TITLE:

On the Activation of Thoria Emitter by Zirconium

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By

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1. Introduction

Since the invention of the thoriated tungsten filament by Langmuir, it has been in general use as an electron emitter. In this type emitter, the original value 4.55 ev of the work function of tungsten can be reduced to 2.63 ev because of the monoatomic layer of thorium coated on the surface of the filament.

This monoatomic layer, however, is not only easily disintegrated by the impact of ions or electrons, but its working temperature is limited within a very narrow range in the vicinity of $1800°$ K. To avoid these two disadvantages, an emitter whose tungsten filament is directly coated with thoria powder has been devised. Although such an emitter has been the subject of research by some persons, its range of operating temperature is narrow, and its action as an emitter is unstable. The author got the idea of placing the thin layer of zirconium between thoria and tungsten to utilize its strong absorption of oxygen.

In this paper, the thoria coated emitter produced by pasting the thoria powder directly on the tungsten filament will be denoted by " ThO_2—W " emitter, and the one firstly coated with zirconium powder and then with thoria will be denoted by " ThO_2—Zr—W " emitter.

In the first place, emissions from both type emitters were measured and reasonable values of the work function derived. It is noticeable that " ThO_2—Zr—W " emitter can give sufficient emission at relatively low temperatures.

Then the evaporation heat of zirconium atom on the emitter surface was measured. The value obtained by the author is reasonable as compared with others' data about other emitters.

The mechanism of electron emission from thoria semiconductor can be explained such that (1) the necessary excess thorium atoms can be produced only on the base metal (tungsten or zirconium), (2) the dissociation

$Th O_2 \rightarrow Th + 2O$ requires considerable energy and it can more easily occur by the presence of zirconium, and (3) excess thorium atoms diffuse through thoria layer towards the emitter surface and compensate the evaporation of thorium atoms there.

The author has verified this view, by ascertaining experimentally that in case of " $Th O_2$—Zr—W " emitter, the emission is limited only by thorium atom diffusion and in case of " $Th O_2$—W " emitter at low temperatures, the emission is limited by the dissociation of thoria on tungsten, but at higher temperatures, the situation is the same as in the former.

The heat of diffusion and the activation energy for reduction were also measured.

2. The work function of thoria emitter with zirconium layer

(1) *Experimental method*

A tube used in the experiments is illustrated in Fig. 1 (a). In the figure, ① is either the " $Th O_2$ — W " emitter or the " $Th O_2$—Zr—W " emitter, ② represents anode to measure emission and ③ are guard rings to prevent the error caused by the lower temperature at the both ends of the filament.
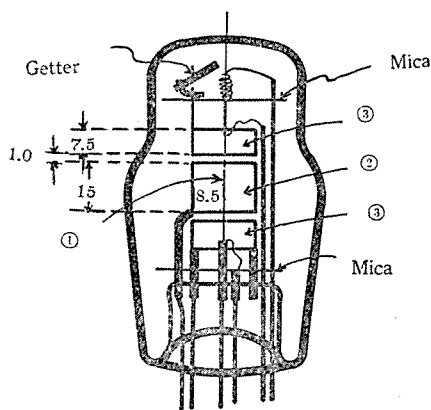

Fig. 1 (a).   Diagram of emission measuring tube.
① Emitter
② Anode
③ Guard rings

The temperature measurement was made by an optical pyrometer, and color temperature was calibrated to the true temperature, taking the radiation constant 0.35 at $\lambda = 0.65 \, \mu$.

The experimental relations between the heater current of the emitter and the temperature are shown in Fig. 2.

The emission currents into the anode ② were measured by the circuit as shown in Fig. 1 (b), which admits measuring in short times ranging from 10^{-3} sec. to 10^{-1} sec. and the initial values were taken.

