Deterioration of Oxide-Coated Cathodes under Low Duty-Factor Operation*†

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The behavior of oxide cathodes coated on a nickel alloy containing about 0.1 percent silicon has been investigated under 100 percent and zero duty-factor operation. The operation of these cathodes at zero duty factor was found to be highly favorable to the development of a high resistance in a layer of BaSO₄ located at the interface between the oxide and the core. The layer itself was present not only in cathodes that had aged without electron emission and had developed interface resistance, but also in cathodes that had aged with electron emission and had not developed interface resistance. A model is presented to account for the experimental observations. Evidence is also presented which shows that an "active" nickel alloy that does not lead to undue interface resistance formation may exist.

I. INTRODUCTION

Oxide cathodes coated on an active-nickel-alloy core often fail before a thousand-hours life when they are operated at a low duty factor, due to the development of a high internal resistance. This failure has been recognized to be a major difficulty by the several groups now engaged in the construction of computers.† Tubes similar to those that failed in computer service have been found to last thousands of hours when they are operated with continuous emission current.

The internal cathode resistance of the failures could be accounted for by the hypothesis of an "interface resistance." The phenomenon of interface resistance has been investigated in connection with cathode sparking by Eisenstein,§ Danforth and Goldwater, Muter, and others. These workers found that in cathodes coated on cores containing impurity concentrations of several percent, a layer of an insulating compound was formed at the interface between the oxide and the core, by chemical reaction between the oxide and an impurity.

The dependence on duty factor, doubted by some, was a fundamental feature of the deterioration that could not be accounted for on the basis of existing knowledge of interface resistance. There was no adequate data to determine whether the deterioration was also associated with a loss of emission, as would be expected from the work of Wright.**

II. EXPERIMENTAL PROCEDURES

The research performed may be divided into two experiments. The first was a study of the behavior of cathodes coated on a commercial active-nickel alloy under high and low duty-factor operation; the second was an investigation into the dependence on the history of electron flow through the interface of the resistance and "activation energy" of an interface resistance on a high silicon nickel core.

A. Experiment I

Diodes similar in electrode structure to the ASTM "Standard Diode"†‖ were chosen for the study of cathode behavior under high and low duty-factor operation, since these diodes could be obtained in the necessary quantities from the Raytheon Manufacturing Company,‡ who produced them under carefully controlled conditions. With the exception of the alumina-coated tungsten heaters and the 699 nickel alloy cathode cores, all metallic parts of the diodes used were of 499 nickel alloy. Typical analyses of the two alloys are as follows:**

699 Si, 0.095 percent; Fe, 0.072; Mn, 0.085; Mg, 0.14; Cu, 0.006; Ti, 0.008
499 Si, 0.008 percent; Fe, 0.033; Mn, 0.008—; Mg, 0.009—; Cu, 0.009; Ti, 0.003.

Forty diodes were aged in four panels of ten tubes each at a cathode temperature of 1100°F. Diodes in

†‖ Developed by American Society of Testing Materials Committee B-4, on Oxide Cathodes.
‡ Under their contract N7-our-389.
** Furnished by Mr. James Cardell of Raytheon, private communication.
Panels I and II were aged with an electron emission of 60 ma per cm$^2$. Tubes in Panels III and IV were aged without electron emission. The tubes of Panel III had their anodes connected to their cathodes, while those of Panel IV had their anodes at -110 volts dc with respect to their cathodes, to simulate the effect of cutoff operation in a pentode or triode.

The tubes were tested periodically for dc emission, pulsed emission, and interface resistance. The dc emission measurement was made at a cathode temperature of about 600°K, with an applied anode potential of 4.5 volts. The average emission obtained at zero hours life was between thirty and forty microamperes.

The pulsed emission measurement was made at a cathode temperature of 940°K by applying to the diode a single one-millisecond 300-volt pulse from a thyratron pulser, and observing the emission by means of a synchroscope with a long-persistence screen. The average pulsed emission obtained at zero hours life was about 0.5 amp per cm$^2$.

