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EVALUATION OF ELECTRON-EMISSON BEHAVIOR
FOR DETECTING CARBON IN TUNGSTEN AND RHENIUM

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EVALUATION OF ELECTRON-EMISSION BEHAVIOR
FOR DETECTING CARBON IN TUNGSTEN AND RHENIUM

by

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September 24, 1963

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EVALUATION OF ELECTRON-EMISSION BEHAVIOR FOR DETECTING CARBON IN TUNGSTEN AND RHENIUM

James B. Baker and Gordon B. Gaines

In a program to develop methods of studying high-temperature metal reactions by means of changes in the thermal-electron-emission behavior when such reactions occur, the thermal-electron-emission behavior of rhenium-carbon and tungsten-carbon alloys was determined. It is shown that the presence of a very small amount of carbon on the surface of rhenium produces an easily detectable increase in the emission current. In the tungsten-carbon system two new emission states were detected. One of these shows emission of a much higher level than that of pure tungsten and appears to occur when the emitting surface is composed of WC. The other shows an emission level slightly lower than that for pure tungsten and appears to occur when the emitting surface is composed of W₂C.

INTRODUCTION

As a part of a program directed toward the study of high-temperature metal reactions, it is the objective of this specific investigation to employ the thermionic-emission behavior and work-function determinations to detect the presence of carbon on the surface of rhenium and tungsten. The knowledge of the emission characteristics of these metals when the surface is covered, either partially or completely, by carbon can then be used in subsequent investigations to measure the rate of arrival of carbon at the surface of specimens in which the carbon is released by a high-temperature reaction within the specimen (or reaches the surface by diffusion through a barrier).

The thermal-electron-emission behavior of most metals is very strongly affected by the conditions at the surface. The presence of certain adsorbed atoms in quantities sufficient to provide only 0.1 monolayer on the surface of the base metal can be detected by a pronounced change in the thermal-electron emission from the metal. A less pronounced, but still easily detectable, emission effect results from a rearrangement of the lattice (recrystallization) at the surface from which the emission is being collected.

The thermal-electron current from a metallic emitter can be represented by the relationship

$$J = AT^2 \exp - \frac{e\phi}{kT} ,$$

known as the Richardson-Dushman equation. In this equation J is the current density in amp per cm^2 , A is a constant which has a theoretical value of $120 \text{ amp}/(\text{cm}^2)(\text{K}^2)$ but for which the experimental values are usually quite different, T is the temperature in degrees Kelvin, e is the electronic charge, k is Boltzmann's constant, and ϕ is the Richardson work function. The quantity $e\phi$ in the Richardson-Dushman equation is the work required to raise an electron at the Fermi surface out through the metal surface and beyond its influence. It is obvious that the sum of all the forces acting upon an escaping electron constitutes the work function. Such forces can be arbitrarily classed

as short-range forces for distances which are of the order of the atomic spacing, say 10 Å, and long-range forces which extend out to about 10^{-4} cm, where in practical cases the electron can be considered to be free of the surface. The short-range forces result from the interaction between atoms. Thus, it can be seen that the work function for different crystallographic faces of the same material could be different and one would expect the work function to be highest for crystals having the closest atomic spacing. Such behavior has been observed for several metals. It might be expected that a nonpolarizable impurity atom on the surface would decrease the emission. In the case of polarizable atoms, dipole forces can be formed which will alter the work function by several electron-volts. Barium and thorium are two polarizable atoms which have been studied extensively.

The long-range forces arise principally from two sources, the image force and patch effects. The image force is visualized to be the electrostatic force acting between the electron and its image charge located within the metal. This force would not be influenced by surface conditions. The other principal long-range force results from the contact potential differences between adjacent "patches" on an inhomogeneous surface. (It should be recognized that the forces due to "patches" can operate as short-range forces also.) It is possible to detect the patch effect experimentally. If a chemical reaction at the surface of a metal (the formation of tungsten carbide by reaction with carbon for example) should proceed by the formation of patches which eventually join to cover the entire surface it might well be possible to "observe" such reactions by means of the electron-emission behavior.

It is known that rhenium does not form a stable carbide but about 10 at/o carbon can be dissolved in it. On the other hand, the solubility of carbon in tungsten is very low but it forms stable carbides. Tungsten carbide has long been of interest in the electron-tube industry because it has been found that the useful life of a thoriated tungsten emitter is increased severalfold if it is carburized. The data reported in the literature concerning the emission properties of tungsten carbide indicate that its emission behavior differs from that of pure tungsten but there is considerable variation in the magnitude of the differences observed by various investigators. Zubenko and Sokol'skaya⁽¹⁾ found a Richardson work function for tungsten carbide of 4.58 eV which is not significantly different from that of pure tungsten (4.52 eV) but their Richardson A value [$190 \text{ A}/(\text{cm}^2)(\text{K}^2)$] was about four times that of the value obtained for pure tungsten. Bas-Taymaz⁽²⁾ found a Richardson work function of 3.85 eV for tungsten carbide but a Richardson A value of only $0.35 \text{ A}/(\text{cm}^2)(\text{K}^2)$. Klein⁽³⁾ studied the surface migration of carbon on tungsten with a field-emission microscope. While he did not determine the emission constants he observed that the emission decreased slightly with increasing carbon deposition and that the work function was decreased very slightly by adsorbed carbon.

No information was found in the literature concerning the emission behavior of carbon on rhenium.

(1) References are at end of report.

EXPERIMENTAL INVESTIGATION

The experimental investigation consisted of measuring the thermal-electron emission from wires of rhenium and tungsten. The emission behavior of tungsten and rhenium wires of the highest purity commercially available was determined, then the emission behavior of wires that had been heated in carbonaceous atmospheres was determined. The emission studies were performed in special tubes in which the wire under investigation was mounted at the axis of a cylindrical anode 0.25 in. (0.635 cm) in diameter. In order to minimize the effects of temperature variations along the length of the wire a guard-ring diode structure was used for the anode. The anode was constructed of three cylinders so that the current emitted by a 1/2-in. (1.27 cm) long section at the mid-point in the wire could be separated from the emission from the rest of the wire. The temperature of the central section of the wire was determined by sighting an optical pyrometer through a small hole in the central anode. The pyrometer temperature readings were converted to true temperatures by using the appropriate values of the spectral emissivities of the various materials. The effect of the glass containment on the pyrometer readings was determined experimentally and was used in calculating the correct temperatures. It was also established experimentally that the presence of the anodes around the wire did not change the apparent spectral emissivity of the wire.

In order to minimize the amount of energy dissipated at the anodes, all emission measurements were made at 200 to 400 v. Two hundred volts is sufficient to insure that all emitted electrons are collected for emission currents up to 13 ma and 400 v is sufficient to provide collection of all electrons up to 37 ma. For cases where the emission current exceeded this value, the electrons were collected by applying pulsed voltages up to 2500 v.