Because of the roughness at the surface of these emitters, the Schottky effect occurs, and the emission current will be given by the equation :

$$I_a = A\rho D T^2 \exp\left(- \frac{e\phi - \sqrt{eV_a}}{kT}\right),\tag{1}$$
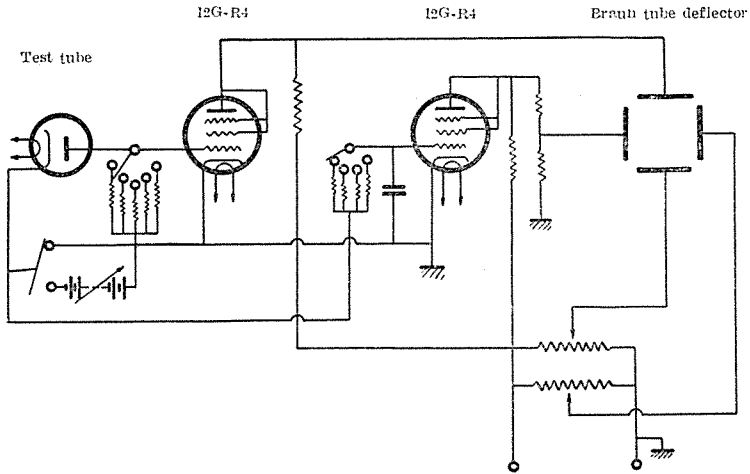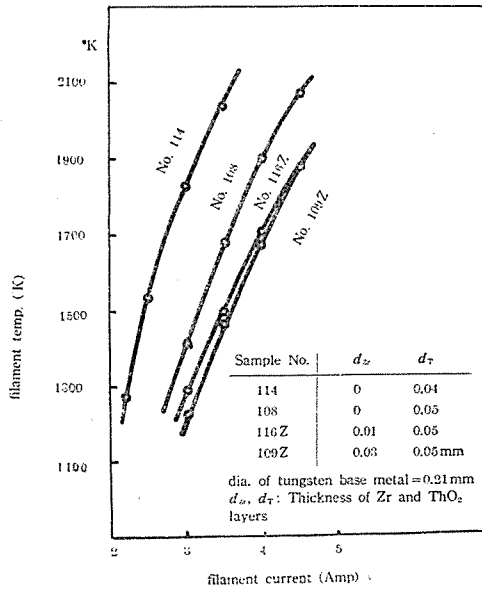
Fig. 1 (b). Diagram of emission measuring circuit.

Sample No.	d_z	d_T
114	0	0.04
108	0	0.05
116 Z	0.01	0.05
109 Z	0.03	0.05 mm

dia. of tungsten base metal = 0.21 mm
d_z, d_T: Thickness of Zr and ThO_2 layers

filament current (Amp)

Fig. 2. Relations between filament heating current
and their temperature for several samples.

where V_a is anode voltage and ρ is roughness factor of the surface of the emitter, instead of Dushman's equation:

$$I = DAT^2 \exp\left(-\frac{e\phi}{kT}\right). \tag{2}$$

The measured values of I_a are plotted in Figs. 3 and 4, forming the Schottky lines. These give zero field emission i_s which corresponds to the value at $V_a \to 0$.
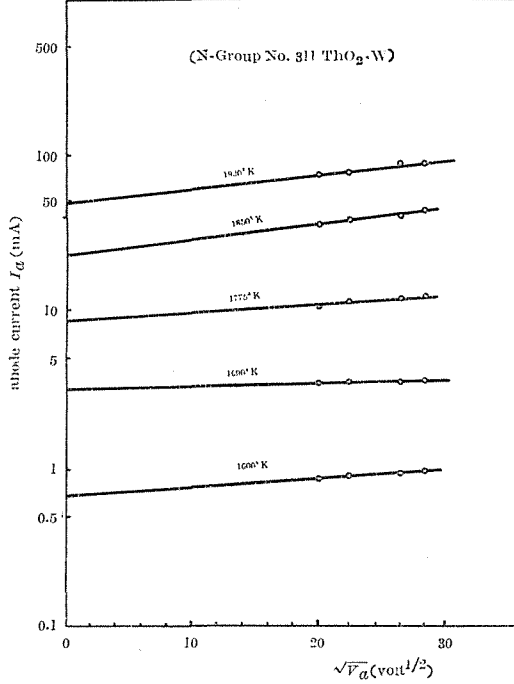

Fig. 3. Schottky lines : $\log I_a = \log I + \dfrac{300\sqrt{e \cdot 10^7}}{kT} \sqrt{V_a}$.