The interface resistance measurement was made by pulsing the diode at constant current space-charge-limited in $2\frac{1}{2}$ microsecond pulses and observing the voltage across the diode during the pulses with a synchroscope. Under these conditions, if the diode has no interface resistance, the voltage pulse appearing across the diode is "square," and equal in height to the potential necessary to draw the constant current pulse, as shown in Fig. 1a. If the diode has an interface resistance, a voltage builds up across this resistance during the pulse, as in Eq. (1):

$$V = IR[1 - \exp(-t/RC)].$$

$R$ and $C$ are the effective interface resistance and capacitance, respectively, and $i$ is the constant pulse current. Since the pulse length is $2\frac{1}{2}$ microseconds and $RC$ is of the order of a microsecond or less, $V$ varies from zero to within a few percent of $iR$ during the pulse.

When the diode is pulsed at constant current space-charge-limited, the potential difference between the surface of the cathode and the anode must remain con-

\[\text{Panel IV}\]

\[\text{Panel III}\]

\[\text{Panel II}\]

\[\text{Panel I}\]

$\text{He Emission}$

\[V_i\]

\[\text{Hours Life}\]

$2000$ $4000$

$\text{Fig. 2. Dc emission.}$

\[A\text{ brief description of the constant-current pulser is given in Appendix I.}\]
hours. The criterion for failure used in plotting Fig. 4 was the presence of any detectable interface resistance. The resistances of failures from Panels III and IV ranged from forty to about a thousand ohms. There was no difference between Panels III and IV.

At the conclusion of the aging program, x-ray diffraction and spectrochemical analyses were performed. For the identification of the interface compound by x-ray diffraction, samples were prepared by molding together (with Duco cement) scrapings from the interfaces of three cathodes whose coatings had been removed.†† One sample was prepared from cathodes with interface resistance from tubes of Panels III and IV, and another from cathodes without interface resistance from tubes of Panels I and II. The layer of interface compound was visible in all of these cathodes as a grayish discoloration of the core; no difference between the two categories could be detected in the layer by visual examination.

Prints made from the patterns obtained from the two samples are shown in Fig. 5. They are quite similar; in each pattern, the heavy lines are caused by nickel, while the fine lines at low angle are due to Ba$_2$SiO$_4$. In each case, Ba$_2$SiO$_4$ is a major constituent of the scrapings from the interfaces. From this evidence, it may be concluded that a layer of Ba$_2$SiO$_4$ is present at the interface, not only in cathodes that have aged without electron emission and have developed interface resistance, but also in cathodes that have aged with electron emission and have not developed interface resistance.

Three categories were chosen for spectrochemical analysis:

A. Tubes without interface resistance (Panels I and II);
B. Tubes with interface resistance (Panels III and IV);
C. Tubes without interface resistance (Panels III and IV).

Four samples were obtained from each of these categories, as follows:

- a. Surface of anode;
- b. Bulk of anode;
- c. Cathode coating plus surface of nickel core;
- d. Bulk of nickel core.

The results of the spectrochemical analyses are shown in Tables I and II. Note that in every case, the concentration of impurities is greater in the anode surface than in the bulk of the anode. This may be ascribed to a contamination of the anode surface by impurities evaporated from the cathode. A comparison of analyses for group A and group B indicates that it is unlikely that the results obtained under the interface-resistance measurement are due to a systematic difference in impurity content between tubes of Panels I and II and tubes of Panels III and IV.

A significant difference in impurity content is shown in the sample labelled “cathode coating plus surface of nickel core” of group C, which consisted of tubes that aged without electron emission without developing interface resistance. The iron concentration in this sample is only one-tenth as great as in the same sample of group B (interface-resistance failures). Meager
though this evidence is, it seems to indicate that an alloy containing as much silicon and manganese as 699, but far less iron, might be significantly better as a base-metal for cathodes to be operated under low duty-factor conditions.