In experiments where one wishes to detect a change in the forces acting upon electrons being emitted by a cathode it is only necessary to observe changes in the emission current. If one wishes to know the nature of these changes, however, the constants ϕ and A to the Richardson-Dushman equation must be evaluated. If the Richardson-Dushman equation is rearranged to read $J/T^2 = A \exp - e\phi/kT$ and then the logarithms are taken, one gets $\log_{10} J/T^2 = \log_{10} A - 0.434 e\phi/kT$. Thus, a plot of $\log J/T^2$ versus $1/T$ gives a line with a slope of $-0.434 \times 11,600 \phi/T$, ($e/k = 11,600$). The emission constants calculated from this line are usually designated as Richardson values and represent the conditions at $T = 0$ K and for zero electric field at the emitting surface. The data obtained at 200 to 400 v were used directly in making Richardson plots of the emission data since the maximum error introduced in the work-function values by this procedure would be only 0.03 ev. [For a discussion of thermionic-emission constants and their interpretation see Reference (4).]

Rhenium-Carbon System

The rhenium-carbon system was chosen for investigation because it was known that rhenium does not form a stable carbide but does have a reasonably high solubility for carbon⁽⁵⁾. It was considered quite probable that by the proper heat treatment under high-vacuum conditions some of the dissolved carbon could be diffused to the surface

and evaporated. Although the vapor pressure of carbon is low, it is still approximately 2 to 3 orders of magnitude higher than that of rhenium.

A 0.015-in. (0.381 mm) diameter rhenium wire was carburized by exposing it to a mixture of dry hydrogen and toluene for 2 minutes at 1980 C. The emission from this wire tended to be unstable, i. e., varied with time even though it was held at a constant temperature, until the wire was heated to 2940 K for 2-3/4 hr. Figure 1 shows the emission behavior of the carburized rhenium wire at a temperature of 2280 K while it was in the unstable condition. The emission obtained from an untreated rhenium wire is also shown. For the untreated wire the actual change in the magnitude of the current is small and it is suspected that the reduction shown is the result of a slight change in the temperature of the wire rather than because of any change in its emission capability. The emission from the carburized wire prior to the stabilization of the emission but measured shortly after the temperature was increased was used to determine the circled data points on the Richardson line shown in Figure 2. The remaining x-points were obtained after the emission had been stabilized by heating the wire to 2940 K. The Richardson line obtained for an untreated rhenium wire over a rather limited temperature range is also shown.

It should be stressed that the time instability of the emission behavior shown in Figure 1 introduces considerable uncertainty into the Richardson plot of the data for carburized rhenium, but within the accuracy of the experiment the slopes of the lines are the same, giving a Richardson work function of about 4.8 ev. Still the emission density from carburized rhenium is about 1.8 times as great as that from uncarburized rhenium.

