Operating Mechanism of the One-Piece Cathode

K. T. Chiang and J. J. Maley — RCA Video Component and Display Division, Lancaster, PA 17604

Originally published in RCA Review, Vol. 45, pp. 379–396, September 1984. Reconstructed with editor's notes by David F. Hakala, Ph.D., NanoTekniks
November 4, 2026

Table of Contents

Note on this reconstruction....1
Abstract....2
1. Introduction....2
2. Experimental Procedures....4
3. Initial Reaction at the Metal/Coating Interface....5
4. Chromium Diffusion in the Base Metal....6
4.1 During Tube Processing....6
4.2 During Life....8
5. Reaction Between Chromium and Oxide Coating....10
5.1 Migration of Chromium....10
5.2 Interface Compound....12
6. Reaction Mechanism....13
6.1 Role of Chromium in Reducing Cutoff Change....13
6.2 Role of Chromium in Increasing Cathode Life....13
7. Summary and Conclusions....14
Acknowledgments....14
References....14
Editor's Notes (2026)....15

Note on this reconstruction

This is a retyped and lightly edited version of the paper as published in *RCA Review*, made from a scanned copy for use with a seminar on materials and processes for color picture tubes. The text follows the original, with optical-character-recognition errors corrected, chemical formulas restored, and SI equivalents added in brackets after dimensions given in mils. The micrographs, microprobe traces, x-ray maps and life-test curves (Figures 1–10) are reproduced from the scan. Figure S1 is a new schematic. The Editor's Notes at the end add checks made in 2026 (Figures S2 and S3).

Abstract

Extensive life testing and metallurgical examinations have been conducted to study the performance characteristics and operating mechanism of the one-piece bimetal cathode. This cathode shows superior emission life and less cutoff change with life. Chromium, originally in the bottom layer of the cathode base metal, is found to diffuse into the nickel portion of the cathode cap and subsequently react with the oxide coating. A reaction in which chromium acts as an activator and chemically reduces barium oxide to free barium is proposed to account for the better emission life. The rate of chromium diffusion, rate of reaction, interface compound formation, and the effect of chromium on cutoff change during life are discussed.

1. Introduction

Oxide cathodes for electron tubes generally consist of a nickel base substrate coated with a porous layer of alkaline earth metal oxide (Ba,Sr,Ca)O. The nickel base contains a low concentration of reducing agents such as Mg, Si, Al, etc. At high temperature the reducing agents continuously diffuse into the oxide coating, reducing a small amount of barium oxide to the metal, thus providing the free barium necessary to activate the oxide emitting surface. A summary of theories advanced to explain the operating mechanism of the oxide cathode is given in Refs. [1] and [2].

In a conventional oxide cathode, the nickel base is a cup-like structure attached to a cylindrical nichrome (Ni–20 wt% Cr) sleeve by welding. The one-piece bimetal cathode design is an integral cathode substrate and sleeve. This cathode structure may be fabricated by deep-drawing blanks from a bimetal laminate strip and then etching away portions of the nickel alloy layer. Aside from the fabrication method, a major difference between the one-piece bimetal cathode and the conventional welded two-piece cathode is the presence of a layer of nichrome beneath the cathode nickel. This difference is illustrated by the cross-sections of the two cathodes shown in Fig. 1 (see also the schematic in Fig. S1).

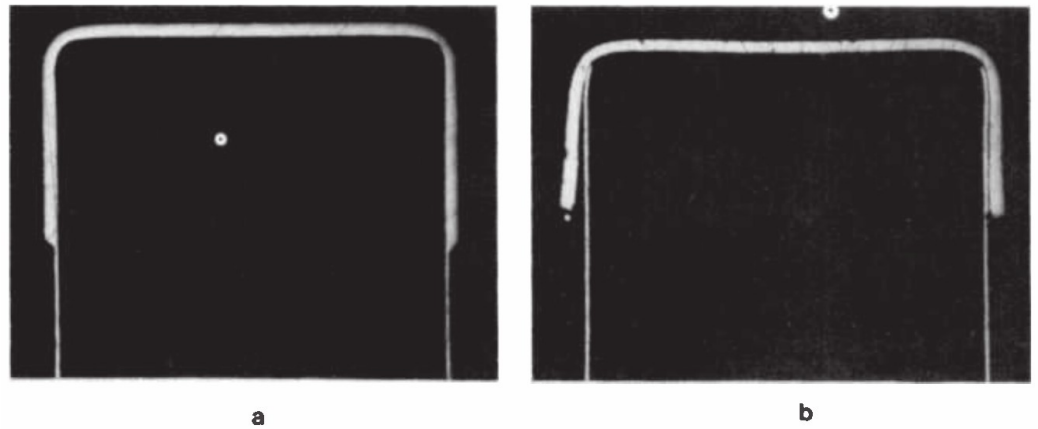


Fig. 1. (a) Cross-section of the one-piece cathode formed by removal of nickel from the sleeve portion of the bimetal; the cathode cap has 2 mils (51 μm) of Ni–4 wt% W on top of 1 mil (25 μm) nichrome. (b) Cross-section of standard KS904 cathode; the 2-mil Ni–4 wt% W cap is welded to the nichrome sleeve. (Enlarged approximately 20×.)

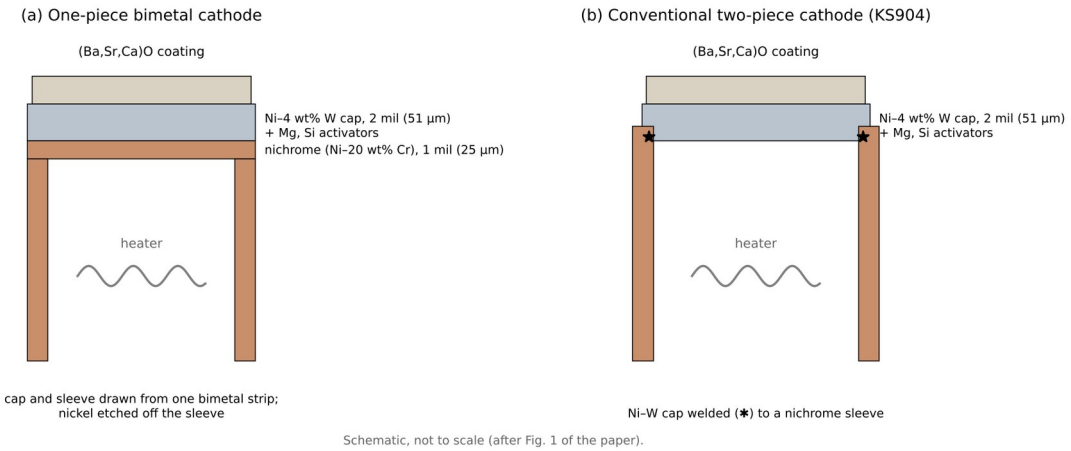


Fig. S1 (new). Schematic cross-sections of (a) the one-piece bimetal cathode and (b) the conventional two-piece KS904 cathode. Not to scale.

Extensive testing of the one-piece bimetal cathode was carried out to determine the emission and other electrical characteristics of the electron gun over an extended life cycle. An important parameter associated with these tests was “cutoff voltage”. Given a specific negative potential applied to the first grid (G1), the cutoff voltage is defined as the positive potential required on the second grid (G2) to start drawing current of approximately 1 microampere. In tube application, the cathode should have a long emission life and a cutoff voltage that is stable over time.