### B. Experiment II

The purpose of the second experiment was to investigate the dependence on the history of electron flow of the resistance and "activation energy" of an interface resistance on a high silicon nickel core. A "sandwich" diode was constructed, in which a wafer of (BaSi)/O was compressed between two flat electrodes, as shown in Fig. 6. The electrode labelled "K1" was of silicon-nickel alloy (about 5 percent Si), while "K2" was of "Grade A" nickel (less than 0.3 percent Si). Two 0.7-mil platinum wire probes imbedded in the wafer, as shown in Fig. 6, permitted the determination of the potential difference across the interface by the "double-probe" method which has been used by Eisenstein and others.

The wafer was constructed by spraying a coating on K1 in three layers with probes between the layers; a single-layer coating was sprayed on K2, and the two were mounted in contact to form the wafer. Since there was apparently a certain amount of potential difference across the junction of the coatings, the probes were used only to measure the potential across the K1 interface. The temperature of this interface was measured with a tungsten-nickel thermocouple. One leg of this thermocouple was the K1 electrode itself, while the other was a three-mil tungsten wire welded to the back of the electrode, as shown in Fig. 6.

In the process of conversion of the carbonates, great care was taken to raise the temperature of the wafer slowly with the pressure monitored by an ion gauge, to prevent excessively rapid liberation of CO2. This was felt to be necessary because of the relatively large volume of the wafer, and the small surface area it presented to the vacuum. After the conversion of the carbonates, the wafer was activated by the passage of electron current at a temperature in excess of 1000°C until no further reduction in resistance took place. At this time, the resistance at 900°C of the wafer (0.2 cm² area of cross section, 0.5 mm thick) was about a meg-ohm. The pressure at seal-off was less than 5×10⁻⁴ mm.

A typical current-voltage characteristic obtained for the K1 interface is shown in Fig. 7. Note the rectifying nature of the interface resistance, similar to that observed by Mutter. The high resistance direction is the direction of electron flow from the core to the oxide. To obtain from these characteristics a value of the "activation energy," use was made of the fact that in the theory of rectifying contacts, the current can be expressed as a function of the voltage by an expression of the form§§

\[ i = A(T) j(V/T) \exp(-e\Phi/kT), \]

where \( \Phi \) is the activation energy in electron-volts, and \( A(T) \) varies as \( T^n \), where \( n \) is of the order of one or two; \( k \) is the Boltzmann constant.

Measurements were taken of the current-voltage characteristic in the high resistance direction at three different temperatures; as few points as possible were read on each curve to avoid difficulties with lack of reproducibility. The logarithm of the current observed at a fixed value of \( V/T \) for each of the temperatures was plotted as a function of \( 1/T \). From the slope of the best straight line that could be drawn through the three points, the activation energy was obtained.

The result of a typical measurement of this kind is shown in Fig. 8. The numbered points are the repro-

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ducibility check points, which were taken with the same potential applied across the wafer after the measurements at 760°FK, 820°FK, and 870°FK, respectively. Note that although the oxide has tended to activate during the measurements, the state of the interface has not changed.

The tube was aged at a wafer temperature of 1000°FK as follows:

- 0–503 hours, electrons flow from oxide to $K_1$ interface;
- 503–668 hours, electrons flow from $K_1$ interface to oxide;
- 668 hours, electrons flow from oxide to $K_1$ interface.

The currents that flowed during the ageing were about ten or twenty microamperes, and the potential difference across the interface was about one or two volts. If a value of $10^{-3}$ cm is assumed for the thickness of the interface region, the electric field in this region can be calculated to have been of the order of one or two thousand volts per cm.

The variation of the activation energy of the interface resistance with time during the ageing is shown in Fig. 9. As long as electrons flowed from the oxide to the interface, the activation energy increased, but when electrons flowed from the interface to the oxide, the activation energy decreased sharply. A similar behavior was shown by the resistance, as may be seen in Fig. 10.

### III. Interpretation

The results that have been obtained have posed a particularly serious question: how can a layer of Ba$_2$SiO$_4$ (an insulator) at the interface between the oxide and the core have a high resistance after ageing with no current flow, and have a low resistance after ageing with electron flow from core to oxide? To answer this question, which I believe to be fundamental to the understanding of the behavior of oxide cathodes under low duty-factor operation, I will propose a model of the interface region and show that it is capable of accounting qualitatively for the observations of both Experiments I and II.