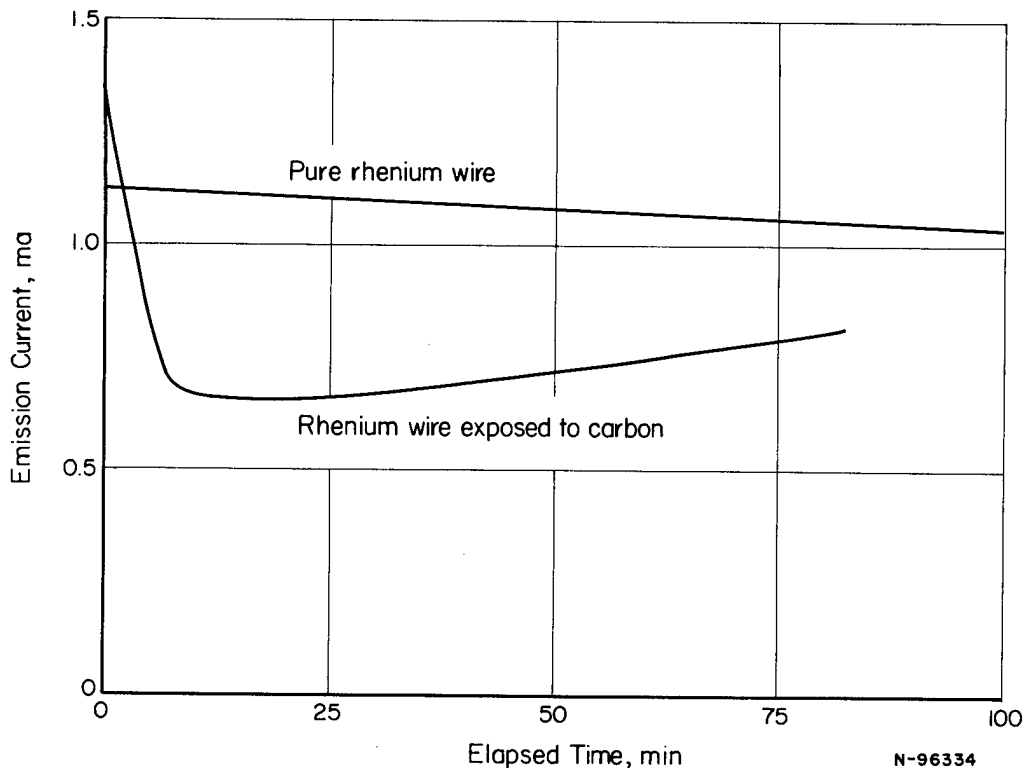


FIGURE 1. EFFECT OF THE PRESENCE OF CARBON UPON THE EMISSION BEHAVIOR OF RHENIUM AT 2280 K

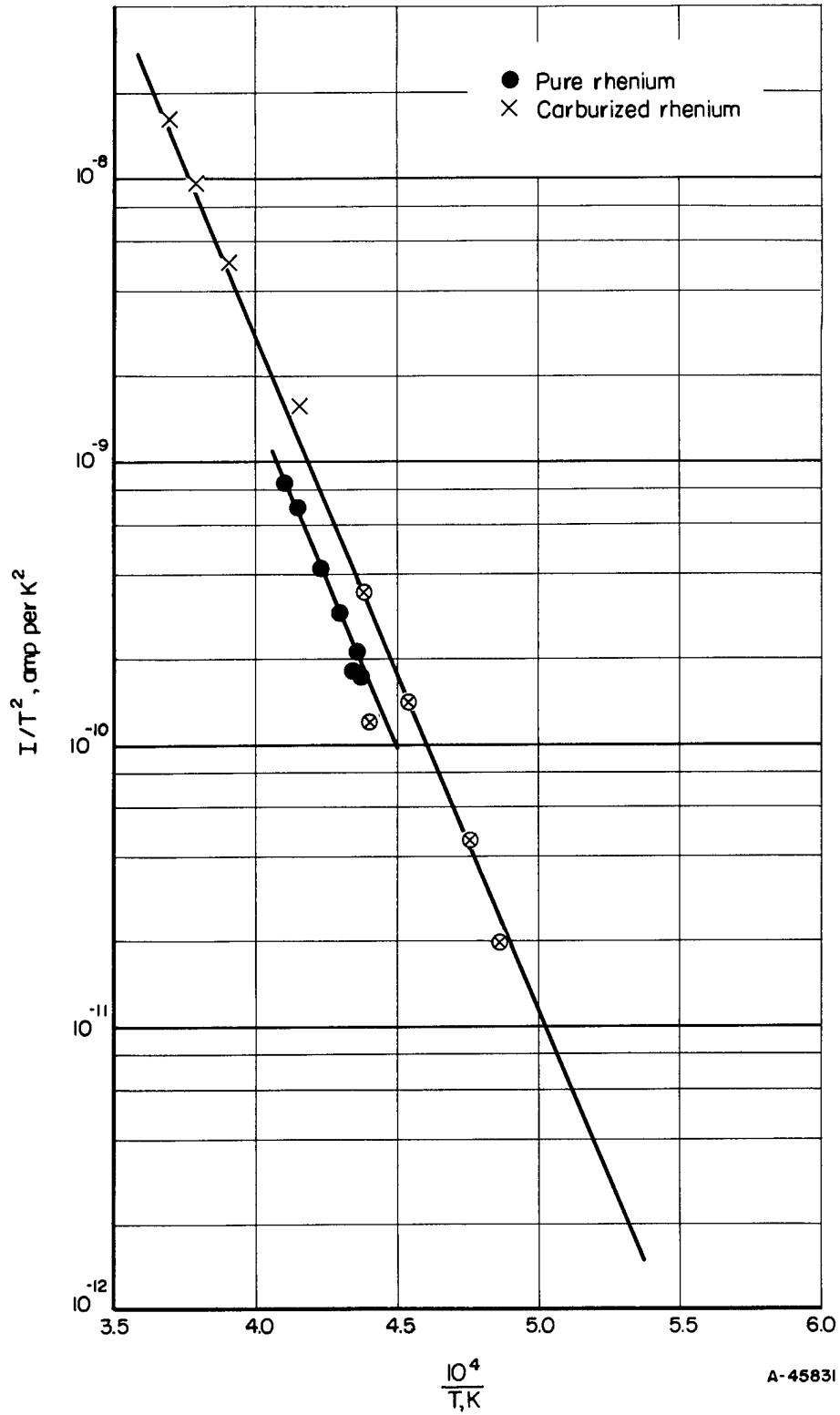


FIGURE 2. RICHARDSON PLOT OF EMISSION DATA FOR RHENIUM WIRES

After the emission data had been obtained for the wire in the stabilized condition it was removed from the tube and Knoop hardness measurements were made on it. Hardness data for a piece of the carburized wire which was cut off prior to the emission studies and those for the wire after it was removed are given in Table 1. These data show that when the emission became stable carbon was no longer present in the wire in sufficient quantity to affect the hardness. Due to the very small size of the test specimen no other means of determining the carbon content was available so that all that is known is that it must have been reduced to a very low level.

The results of the emission studies of the rhenium-carbon system show clearly that the emission is sensitive to the presence of carbon on the surface but additional experiments would be required to definitely explain the observed behavior. Since this system was chosen only to establish whether carbon could be detected on the surface no further studies were undertaken. By analogy with the behavior of other film-type cathodes and with the knowledge gained in subsequent work on tungsten a possible explanation can be suggested. Generally it would be expected that when the temperature of a refractory wire is first increased, the surface would tend to "clean-up". It is usually found that the forces holding the last monolayer of an impurity on a surface are much greater than those holding the preceding layers. The treatment at 2940 K was apparently sufficient to remove all of the carbon from the wire except about one monolayer on the surface. It must be then that a small amount of carbon, of the order of a monolayer, results in a substantial increase in the emission capability of rhenium. The unstable emission behavior at low temperature probably results from a variation in the carbon concentration due to the competing processes of diffusion of carbon to the surface and evaporation from the surface. Carbon in excess of a monolayer probably results in a reduction of the emission capabilities.

Tungsten-Carbon System

The tungsten-carbon system was studied in considerable detail by observing the emission behavior of a number of tungsten wires that were carburized under somewhat varying conditions. One 0.015-in. (0.38 mm)-diameter undoped tungsten wire (Sample 1) was carburized by heating it for 100 hr at 1000 K in methane. Sample 2 was prepared by exposing a 0.010-in. (0.254 mm)-diameter Type 218 tungsten wire to toluene vapor after it was installed in a guard-ring diode tube. The temperature of Sample 2 was 2450 K when the toluene vapor was admitted but upon admission of the gas the temperature dropped several hundred degrees. The wire was heated for a total of 12 min in the toluene. The third method of carburizing wires consisted of heating the wires to 1700 to 2100 K in a mixture of toluene and extra-dry hydrogen. This method of carburization produced a structure that was very useful for the emission studies so a number of these wires were investigated. Sample 3 was prepared by this method.

In order to have some idea of the initial composition of the carburized wires, Knoop hardness data were taken on a section of Sample 1 and two wires carburized by Method 3 (in a mixture of extra-dry hydrogen and toluene). Since Sample 2 was carburized in a guard-ring diode tube, it was impossible to obtain such data for it. The hardness data and metallographic examination revealed that Sample 1 did not contain sufficient carbon to be detected by these means. The wires carburized in the toluene-hydrogen mixture had a structure (shown in Figure 3) consisting of two carbide

TABLE 1. KNOOP HARDNESS DATA FOR CARBURIZED RHENIUM WIRE

Distance From Edge, cm	Knoop Hardness Number, 100-G Load	
	Before Emission Studies	After Emission Studies
0.002	715	238
0.004	644	
0.005		281
0.008		285
0.009	795	
0.010		270
0.014	745	223
0.017		300
0.019	605	
0.021		296
0.024	684	263
0.028		281
0.029	855	
0.030		253
0.034	700	
0.0365	669	

layers around a matrix of unreacted tungsten. Hardness data indicated that the very thin outside zone was WC and the intermediate zone W_2C . This was verified by X-ray diffraction of another piece of this wire.