The life tests were done at the normal filament voltage of 6.3 volts and at accelerated test conditions of 6.9, 7.5, and 8.1 volts. The major conclusions from these tests were that (1) the emission life of the one-piece bimetal cathode is superior to that of the conventional two-piece cathode and (2) the cutoff change with life is less for the one-piece bimetal cathode than for the two-piece cathode. Results of the typical life tests for emission and cutoff voltage are presented in Figs. 2 and 3, respectively.

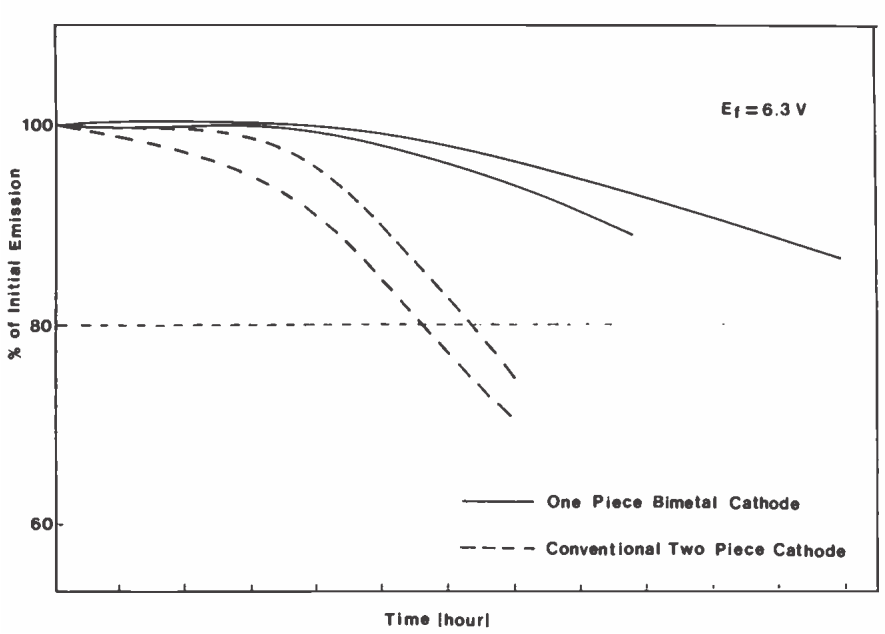


Fig. 2. Cathode emission versus time ($E_f = 6.3$ V). Solid lines: one-piece bimetal cathode; dashed lines: conventional two-piece cathode. (The time axis is unscaled in the original.)

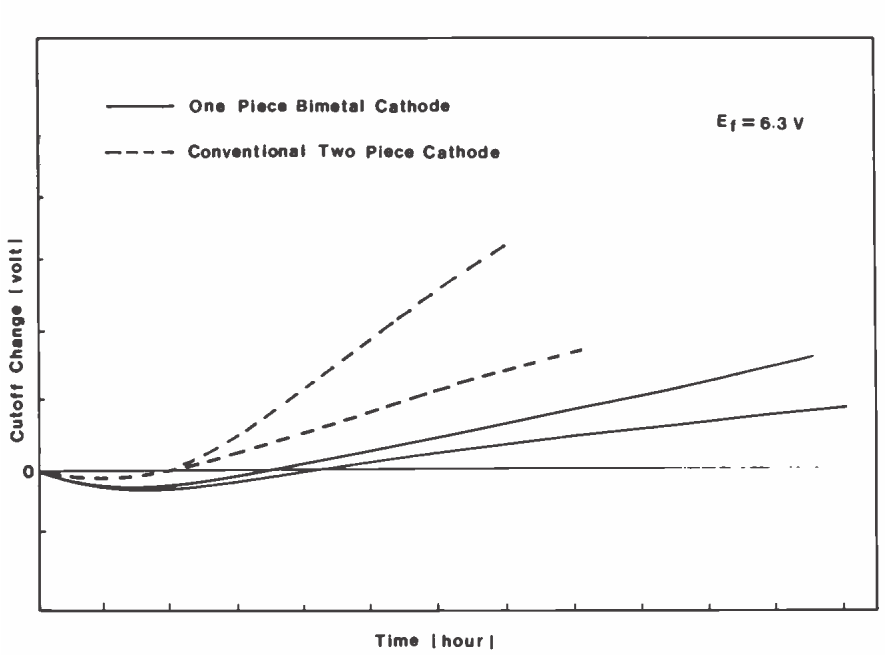


Fig. 3. Cutoff voltage change versus time (E_f = 6.3 V). Solid lines: one-piece bimetal cathode; dashed lines: conventional two-piece cathode. (Axes unscaled in the original.)

To explain these test results, we initiated a program to study the operating mechanism of the one-piece bimetal cathode. An understanding of the operating mechanism is essential to the manufacture, processing, and use of this cathode, as well as for future cathode development. A survey of scientific literature on oxide-coated cathodes [3–5] revealed that chromium above 0.003 wt% has never been intentionally added or present in cathode nickel. Special attention was therefore paid to the study of the migration of chromium and its effect on cathode performance. Specifically, it was intended to answer the following questions concerning the presence of chromium in the one-piece cathode.

1. Earlier researchers [6] have reported the formation of a high-resistance interface layer on cathodes made from chromium-plated nickel. Does a similar reaction occur on the one-piece cathode?
2. How long does it take for chromium to diffuse through the nickel portion of the cathode cap at the normal operating voltage of 6.3 V E_f and at accelerated test conditions?
3. After reaching the oxide-coating/metal interface, how does chromium react with the oxide coating? Does the reaction compound form an interface barrier?
4. What is the role of chromium in improving the emission and cutoff characteristics of the cathode during life?

All of these aspects were carefully examined during the course of this study. As a result, an operating mechanism that extended over all stages of the cathode life was defined.

2. Experimental Procedures

The experimental methods used for analysis involved x-ray diffraction, optical metallography, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and electron microprobe analysis.

Most long-term-life-test samples had at least 15,000 hours of life. After life test, the cathodes were visually inspected to determine the extent of coating discoloration. Cross-sections of the cathodes were then prepared for further analysis using optical-microscope and scanning-electron-microscope techniques. For selected samples, parts of the oxide coating were scraped from the cathode and analyzed by x-ray diffraction. This technique offered information on the crystal structure of the reaction product and allowed new phases to be identified.

To study chromium diffusion in the base metal, microprobe scans were made on cross-sectional samples along a line perpendicular to the cathode surface. A series of samples with different life-test conditions and operating times were examined. The tube operating conditions included filament voltages (E_f) of 6.3, 6.9, 7.5, and 8.1 V. The corresponding cathode temperatures, in terms of optical brightness, were approximately 1075, 1120, 1150, and 1200 K. For operating filament voltages of 6.3 and 6.9 V, the cathodes were examined after interrupting the life tests at 1, 3, 5, 11, and 15 weeks. At filament voltages of 7.5 and 8.1 V, the life tests were interrupted at 1, 2, 3, 5, and 7 weeks.

Cathodes operated for even longer times were chosen for the study of the migration of chromium into the oxide coating. Energy dispersive analysis of x-rays (EDAX) was used to identify the elements present in the coating. Scanning electron micrographs and x-ray dot maps were taken to show the distribution of chromium in the base metal as well as in the oxide coating. In this analysis, the detector was tuned to respond to the x-ray wavelength characteristic of chromium. The density of the white dots therefore provided information on the abundance of chromium in the examined areas. To study the interface compound between the oxide coating and the base metal, similar x-ray maps of barium, tungsten, oxygen, and nickel were also obtained.