During the process of activation of a cathode coated on a silicon-bearing nickel core, a layer of Ba$_2$SiO$_4$ forms at the interface by a reaction between silicon in the core and BaO of the coating. This reaction is probably at least partly responsible for the formation of the stoichiometric excess of barium necessary for an active cathode. Some of this excess of barium undoubtedly remains in the layer of interface compound, providing it with donor centers which transform it from an insulator to an "excess" or $N$-type semiconductor. The conductivity of the Ba$_2$SiO$_4$ in this state is high enough that the cathode has a negligible interface resistance.

The energy-level configuration of the interface region in this state would be as shown in Fig. 11. The diagram has been drawn in accordance with the views of Slater concerning the junction between conductors and semiconductors, with the $a$ $priori$ assumption that the work-function of the activated Ba$_2$SiO$_4$ does not differ greatly from the work-function of the activated oxide, but that the work-function of the nickel is greater than either. In all probability, the Schottky "depletion-layer" barrier at the interface between the nickel and the Ba$_2$SiO$_4$ has a negligible resistance, because the boundary is undoubtedly not abrupt, as shown, but much more "diffuse."

As the cathode is aged, the layer of Ba$_2$SiO$_4$ thickens to the point where reaction between silicon of the core and BaO of the coating becomes negligible. The behavior of the concentration of donor centers in the layer during the ageing will depend on whether an electric field is present, because the donor centers behave on the average as positive charges.

If no electron emission is drawn from the cathode, there is no electric field in the interface region, and the donor centers can migrate out of the layer of interface compound by thermal diffusion. The concentration of donor centers in the layer is reduced to the extent that it is insufficient to maintain a negligible resistance; the cathode has then developed an interface resistance.

If the cathode is aged delivering electron emission, an electric field directed from oxide to core exists in the interface region. Field-induced migration of donor centers into the layer of interface compound and thermal diffusion of donor centers out of the layer of oxide.
interface compound are then in competition. The equilibrium concentration of donor centers in the Ba₂SiO₄ layer is greater than it would be if thermal diffusion were the only migration process. If the field is strong enough, the equilibrium concentration of donor centers is sufficient to maintain the conductivity of the interface compound. The cathode does not develop an interface resistance.

The energy level configuration of the interface region of a cathode that aged delivering electron emission and did not develop interface resistance would probably be quite similar to that shown in Fig. 11, with the exception that the layer of interface compound would be thicker. For a cathode that did develop interface resistance, the energy level configuration would be as shown in Fig. 12.

In Fig. 12, the levels of the Ba₂SiO₄ have been shifted upward relative to the levels of the nickel and the oxide, because of the dependence of the Fermi level (μ) in the Ba₂SiO₄ on the concentration of donor centers. Since the resistance of the Schottky “depletion-layer” barrier can still be neglected, the activation energy of the interface resistance would be equal to Φ, the energy difference in electron volts between the Fermi level (μ) and the bottom of the conduction band in the Ba₂SiO₄, as shown in the figure.

If the cathode were aged with electrons flowing from the oxide to the core, an electric field directed from the core to the oxide would exist in the interface region. The field-induced migration of donor centers would then be in such a direction as to reduce the concentration in the interface compound, and would aid rather than retard the development of an interface resistance. Furthermore, a comparison of Figs. 11 and 12 shows that as the concentration of donor centers decreases and the resistance increases, the activation energy also increases.

This is exactly what was observed in Experiment II; as long as the interface was aged with electrons flowing from the oxide to the core, the resistance and activation energy increased. The fact that resistance and activation energy could be reduced by the passage of electron current from the core to the oxide is also in agreement with the features of this model, since there is no reason why a low concentration of donor centers could not be increased by the establishment of field-induced migration in the proper direction.