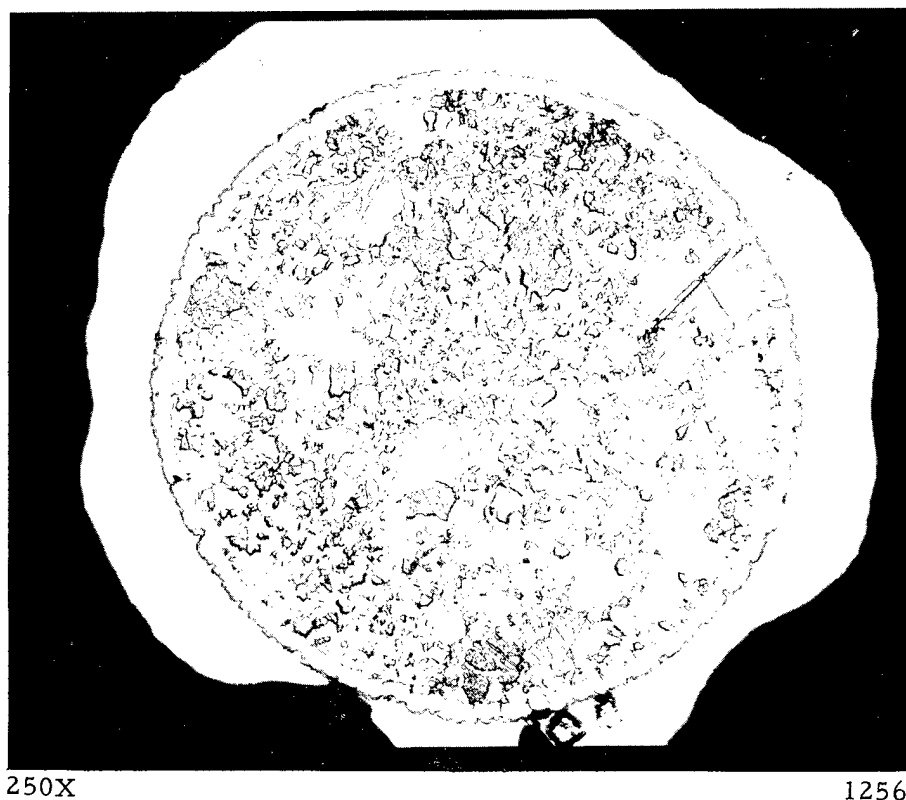


FIGURE 3. WC AND W_2C ZONES ON CARBURIZED TUNGSTEN (SAMPLE 3)

The bright white outer layer is nickel used for metallographic mounting purposes. The next layer which is dark gray is WC, and the next layer, a fairly uniform layer of considerable thickness, is W_2C .

Richardson plots showing the emission behavior of the carburized wires are shown in Figures 5 through 7. Figure 4 shows the experimental data for two samples of untreated tungsten wire. One of the untreated samples was a 0.015-in. (0.381 mm)-diameter undoped wire and the other was the 0.010-in. (0.254 mm)-diameter Type 218 wire that was subsequently carburized to form Sample 2. The Richardson lines determined from the plots of the experimental data shown on the curves of Figures 4 through 7 have been transferred to Figure 9 so that they may be compared more easily.

The two lines shown on Figure 5 indicate that a rather abrupt change occurred in the conditions at the emitting surface of Sample 1 (heated in methane at 1000 K) when the temperature exceeded 2000 K. The Richardson line determined by the open circles is for the cathode in a stable condition after it had been heated to 2470 K. This line is extremely close to the Richardson lines obtained for untreated tungsten wires. It can be seen then that the emission level during the first time the wire was heated was substantially higher than would be expected from pure tungsten. It can also be seen that