XPS analysis was carried out to study the cathode surface before spraying the alkaline-earth carbonate coating. This surface-sensitive technique offered chemical-element and chemical-bonding information within a 100 Å (10 nm) range of the sample surface.

3. Initial Reaction at the Metal/Coating Interface

To study the surface reaction between the oxide coating and the base metal, three sets of cathode samples were prepared for XPS analysis:

1. One-piece bimetal cathode before and after H_2 firing.
2. Nichrome cathode before and after H_2 firing.
3. Standard KS904 cathode before and after H_2 firing.

The nichrome cathode was made by removing all the nickel from the one-piece bimetal cathode. XPS analysis showed the following results [7]:

1. Approximately 10 nm of nickel oxide was observed on the unfired nickel surface of the one-piece bimetal cathode, composed of NiO and a nickel suboxide NiO_x (or perhaps a partial hydroxide NiOOH). After H_2 firing, the oxide was somewhat thinner and richer in NiO. The oxide on the standard cathode closely resembled the one-piece cathode.
2. The surface of the unfired nichrome cathode was chromium enriched and contained a mixture of Cr_2O_3 and nickel oxides. No nickel–oxygen bonding was present after firing, but the Cr_2O_3 was unaffected.

The results are as expected from a thermodynamic perspective. The atmosphere of the hydrogen firing furnace is slightly reducing for nickel oxide on the cathode caps of the standard and the one-piece bimetal cathode. For the nichrome cathode, however, Cr_2O_3 is present on the cathode surface and is

stable in the H_2 firing atmosphere. The Cr_2O_3-enriched layer continues to grow during subsequent cathode processing and tube processing. As a result, after the cathode activation process at a cathode temperature of about 1250 K, the interface reaction compound on the nichrome cathode surface is of the form $BaO{\cdot}Cr_2O_3$. This interface layer is similar to that in chromium-plated nickel. The higher resistance of this compound [6] may cause difficulty in drawing current through the coating. In addition, the coefficient of thermal expansion of this layer may be different from the cathode substrate body, causing peeling of the oxide coating. Both these effects were observed for nichrome cathodes at 8.1 V E_f life test. The nichrome cathodes had early emission failures at 8.1 V E_f life test and many of the cathodes had poor coating adherence. For the standard cathode and the one-piece bimetal cathode, the interface reaction between the oxide coating and the substrate is of the form BaO·NiO. This reaction forms a strong bond between the oxide coating and base metal and is responsible for the good adherence of the cathode coating.

This analysis shows that the detrimental effect of high-resistance chromium compound formation was avoided due to the presence of a 2-mil (51 µm) layer of cathode nickel.

4. Chromium Diffusion in the Base Metal

4.1 During Tube Processing

Fig. 4a shows an optical micrograph of the one-piece cathode before tube processing. The two-layer structure is clearly visible. The 2-mil (51 µm) cathode nickel (with 4 wt% W and trace amounts of Mg and Si as reducing impurities) was hot bonded to the 1-mil (25 µm) nichrome alloy (Ni–20 wt% Cr). Microprobe traces of Ni and Cr (Fig. 4b) across the cap indicated chromium was confined to the bottom 1-mil layer, and the top layer contained higher nickel concentration. This result is as expected, since the initial cathode nickel contained 96 wt% nickel as compared to about 80 wt% in the nichrome layer. After tube processing, a significant amount of chromium had already diffused into the nickel portion of the cap. At the same time, some nickel diffused back to the nichrome portion. The interdiffusion zone is seen in the cross-section (Fig. 5a) as the slightly darker area around the original nickel/nichrome interface. The interdiffusion of nickel and chromium is clearly evident from the concentration profiles of the two elements as shown in Fig. 5b.

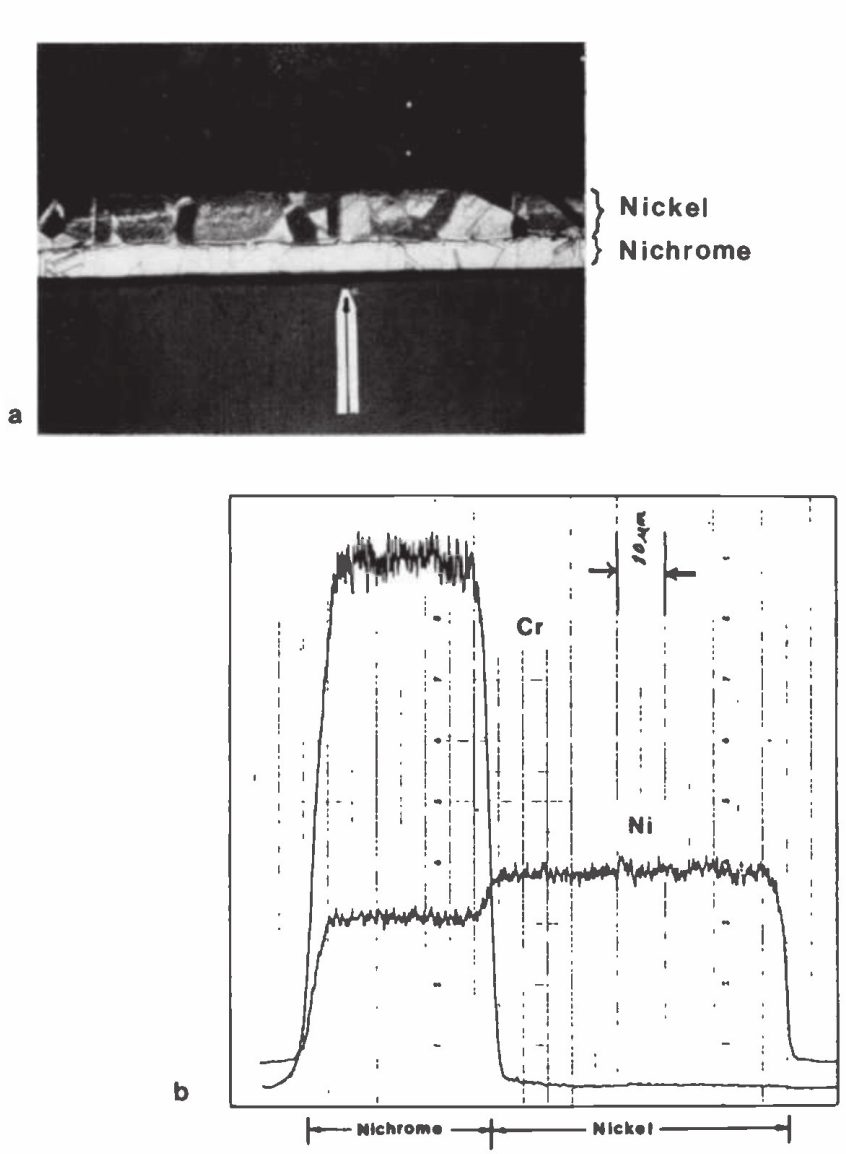


Fig. 4. (a) Cross-section of the one-piece cathode cap before tube processing (approx. 130×). (b) Ni and Cr concentration profiles along the line of traverse indicated by the arrow in the photo.

