 max	3.75-4.25
Active-Commercial	0.03-0.10	0.02-0.07	0.05 max	—
Normal	0.02 max	0.02-0.07	0.02-0.06	—
Passive	0.01 max	0.01 max	0.01 max	—

(Carbon should average about 0.02 per cent per 0.001-inch of strip or wall thickness.)

These alloys would all have low rate of sublimation and low interface impedance values. They would provide three levels of saturated emission (both dc and pulsed), and three levels of rate of free Ba evolution. Their rates of activation can be controlled by tube exhaust and processing schedules.

It is likewise important that these future alloys be capable of commercial melting and metallurgical processing. In addition, they should be closely reproducible from melt to melt or produced in sufficiently large melts to provide a continuity of tube production not requiring major tube process changes. It is believed that these suggested future alloys are capable of meeting these requirements.

During the past ten years tremendous strides have been made in acquiring knowledge concerning the mechanism of thermionic emission from oxide cathodes. Some of this progress has resulted through considering the effects of each assembly constituent as though it was an independent entity. In this manner the basic concepts have been clarified concerning the effect of nickel analysis and treatment upon activation, emission level, and life expectancy. It is necessary occasionally to stop and take stock, to recognize the omissions and simplifications, and then to go forward more carefully considering all of the combined factors bearing on the problem.

ACKNOWLEDGMENTS

The authors wish to express their thanks to P. N. Hambleton, R. B. Yeaton, and A. J. Zvarick, of Superior Tube Company Laboratories, for their extensive vapor pressure calculations.

BIBLIOGRAPHY

1. "The Romance of Nickel," International Nickel Company, New York, N. Y.; 1947.
2. B. Stoughton and A. Butts, "Engineering Metallurgy," McGraw-Hill Book Publishing Co., Inc., New York, N. Y.; 1938.
3. D. M. Liddell, "Handbook of Non-Ferrous Metallurgy," McGraw-Hill Book Publishing Co., Inc., New York, N. Y.; 1926.
4. W. A. Mudge, "The Melting of Nickel," American Institute of Mining and Metallurgical Engineers, New York, N. Y.; 1946.
5. R. F. Mehl, "Diffusion in solid metals," *Trans. AIME*, vol. 122; 1936.
6. "The Iron Age," Chilton Co., Inc., Philadelphia, Pa., vol. 161, no. 9.
7. "Metals Handbook," 1948 Ed. Am. Soc. for Metals, Cleveland, Ohio, p. 28.

²² F. Violet and J. Riethmuller, "Contribution to the study of oxide cathodes," *Ann. Radioelect.*, vol. 4, pp. 148-215; July, 1949.