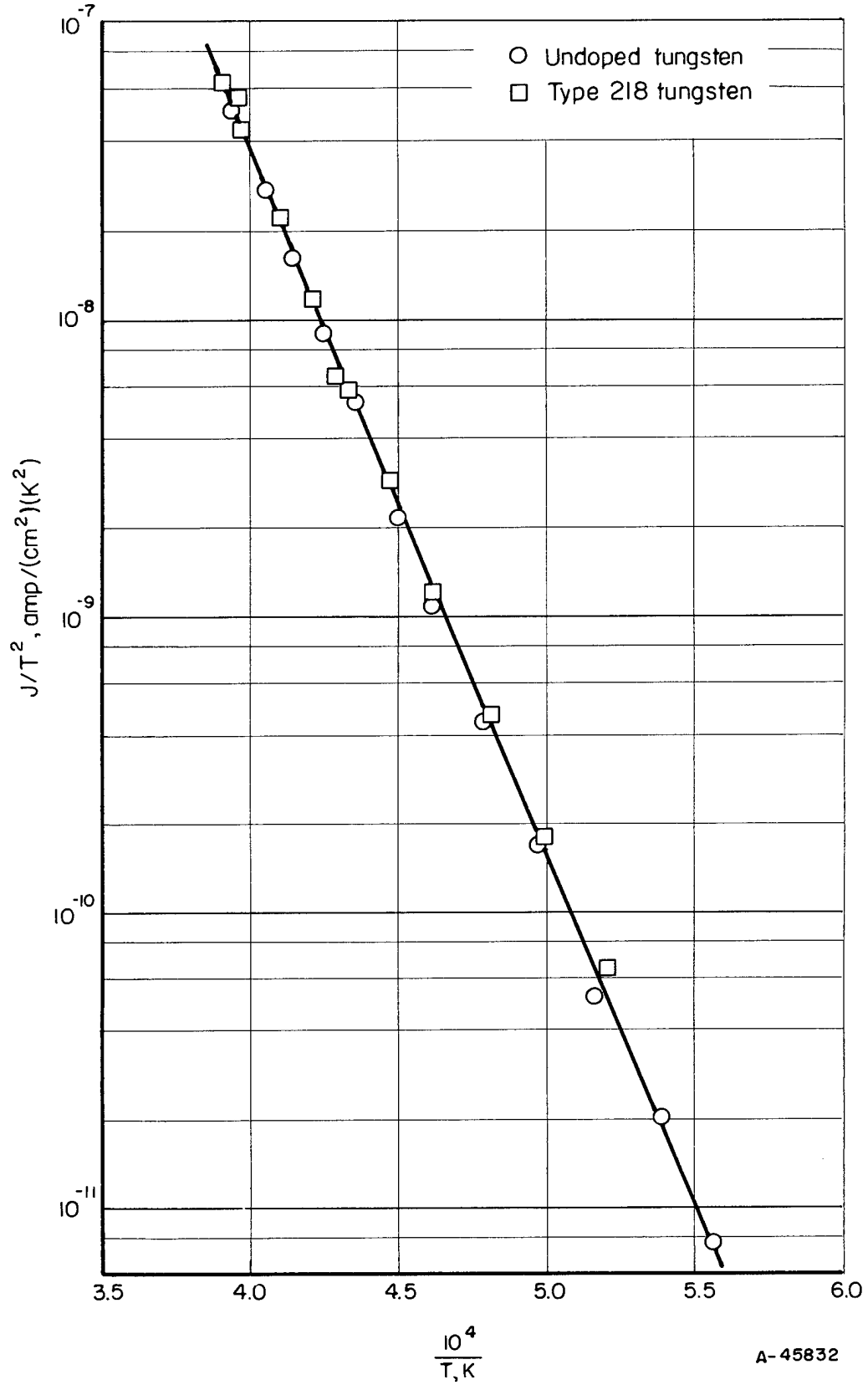


FIGURE 4. RICHARDSON PLOT OF EMISSION DATA FOR UNTREATED TUNGSTEN WIRES

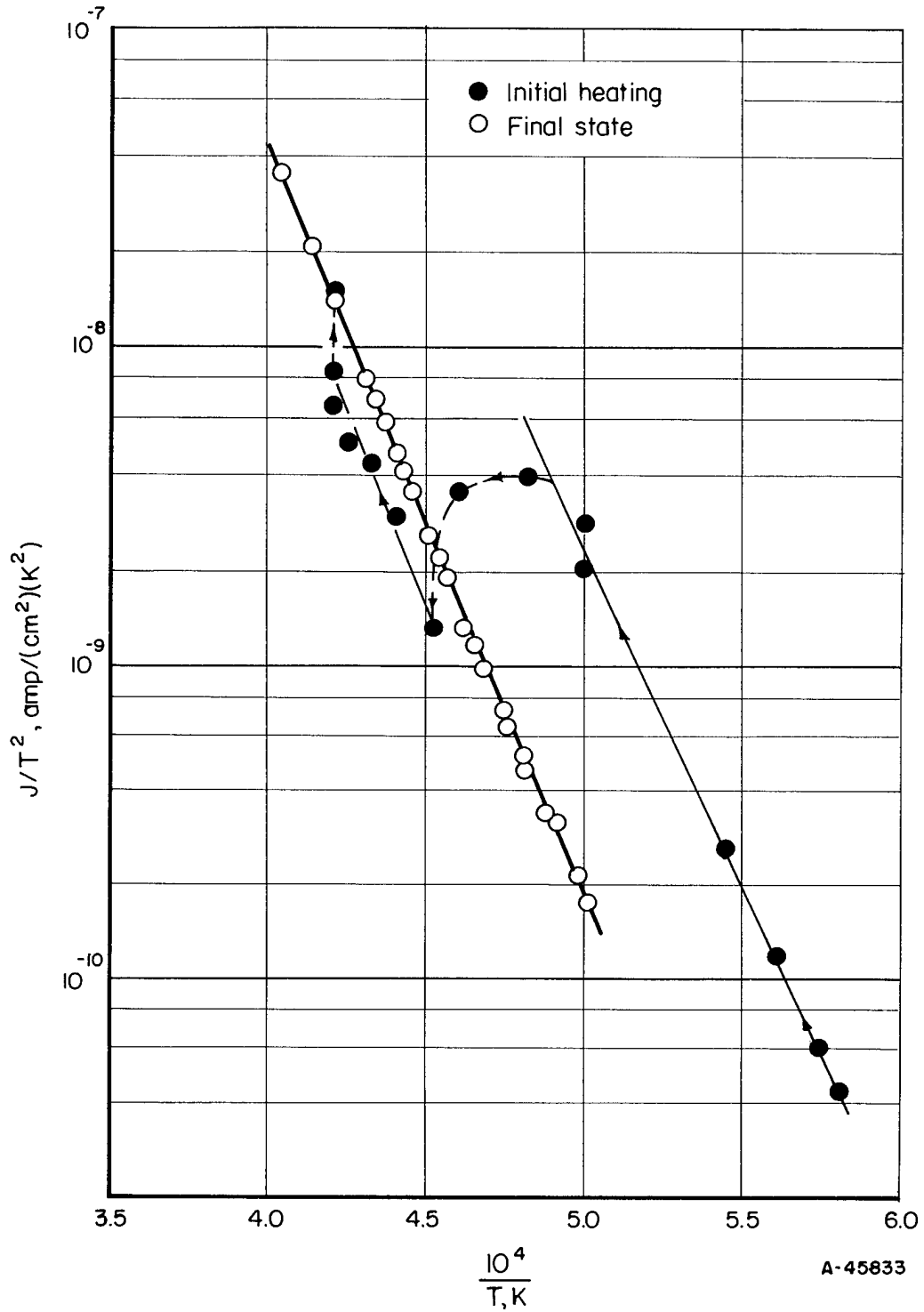


FIGURE 5. RICHARDSON PLOT OF EMISSION DATA FOR TUNGSTEN WIRE CARBURIZED IN METHANE AT 1000 K (SAMPLE 1)