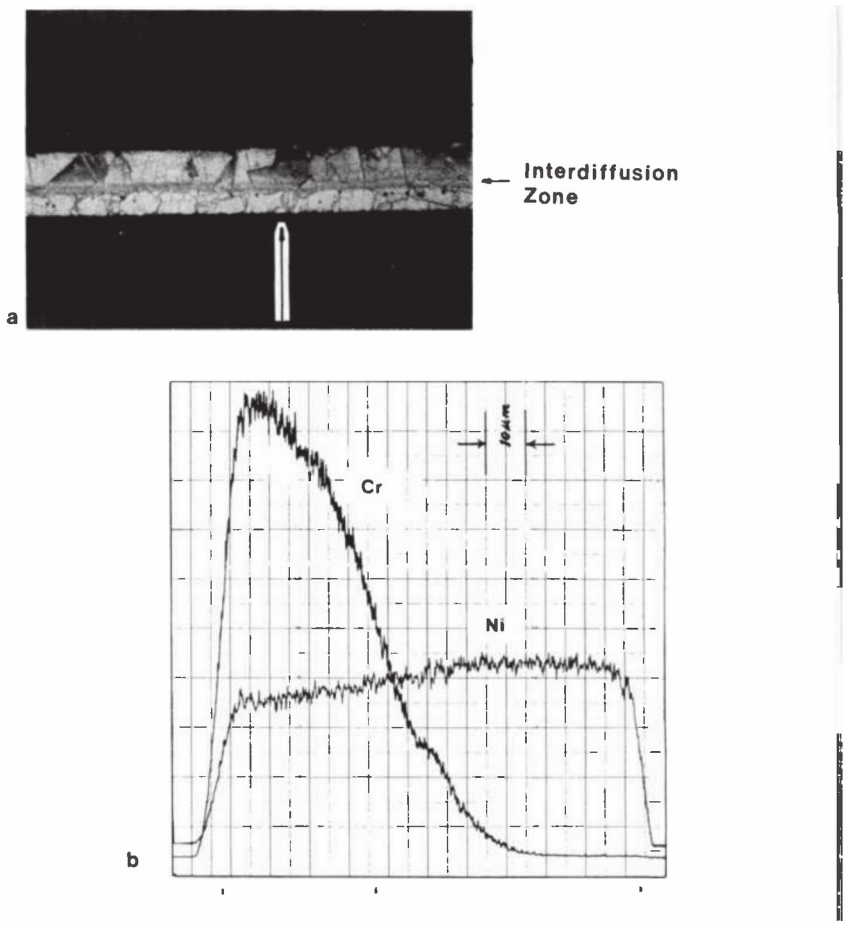


Fig. 5. (a) Cross-section of the one-piece cathode cap after tube processing (approx. 130×). (b) Ni and Cr concentration profiles along the line of traverse indicated by the arrow in the photo.

4.2 During Life

Chromium profiles across the cathode cap after different operating times at filament voltages of 6.3, 6.9, 7.5, and 8.1 volts are presented in Figs. 6(a), (b), (c), and (d). Different samples were examined for different operating voltages and operating times. It is noted that in all cases, chromium diffusion progresses at a rapid rate. As shown in Fig. 6(a), at a filament voltage of 6.3 V, it takes about 3 weeks for chromium to diffuse through the nickel portion of the cap and to reach the metal/oxide coating interface. At an operating filament voltage of 8.1 V, it takes only one week for chromium to diffuse to the interface (Fig. 6(d)). Similarly, only one to two weeks are needed for chromium to reach the metal/oxide coating interface at filament voltages of 6.9 and 7.5 V (Figs. 6(b) and 6(c)). This rapid diffusion rate can be explained by diffusion through easy diffusion paths, such as grain boundaries that are present in both the nickel and nichrome portions of the cap. The grain structure in the cathode cap is shown in Fig. 7a. The grain structure in the nichrome alloy is shown in Fig. 7b. The rapid diffusion along these grain boundaries, followed by volume diffusion within the grains, allows chromium to diffuse into the nickel lattice during early stages of the cathode operation (see Editor's Note 2 and Fig. S3).

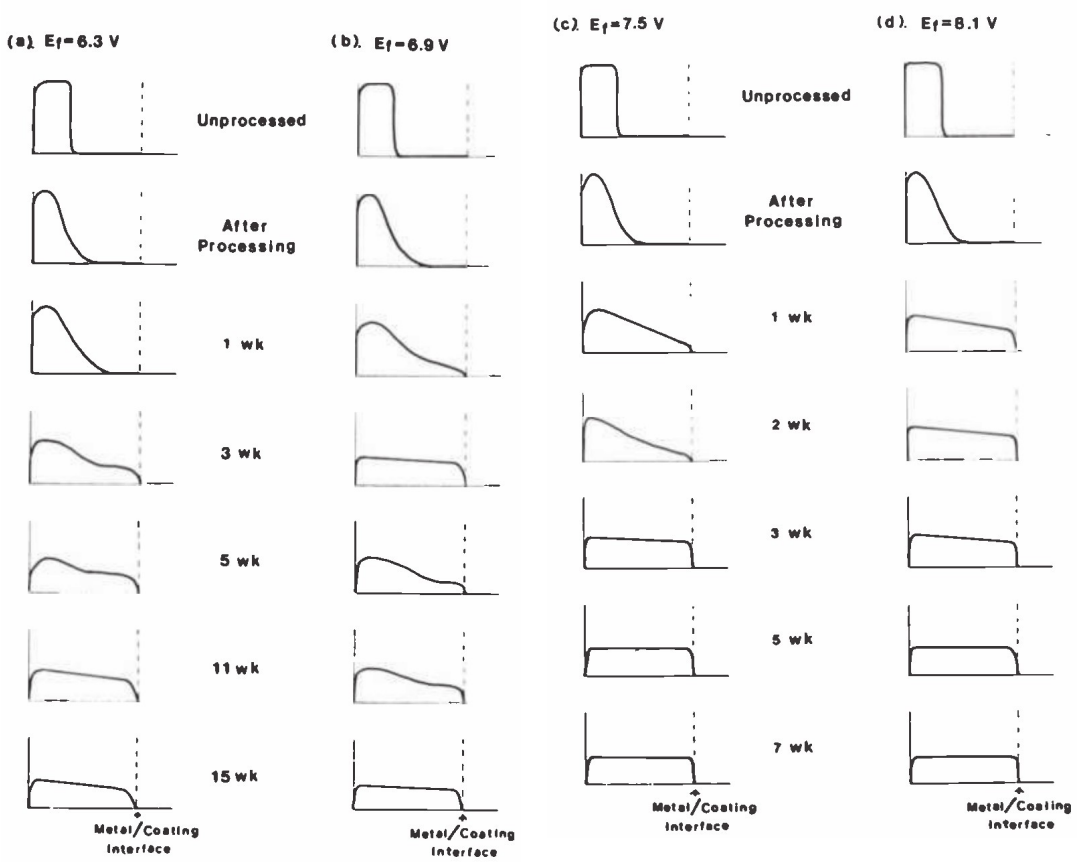


Fig. 6. Cr concentration profiles across the one-piece cathode cap after different times on life at filament voltages of (a) 6.3 V, (b) 6.9 V (unprocessed; after processing; 1, 3, 5, 11 and 15 weeks), (c) 7.5 V and (d) 8.1 V (unprocessed; after processing; 1, 2, 3, 5 and 7 weeks). The dotted line marks the metal/coating interface.