To account for one of the results of Experiment II, it is necessary to modify the model slightly, without altering the fundamental features already outlined. An examination of Figs. 9 and 10 shows that the resistance is not related to the activation energy by the simple expression

$$Ra \exp(e\Phi/kT),$$

as would be expected on the basis of Eq. (2). The variation observed in R is not nearly as great as would be expected from the variation observed in Φ.

This can be accounted for by the fact that the interface layer is probably not at all homogeneous, but varies in thickness and in donor center concentration. Conduction through it depends on parallel conduction through many “patches” of different thickness, conductivity, and activation energy. The experimental measurements of resistance and activation energy represent two different methods of averaging over the patches. Since the degree of inhomogeneity, on which the resistance strongly depends, can be quite different for two states of the interface barrier having the same observed activation energy, it is not surprising that the resistance and activation energy fail to be related in the simple manner expressed by Eq. (3).

IV. SUMMARY AND CONCLUSIONS

The results obtained in this work have shown that the anomalous deterioration that occurs in oxide cathodes coated on silicon-bearing nickel cores when they are operated at a low duty factor is due entirely to the development of a high resistance in a layer of Ba₂SiO₄ located at the interface between the oxide and the core. The layer itself was found to be present not only in cathodes that had developed interface resistance, but also in cathodes that had not. The development of a resistance in this layer was heavily favored by the absence of electron emission from the cathode during life.

Further investigation of the properties of an interface resistance on a high silicon nickel core has shown the resistance and activation energy to be strikingly dependent on the history of electron flow through the interface. A model has been presented that appears
Fig. 12. Energy level system of cathode with interface resistance.

The application of this understanding to the engineering problem of developing cathodes that do not deteriorate when they are operated at a low duty factor leads to two main avenues of approach.

(1) Use nickel containing less silicon and other impurities; the layer of interface compound will be thinner, and will have less resistance.

(2) Search for other substances that can be added to the interface compound to provide it with permanent donor centers that will persist in the layer irrespective of duty factor.

The first of these avenues is currently being exploited by most of the major tube manufacturers, although it suffers from two faults. First, there is enough variation in impurity content among different melts of what is nominally the same alloy that different production lots of the same tube can have widely different life expectancies. Second, the use of alloys containing appreciable amounts of impurities (i.e., "active" alloys) is often highly desirable as an aid to easy activation of the cathodes.

That the second avenue is not beyond the realm of possibility appears to be indicated by the results of the spectrochemical analyses of diodes that had aged 4316 hours with no electron emission without developing interface resistance. The cathodes of these diodes were found to contain far less iron in the "cathode-coating-plus-surface-of-nickel-core" sample, which contains the interface, than cathodes that had developed interface resistance. It is conceivable that in cathodes containing very little iron, the presence of BaMnO$_4$ in the Ba$_2$SiO$_4$ lattice might provide just such permanent donor centers. The dependence on the iron content stems from the fact that the coexistence of BaMnO$_4$ and Fe side by side at a temperature of 1100°C for 4000 hours would be extremely improbable, because the MnO$_4^{2-}$ ion is a strong oxidizing agent.

However meager the data, and whatever the mechanism may be, these results appear to indicate at first sight that a nickel alloy containing all impurities except iron to the extent that they are found in 699 nickel alloy might be a satisfactory active nickel alloy for cores of cathodes to be operated at a low duty factor.

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APPENDIX I. CONSTANT-CURRENT PULSER

A diagram of the essential features of the constant current pulser is shown in Fig. 13. The grid of the 6AN5, which is normally biased beyond cutoff, is supplied with flat-topped pulses from a voltage-pulse generator. The pulse amplitude is adjusted until the current through the diode during the pulse is 50 ma. Under these conditions, the potential across the diode during the pulse is about 45 volts.

The plate current of a 6AN5 drawing 50 ma with 120 volts screen voltage and 250 volts plate voltage is approximately independent of plate voltage. When the total drop across the diode increases by four or five volts during the pulse because of interface resistance, the plate voltage of the 6AN5 is reduced by the same amount, but the plate current is not affected. The current through the diode is constant during the pulse irrespective of whether or not the diode has an interface resistance.