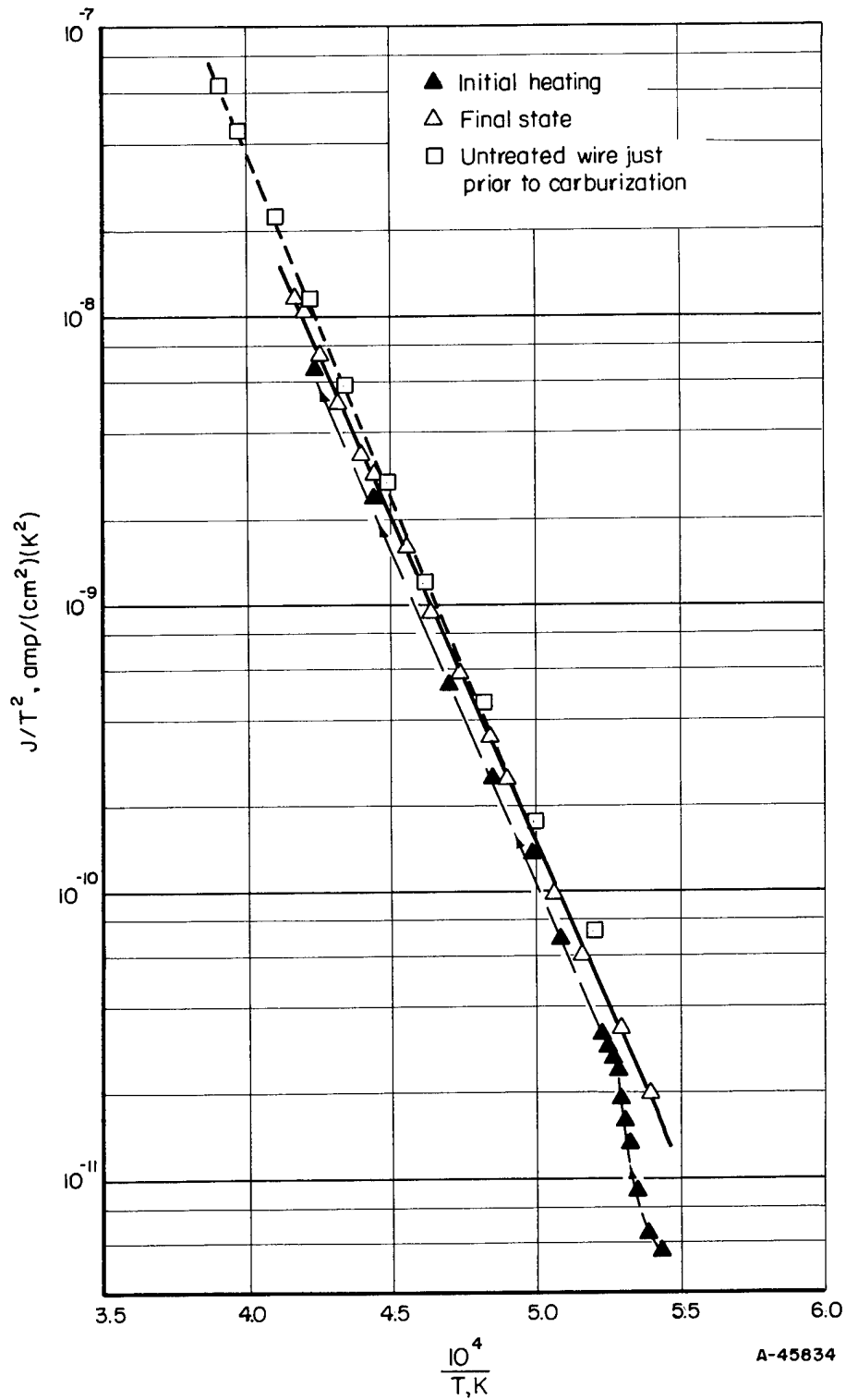


FIGURE 6. RICHARDSON PLOT OF EMISSION DATA FOR TUNGSTEN WIRE COMPLETELY CARBURIZED TO W_2C IN TOLUENE VAPOR AT ABOUT ~ 2450 K (SAMPLE 2)

the emitting surface changed to a condition which had lower emission capabilities than those of pure tungsten for the temperature range of 2210 to 2380 K. At 2380 K the emission slowly increased until it reached the level of pure tungsten. Subsequent increases in temperature up to 2470 K did not produce any further change in the emission behavior.

Figure 6 shows that the exposure of Sample 2 to toluene vapor at an unknown temperature near 2450 K resulted in a slight reduction in the emission capabilities of the wire. The data points used to determine the Richardson line shown, i. e., those for the cathode in its "final" state were obtained after the cathode had been heated for 1/4 hr at 2430 K. By comparison of the data points for the initial heating it can be seen that a slight shift toward the emission level of pure tungsten appears to have resulted from this treatment. When the temperature of this wire was increased to 2570 K the wire burned out and all but a very short section at one end was lost. Metallographic examination of this short section revealed the structure to be a central core of tungsten covered by a layer of W_2C saturated with tungsten.

The data points obtained on Sample 3 (carburized in toluene-hydrogen mixture at 2100 K) tended to follow those of Sample 2 very closely on initial heating until a temperature of 1975 K ($10^4/T = 5.07$) was reached (Figure 7). At that point, however, the emission from Sample 3 began to have higher values and eventually rose to a level comparable to that of the active state of Sample 1. At the same time this increase in emission was occurring, a gradual increase in the brightness temperature occurred (even though the power setting of the filament supply was not changed) until the temperature reached 2010 K. At this temperature the heater power was reduced slightly to give a brightness temperature of 1965 K. At this point the temperature was essentially stable. Figure 8 shows a plot of the heating current through Sample 3 versus the observed (brightness) temperature. The initial heating data from 1466 to 1574 C cover the range where the indicated temperature increased while the heater power setting was held constant. The power supplied to the filament is voltage regulated to a high degree which means that the resistance of the wire had to be increasing during this period. A plot of the resistance of the wire versus temperature gave a smooth curve through this temperature range, however, showing that the abrupt irreversible decrease in the heating current requirement did not result from a change in resistivity. It must be then that the total emissivity of the surface decreased substantially so that the power lost by radiation was reduced. The most probable explanation for this is that the original surface was covered by a layer of carbon for which the total emissivity is near 1. As the temperature increased, this carbon probably diffused into the wire and eventually left a surface of tungsten carbide. It has been reported⁽⁶⁾ that the total emissivity of tungsten carbide is not much different from that of tungsten which is about 0.22 at 1540 C brightness.

The emission behavior of Sample 3 appears to be explained as follows: first, a layer of uncombined carbon on the surface causes a reduction in the emission compared with that of pure tungsten (this is in agreement with the work by Klein); at 1880 K the uncombined carbon begins to react with the base metal and as it does so the emission increases with time to a level which is much higher than that of pure tungsten. This level is probably a characteristic of clean WC. On continued heating to about 2000 K, the WC reacts with additional base-metal tungsten to form additional W_2C leaving a surface composed of W_2C , which must have emission capabilities lower than those of pure tungsten.