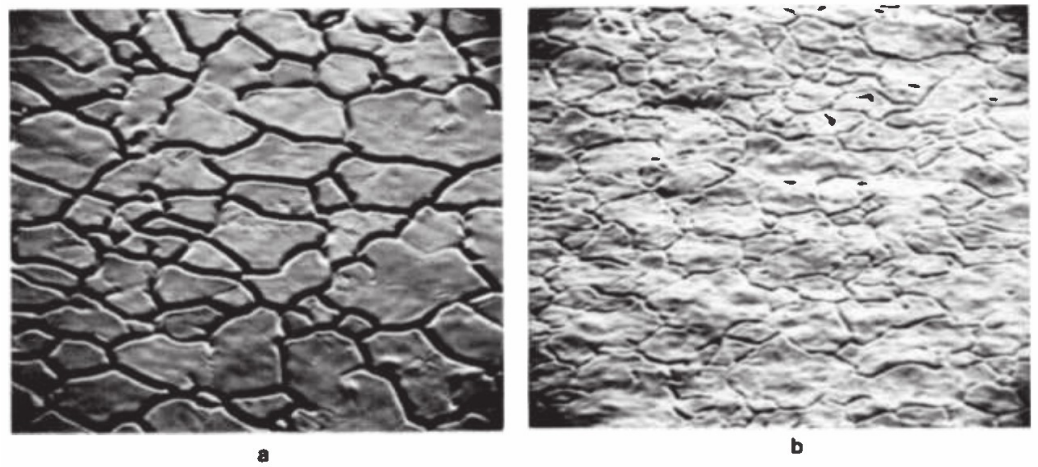


Fig. 7. Surface micrograph of the one-piece cathode showing grain boundaries within the base metal (approx. 100×): (a) grain structure of cathode cap and (b) grain structure of nichrome alloy.

5. Reaction Between Chromium and Oxide Coating

5.1 Migration of Chromium

Two one-piece bimetal cathodes after long-term life tests at 6.3 and 5.7 V E_f and one similar cathode after an accelerated life test at 8.1 V E_f were selected for this study. All three cathodes outlived their two-piece cathode counterparts. The operating conditions, time on life, and cathode emission levels when the tubes were opened are as follows:

E_f	Time on life	Emission when opened
6.3 V	110 weeks	greater than 80% of initial
8.1 V	10 weeks	approximately 80% of initial
5.7 V	110 weeks	greater than 80% of initial

The heating cycle of the life test is 2¾ hours on and ¼ hour off. One hundred and ten weeks of life test corresponds to about 17,000 hours of cathode working life.

Fig. 8a shows the cross-section of the 6.3 V E_f cathode. EDAX of the outer part of the coating shows Ba, Sr, and Ca, which are the constituents of the oxide coating (Fig. 8b). The inner part of the coating contains Cr in addition to Ba, Sr, and Ca (Fig. 8c). The migration of chromium into the oxide coating is clearly indicated. X-ray powder diffraction of the coating scraped from the 6.3 V E_f sample and from 8.1 V E_f samples showed the chromium-containing phase was in the form of $Ba_3(CrO_4)_2$ [8]. This phase is yellow and can be visually detected in cathodes after accelerated life test.

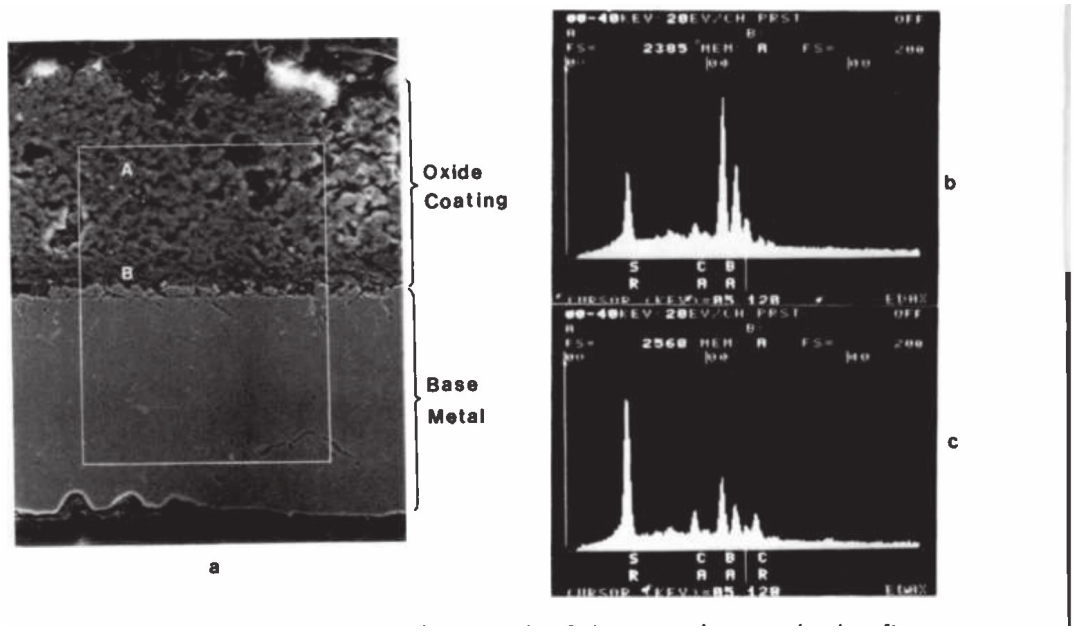


Fig. 8. (a) Scanning electron micrograph of the one-piece cathode after 110 weeks at E_f = 6.3 V (approx. 400×); (b) EDAX of outer part of oxide coating (point A) and (c) EDAX of inner part of oxide coating (point B).

To compare the extent of chromium migration into the oxide coating at different operating temperatures, chromium x-ray maps were taken of the three samples. Fig. 9a shows that after 110 weeks at 6.3 V E_f, a small amount of chromium was present in the inner part of the coating. For the cathodes

after 10 weeks at 8.1 V E_f, massive migration of chromium into the coating was observed (Fig. 9b). In some areas, migration through the oxide was complete. The chromium concentration in the oxide coating was estimated to be between 10 and 50 times higher than in the chromium-containing region of the 6.3 V E_f cathode. In contrast, no detectable chromium was found in the oxide coating of the 5.7 V E_f cathode (Fig. 9c). Although Cr may be present in the oxide in a small amount, it is below the detection limit of this technique. Some background x-rays are seen in the coating part of the micrograph.