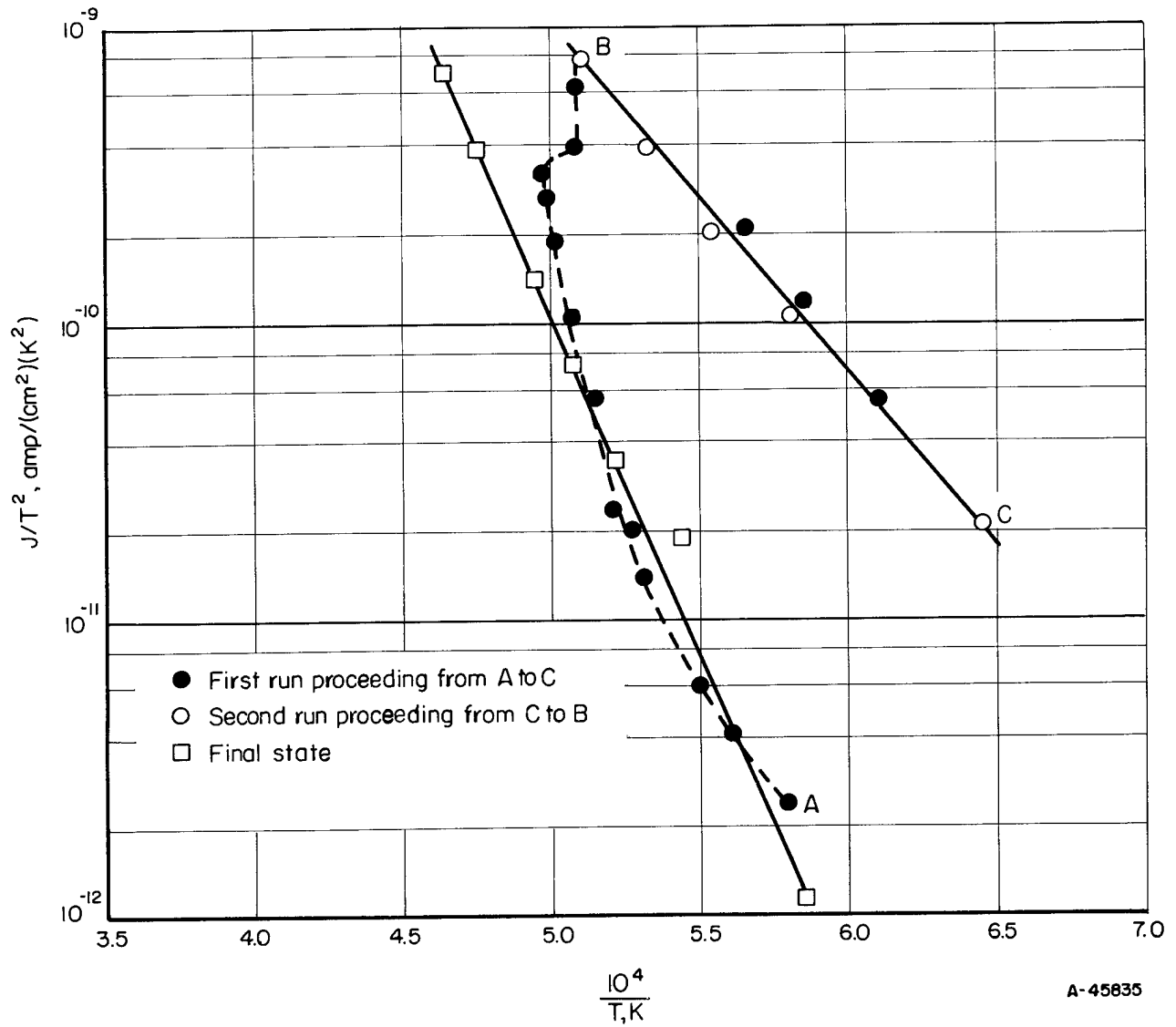
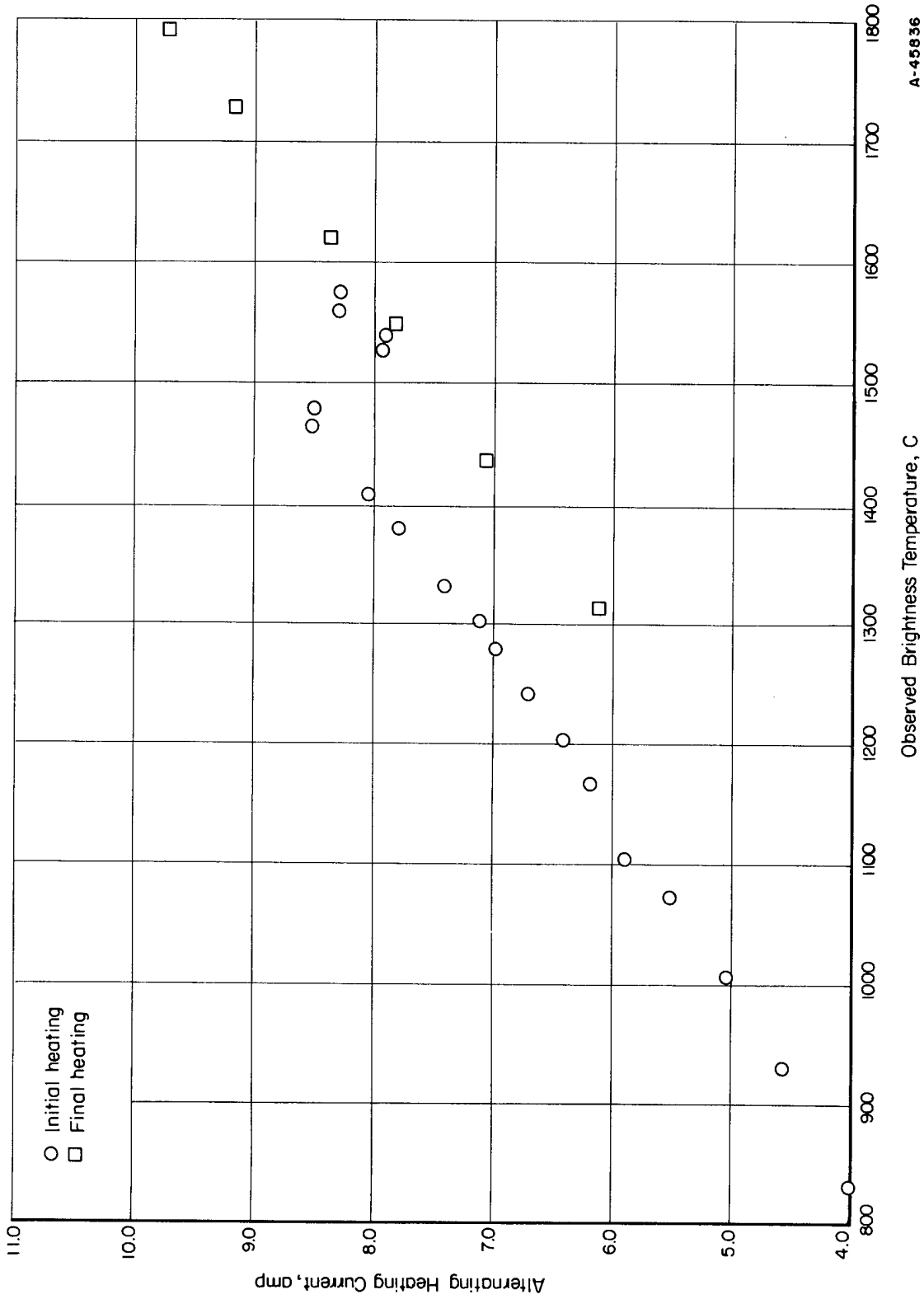


FIGURE 7. RICHARDSON PLOT OF EMISSION DATA FOR TUNGSTEN WIRE CARBURIZED IN TOLUENE-DRY HYDROGEN MIXTURE AT 1660 TO 2100 K (SAMPLE 3)



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FIGURE 8. PLOT OF THE RELATIONSHIP BETWEEN HEATING CURRENT AND OBSERVED BRIGHTNESS TEMPERATURE FOR 0.381-MM-DIAMETER CARBURIZED TUNGSTEN WIRE (SAMPLE 3)