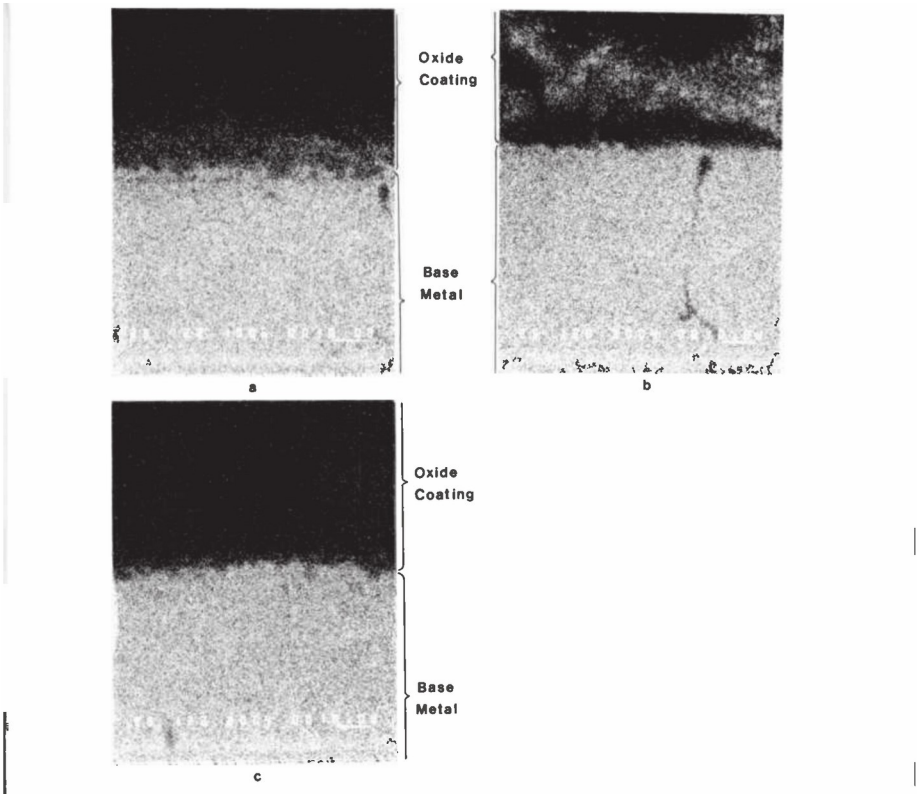


Fig. 9. Chromium Kα x-ray maps of the one-piece cathode: (a) after 110 weeks at E_f = 6.3 V (area outlined in Fig. 8a), (b) after 10 weeks at E_f = 8.1 V, and (c) after 110 weeks at E_f = 5.7 V.

The aforementioned results show that the rate of chromium migration is highly temperature dependent in the temperature range of the life tests. Other significant results from these data are:

1. In all three cases, chromium is uniformly distributed in the base metal, including the portion originally containing only cathode nickel (see Figs. 9a, b, c). These data confirm the results of the microprobe trace study of diffusion of chromium in the base metal.
2. In all three cases, there was no accumulation of chromium at the oxide-coating/metal interfaces (see Figs. 9a, b, c).

If the reaction between chromium and the oxide coating were controlled by solid-state diffusion of chromium in the base metal, a high concentration of chromium in the interface would be expected. The observation that chromium works its way up through the highly porous cathode coating instead of accumulating in an interface layer strongly suggests that the migration is through a vapor transport process.

The vapor pressure of chromium at various temperatures can be calculated from Ref. [9]. At filament voltages of 5.7, 6.3, and 8.1 V, the vapor pressures of chromium are 4.08×10^{-11}, 8.05×10^{-11}, and 4.02×10^{-9} atm, respectively. The vapor transport rate of chromium was increased by a factor of 2 when the filament voltage was increased from 5.7 V to 6.3 V, and by a factor of 50 when the filament voltage was

increased from 6.3 V to 8.1 V. These data show that the vapor transport mechanism is consistent with the observed temperature-dependent nature of the chromium migration (see Editor's Note 3 and Fig. S2).

5.2 Interface Compound

To complete the description of the coating/metal interface reaction for the one-piece cathode, nickel, tungsten, barium, and oxygen x-ray maps were taken of the interface region of the 6.3 V E_f cathode. The region examined is the blocked area shown in Fig. 8a. Nickel stays in the base metal (Fig. 10a). An accumulation of tungsten at the coating/metal interface is clearly seen (Fig. 10b). This layer is also enriched with barium and contains oxygen (Figs. 10c and 10d), suggesting that the interface compound is barium tungstate (possibly $3BaO{\cdot}WO_3$). The formation of the barium tungstate interface layer is expected and observed for all KS904 cathodes using Ni–4 wt% W cathode nickel [10]. Some penetration of barium and oxygen into the metal substrate is also noted in Figs. 10c and 10d.

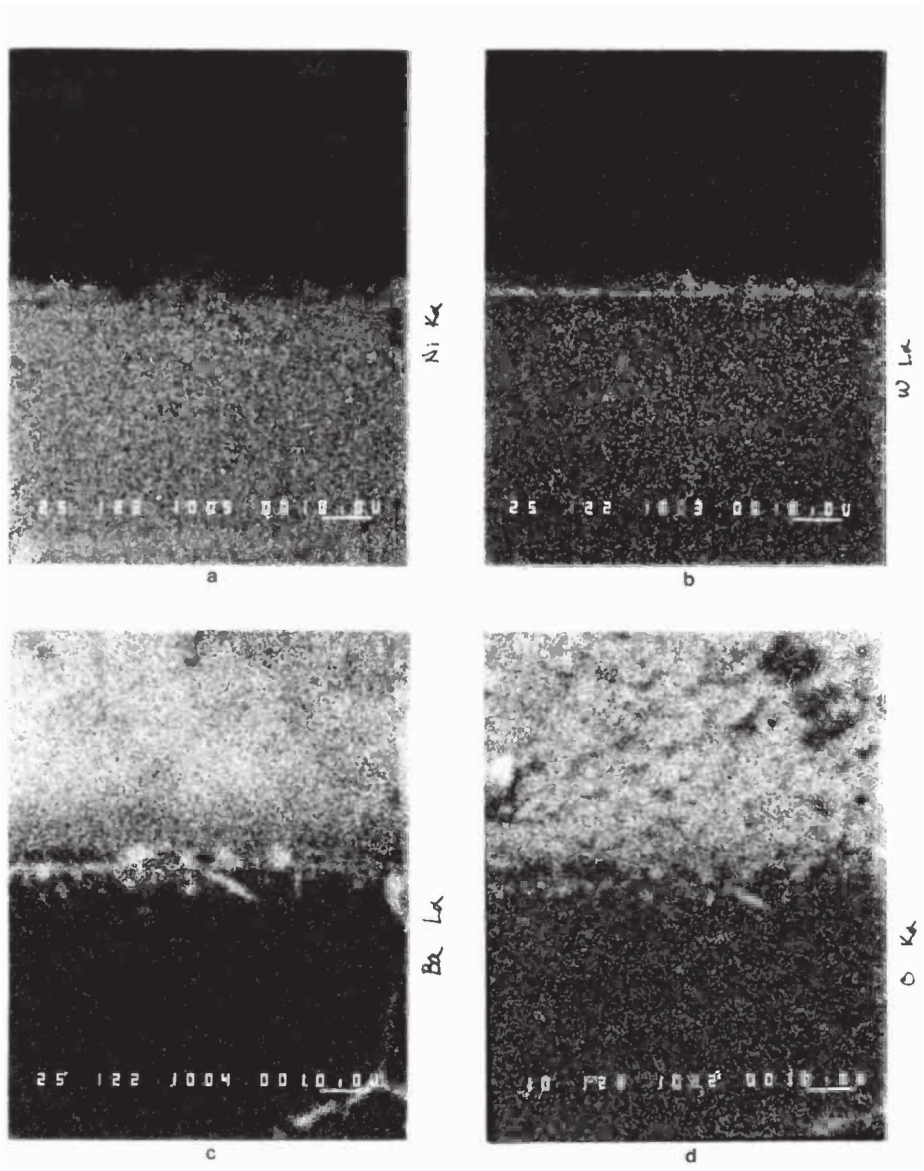


Fig. 10. Distribution of nickel, tungsten, barium, and oxygen in the area outlined in Fig. 8a: (a) Ni Kα x-ray map, (b) W Lα x-ray map, (c) Ba Lα x-ray map, and (d) O Kα x-ray map.

This analysis shows the interface compound of the one-piece bimetal cathode to be similar to that of the standard KS904 cathode. Chromium does migrate into the coating and reacts with the oxide to form a compound of $Ba_3(CrO_4)_2$. The reaction is controlled by vapor transport of chromium and does not concentrate in an interface layer. Cathodes with this compound in the oxide coating have very long emission life. This is further evidence that the chromium migration does not cause excessive bulk or interface resistance or loss of coating adherence.

6. Reaction Mechanism

6.1 Role of Chromium in Reducing Cutoff Change

Cutoff voltage is an electrical characteristic of the electron gun that is sensitive to cathode-to-grid (G1) spacing [11]. An increase in cutoff voltage during life usually represents an increase in cathode–G1 spacing. Contributors to this increase are sintering of the cathode coating during life, thinning of the coating due to evaporation of coating material, and the thermal deformation of the cathode cap and sleeve. Comparing the one-piece bimetal cathode and the standard two-piece cathode, the effects of coating sintering and evaporation are the same. The initial slight decrease in cutoff voltage of the one-piece cathode in life testing may be due to the elimination of cathode cap–sleeve welding and related to the interdiffusion of nickel and chromium. Details of this process are not yet completely understood.

After several weeks of life test, nickel and chromium are uniformly distributed throughout the cathode cap by diffusion. The presence of chromium in the nickel alloy strengthens the nickel lattice and results in smaller cap deformation during life. Consequently, the net cutoff increase in the same operating time period is reduced. The solid-solution strengthening effect of chromium on nickel-base alloys at high temperature is well documented in the literature [12, 13].

6.2 Role of Chromium in Increasing Cathode Life

Maintenance of emission levels is dependent upon a delicate balance of the amount of free alkaline-earth metal (Ba or Sr). A continuous production of free Ba is required, because a constant evaporation of the metal from the oxide surface takes place during tube operation. The production of free Ba is determined by the transport and availability of the activators. As the operating time of a cathode increases to thousands of hours, the supply of activators (Mg or Si) can be gradually depleted in two ways.

First, evaporation and activation reaction at the coating/metal interface gradually deplete the core metal of its activators [14]. Consequently, the flux of activators to the interface is reduced. Second, BaO dissociates into Ba and O. Oxygen and part of the barium diffuse back into the nickel cap [15]. Mg and Si may be oxidized inside the base metal through the reactions:

$$Mg + O \rightarrow MgO$$

$$Si + 2O \rightarrow SiO_2$$

Barium may precipitate along these oxides at grain boundaries. Subsequent diffusion of free activators is partly inhibited by these internal oxides.

For the one-piece bimetal cathode, chromium diffuses into the nickel portion of the cathode cap during the first several weeks of tube operation. After diffusing to the coating/metal interface, chromium migrates via vapor transport to react with the oxide coating. A reaction such as

$$8BaO + 2Cr \rightarrow Ba_3(CrO_4)_2 + 5Ba$$

occurs in the coating. In this reaction, chromium acts as an activator to chemically reduce barium oxide and thus provide an excess of free metallic barium. The life of the cathode is prolonged by this reaction when original activators are depleted by the two aforementioned processes.

Although there is not much difference in the time needed for chromium to diffuse to the oxide/metal interface at different operating temperatures (about 1 week at 8.1 V E_f, 3 weeks at 6.3 V E_f), the migration rate of chromium into the oxide coating changes greatly with different operating temperatures. At the normal operating temperature of 6.3 V E_f, chromium is metered out slowly and the cathode activity is maintained over a long period of time.

7. Summary and Conclusions

The one-piece bimetal cathode is a system that shows superior emission life and less cutoff voltage change with time than a conventional cathode. The major structural difference between the one-piece bimetal cathode and the standard two-piece cathode is the presence of a 1-mil (25 µm) nichrome layer beneath the cathode nickel.

Initial activation of the one-piece cathode is accomplished by the activators (Mg and Si) present in the cathode nickel, as in the case of the standard cathode. The interface reaction between the oxide coating and the substrate is of the form BaO·NiO. During tube processing and the initial stage of cathode life, chromium diffuses into the nickel portion of the one-piece cathode cap. The process involves grain-boundary diffusion and progresses at a rapid rate. Only one to three weeks are needed for chromium to reach the oxide-coating/metal interface. Chromium subsequently migrates via vapor transport to react with the oxide coating. In this reaction chromium acts as an activator and prolongs the cathode emission life.

The decrease in cutoff voltage change with time for the one-piece cathode is related to the elimination of cathode cap–sleeve welding and to solid-solution strengthening of the nickel lattice by chromium.

Acknowledgments

The authors gratefully acknowledge the contributions of J. C. Bridgeman, L. J. Royer, R. H. Woods, K. M. Finlayson, J. M. Wolfe and Dr. R. W. Heiden of the RCA VC&DD Analytical Laboratory and S. J. Kilpatrick of RCA Laboratories' Analytical Laboratory.

References

1. G. Hermann and S. Wagener, *The Oxide-Coated Cathode*, Volumes 1 and 2, Chapman and Hall, London (1951).
2. P. Zalm, "Thermionic Cathodes," in *Advances in Electronics and Electron Physics*, **25**, pp. 211–275 (1968).
3. J. C. Turnbull, RCA Technical Note 1159 (1976).
4. C. H. Meltzer and E. G. Widell, "Nickel Base Metal for the Oxide Cathode," in *Electron Tube Design*, pp. 64–76 (1962).
5. W. H. Kohl, "Cathodes and Heaters," in *Handbook of Materials and Techniques for Vacuum Devices*, Chapter 16 (1967).

6. A. Fineman and A. Eisenstein, “Studies of the Interface of Oxide Coated Cathodes,” *J. Appl. Phys.* **17**, p. 663 (1946).

7. S. J. Kilpatrick, private communication.

8. JCPDS Powder Diffraction File (1979).

9. JANAF Thermochemical Tables, 1975 Supplement, Reprint No. 60 from *J. Phys. Chem. Ref. Data* **4** (1975).

10. E. J. Hannig, “The Interface and Other Oxide-Cathode Impedances,” in *Electron Tube Design*, pp. 77–89 (1962).

11. H. Moss, *Narrow Angle Electron Guns and Cathode Ray Tubes*, *Advances in Electronics and Electron Physics*, Supplement 3 (1968).

12. K. Jackson and R. O. Jenkins, “Nickel in Electronics,” *Metallurgia* **47**, p. 277 (1953).

13. R. M. Brick, R. B. Gordon, and A. Phillips, “Metals for High Temperature Service,” in *Structure and Properties of Alloys*, Chapter 14 (1965).

14. E. S. Rittner, “A Theoretical Study of the Chemistry of the Oxide Cathode,” *Philips Res. Repts.* **8**, p. 184 (1953).

15. A. C. Aten, J. C. Duran, J. J. Guerts, and A. J. Griffioen, “Chemical Transport in Oxide Cathodes,” *Philips Res. Repts.* **26**, p. 519 (1971).

Editor’s Notes (2026)

1. **Transcription.** The text was recovered by optical character recognition from the scanned journal pages and checked against the page images. Corrections include the chemical formulas ($Ba_3(CrO_4)_2$, Cr_2O_3, $BaO{\cdot}Cr_2O_3$, NiO_x, H_2 firing, $3BaO{\cdot}WO_3$), subscripted symbols (E_f), and “°K,” which is now written as K. The exponent of the 8.1 V vapor pressure is unclear in the scan; 4.02×10^{-9} atm is consistent with the factor of 50 stated in the text. The authors’ names are as printed: K. T. Chiang and J. J. Maley. In the original the two-piece cathode is called the “standard KS904 cathode.”