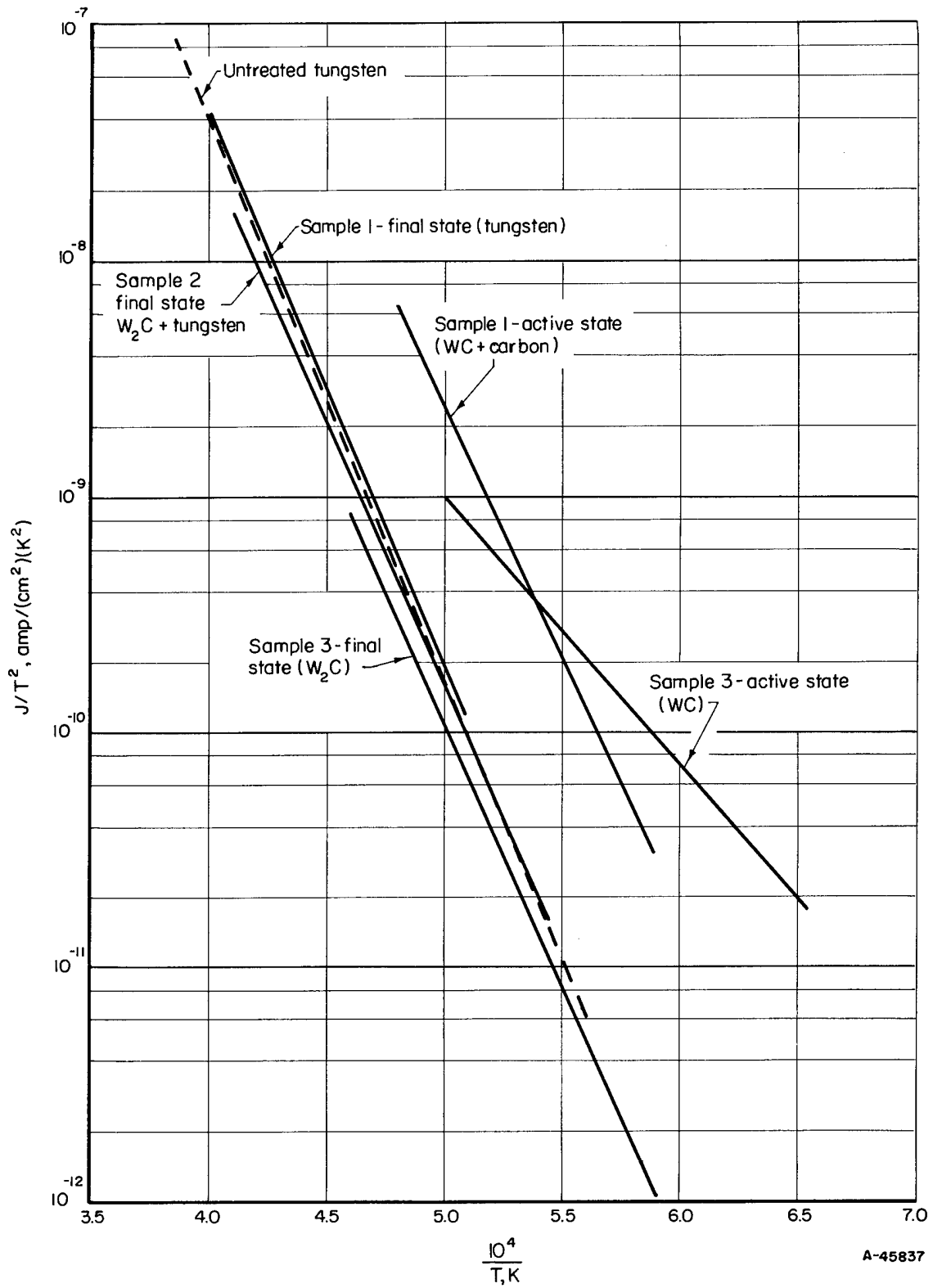


FIGURE 9. RICHARDSON LINES FOR ALL SAMPLES

The emission behavior of several other wires having the same structure as Sample 3 was essentially the same as that of Sample 3 but it was found that the level of the emission in the active state and the length of time the active condition prevailed at 2000 K could vary considerably from sample to sample. The value of the Richardson work function for the "active" surface also showed considerable variation. It seems probable that the variation in emission behavior arises from differences in the thickness of the WC layer and in the amount of free carbon originally on the surface.

An X-ray diffraction pattern for Sample 3 taken after the emission studies revealed only W_2C on the surface of the wire. This result is in agreement with the emission data for the final condition of this wire and with the model proposed above.

The emission behavior observed for Sample 1 (Figure 5) would fit this model if it is assumed that the surface of the wire was covered by a very thin layer of a mixture of free carbon and WC, a layer which reacted very quickly with the base metal as the temperature was increased to give W_2C which in turn dissolved in the base metal at even higher temperatures to leave a nearly pure tungsten surface. In the case of Sample 2, it is only necessary to assume that the surface of the entire wire was composed of carbon-rich W_2C at the outset and that the emission level was increased slightly by the heat treatment at high temperatures because the wire was partly decarburized or homogenized to produce a carbon-lean W_2C and possibly some free tungsten at the surface.

The Richardson work functions have been calculated from the slopes of the various lines shown in Figure 9 and are given in Table 2.

TABLE 2. RICHARDSON WORK FUNCTION VALUES FOR CARBURIZED AND UNTREATED TUNGSTEN WIRE

	Work Function, ev
Sample 1 - active state (WC + C)	$\phi_R = 4.25$
Sample 1 - final state (W)	$\phi_R = 4.65$
Sample 2 - final state (W_2C + W)	$\phi_R = 4.49$
Sample 3 - active state (WC)	$\phi_R = 2.24^{(a)}$
Sample 3 - final state (W_2C)	$\phi_R = 4.41$
Untreated tungsten	$\phi_R = 4.71$

(a) Values for other wires with this structure ranged from 2.54 to 3.22 ev.

The limits of precision were not determined for these values but a good idea of the confidence that can be placed in a given value can be obtained from the scatter in the data from which the Richardson line was drawn. In view of the materials involved, the value of 2.24 ev for Sample 3 in the active state is surprisingly low and indicates the possibility that some other impurity may be still present on the surface.

CONCLUSIONS

The emission behavior of rhenium which has been exposed to carbon is substantially different from that of unexposed rhenium. The emission level appears to depend very strongly upon the amount of carbon present at the surface. If the carbon concentration is near optimum the emission level is about 1.8 times that of the clean metal. For less optimum concentrations (probably excess carbon) the emission can be somewhat lower than for unexposed rhenium.

At least for the temperature range of 2000 to 2350 K the emission of tungsten is reduced by about 25 per cent due to the formation of W_2C on the emitting surface. If the surface changes to WC, the emission increases to a level several times greater than that of tungsten. If there is any unreacted tungsten available in the core, the WC surface is unstable at 2000 K and above and changes to W_2C .

Thus, while additional studies of the emission behavior of phases in the tungsten-carbon system will be performed in order to verify or disprove the model proposed in this report, enough information is now available so that one can anticipate with some confidence that the arrival of carbon from within or through a tungsten specimen can be detected. Subsequent experiments will be designed so that information concerning the diffusion of carbon in tungsten can be obtained in addition to that mentioned above.

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