2. **Grain-boundary diffusion (Fig. S3).** For lattice diffusion of Cr in Ni a representative literature value is $D \approx 1.1 \exp(-272\ \text{kJ mol}^{-1}/RT)\ \text{cm}^2\ \text{s}^{-1}$. At the 6.3 V brightness temperature of 1075 K this gives $D \approx 7 \times 10^{-14}\ \text{cm}^2\ \text{s}^{-1}$, and a diffusion distance $\sqrt{(Dt)}$ of only about 3.5 µm in 3 weeks, against the 51 µm of cathode nickel that chromium crossed in that time. Crossing 51 µm in 3 weeks needs an effective diffusivity of about $1.4 \times 10^{-11}\ \text{cm}^2\ \text{s}^{-1}$, roughly 200 times the lattice value. At 8.1 V (1200 K) and 1 week, the factor is about 27. Both strongly support the authors’ explanation that chromium moves along grain boundaries.

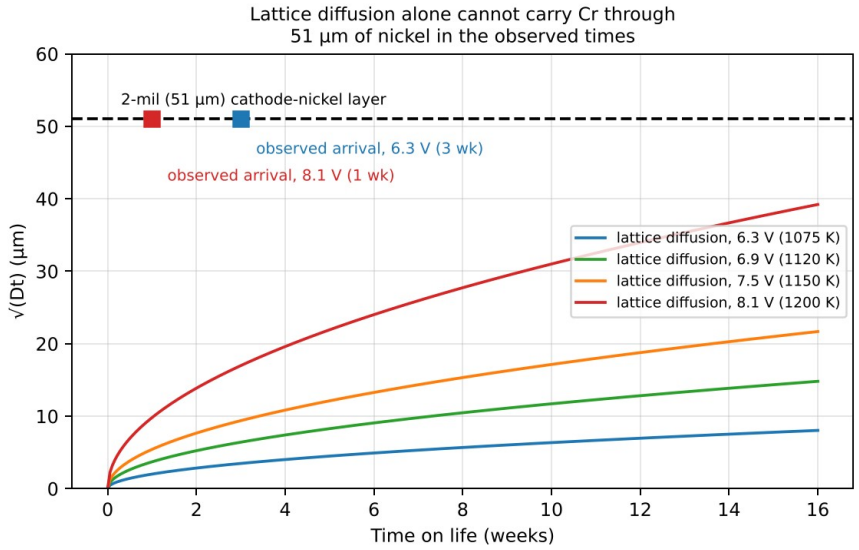


Fig. S3 (new). Lattice-diffusion distance √(Dt) of Cr in Ni against time at the four life-test temperatures, compared with the 51 µm cathode-nickel layer and the observed arrival times of chromium at the metal/coating interface.

3. **Chromium vapor pressure (Fig. S2).** A modern evaluation of the vapor pressure of solid chromium (Alcock, Itkin and Horrigan, 1984) gives about 7.0×10^{-12} atm at 1075 K and 7.5×10^{-10} atm at 1200 K. The paper's values are higher: they correspond to temperatures about 50–60 K above the stated brightness temperatures. That is consistent with the true temperature of a cathode exceeding its optical brightness temperature, since its emissivity is below one; an emissivity of about 0.3 at 650 nm would account for the difference. With the modern data at the brightness temperatures, the vapor pressure rises by a factor of about 100 between 6.3 V and 8.1 V, against the paper's factor of 50. The conclusion that chromium migration is strongly temperature dependent, and consistent with vapor transport, is unchanged and somewhat strengthened. The paper does not give a temperature for 5.7 V.

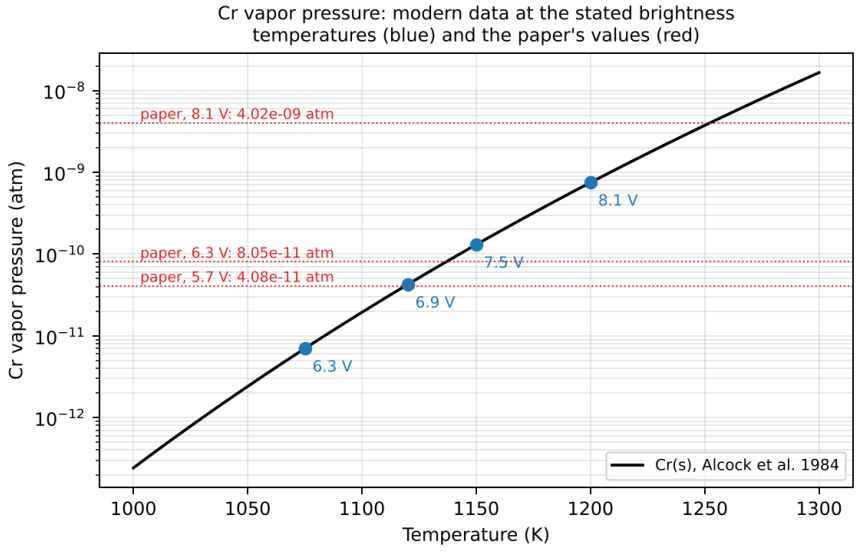


Fig. S2 (new). Vapor pressure of solid chromium against temperature (Alcock et al., 1984) with the values at the stated brightness temperatures (points) and the values quoted in the paper (dotted lines).

4. **The activation reaction and the oxidation state of chromium.** The proposed reaction balances with chromium ending as Cr(V). In $Ba_3(CrO_4)_2$ ($Ba_3Cr_2O_8$, tribarium bis(chromate(V)) [E3]) three Ba^{2+} carry +6, so each CrO_4 group is CrO_4^{3-} and chromium is +5. Each chromium atom gives up five electrons and frees 2.5 Ba:

   $8BaO + 2Cr \rightarrow Ba_3(CrO_4)_2 + 5Ba$ ($Cr^0 \rightarrow Cr^{5+}$)

   If chromium went on to Cr(VI), the product would be ordinary barium chromate, with three Ba freed per chromium atom:

   $4BaO + Cr \rightarrow BaCrO_4 + 3Ba$ ($Cr^0 \rightarrow Cr^{6+}$)

   Either way chromium frees more barium per atom than magnesium (one Ba per Mg) or silicon (two Ba per Si, forming Ba_2SiO_4), so the activation argument holds.

   The paper's evidence is mixed on which product forms. The x-ray diffraction match is to $Ba_3(CrO_4)_2$, and Cr(V) is what would be expected in an operating cathode: a strongly reducing BaO matrix containing free barium, in vacuum at about 1100 K. But the phase is described as yellow, which is the characteristic color of chromate(VI) such as $BaCrO_4$. One possible reconciliation is that Cr(V) formed in the tube and was partly converted afterward. Chromate(V) is unstable in air and moisture and disproportionates to Cr(VI) and Cr(III). Both the color and the diffraction were observed on cathodes taken from opened tubes. The color of $Ba_3(CrO_4)_2$ itself, and whether $BaCrO_4$ lines were also present in the diffraction patterns, would settle the point.

5. **Dimensions.** 1 mil = 25.4 µm; the 2-mil cathode nickel is 51 µm and the 1-mil nichrome 25 µm.

Additional references for the Editor's Notes

- C. B. Alcock, V. P. Itkin and M. K. Horrigan, "Vapour pressure equations for the metallic elements: 298–2500 K," *Canadian Metallurgical Quarterly* **23**, 309–313 (1984).
- Representative Cr-in-Ni lattice diffusion data: K. Monma, H. Suto and H. Oikawa, *J. Japan Inst. Metals* **28**, 188–192 (1964).
- [E3] H. Mattausch and Hk. Müller-Buschbaum, "Zur Kristallstruktur von $Ba_3(CrO_4)_2$," *Z. Naturforsch. B* **27**, 739–744 (1972).