(11) *Experimental results and discussion*

Different from the thoriated tungsten filament, the thoria coated emitter is the so-called metallic excess type semi-conductor. Accordingly, both the number n_0 of excess thorium atoms and that N of crystal lattice vacancies or frozen-in holes produced by the thermal treatment, supply free electrons n in conduction band. In thermal equilibrium at certain temperature, the following relation is given from the theory of semi-conductor by Nijiboer (6) :

$$\frac{n(n + N)}{n_0 - n} = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} \exp\left(-\frac{eE}{kT}\right). \qquad (3)$$

The emission current will be as follows :

$$I = ne\rho D \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \exp\left(-\frac{e\chi}{kT}\right), \qquad (4)$$
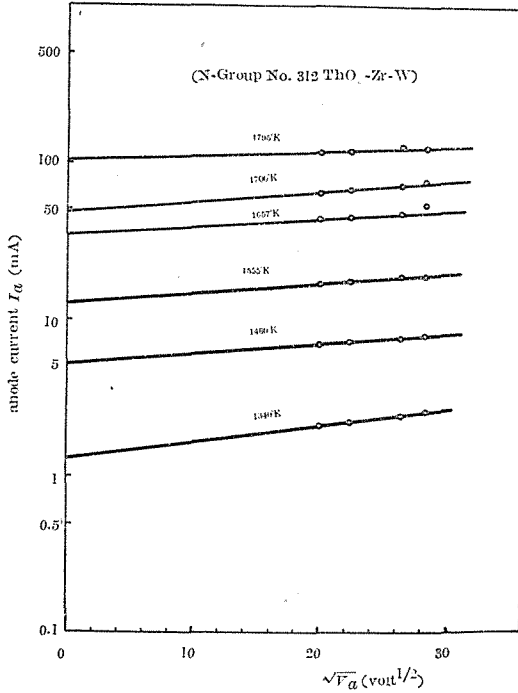
Fig. 4. Schottky lines.

where E denotes potential difference between the impurity level and the bottom of conduction band and χ that between the bottom of conduction band and the level outside of the crystal (see Fig. 5).

In case when $n \ll N$, Eqs. (3) and (4) become respectively

$$n = \frac{n_0}{N}\left(\frac{2\pi m\,kT}{h^2}\right)^{\frac{3}{2}} \exp\left(-\frac{cE}{kT}\right),$$

and

$$I = A_1 D_1 n_0 T^2 \exp\left(-\frac{e(E + \chi)}{kT}\right). \quad (5)$$

In case when $n \ll N$, the corresponding equations are

Fig. 5. Potential diagram of semiconductor.

$$n = n_0^{\frac{1}{2}}\left(\frac{2\pi m\,kT}{h^2}\right)^{\frac{3}{4}} \exp\left(-\frac{cE}{2kT}\right),$$

and

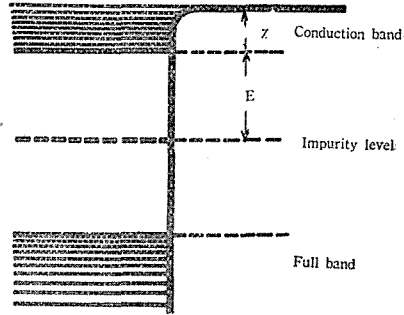$$I = A_2 D_2 n_0^{\frac{1}{2}} T^{\frac{3}{2}} \exp\left(-\frac{e(E/2 + \chi)}{kT}\right). \quad (6)$$

The value of n is small when low temperature prevents the full activation and large when activation is sufficiently carried out. It can be known from above equations that, in the medium cases, the work function distributes from $(E + \chi)$ to $(E/2 + \chi)$, according to the emitter's production process. Equation (6) is further modified to

$$\log(I/T^{\frac{5}{4}}) = \text{const} - \frac{e\phi}{kT}, \qquad (7)$$

or

$$\log_{10}(I/T^{\frac{5}{4}}) = \text{const} - 5040 \, \phi/T, \qquad (7')$$

which represents the Richardson line. From the slope of the line, the work function can be calculated. (The difference between the values of ϕ obtained from equation (7) and those obtained from the equation (5) caused by the difference between the terms $T^{\frac{5}{4}}$ and T^2 is less than 10 %.) Figs. 6, 7, and 8 show the Richardson lines, where three groups N, S and T correspond to the different refining processes of thoria, and in one group the lines differ according to various exhaustion process.
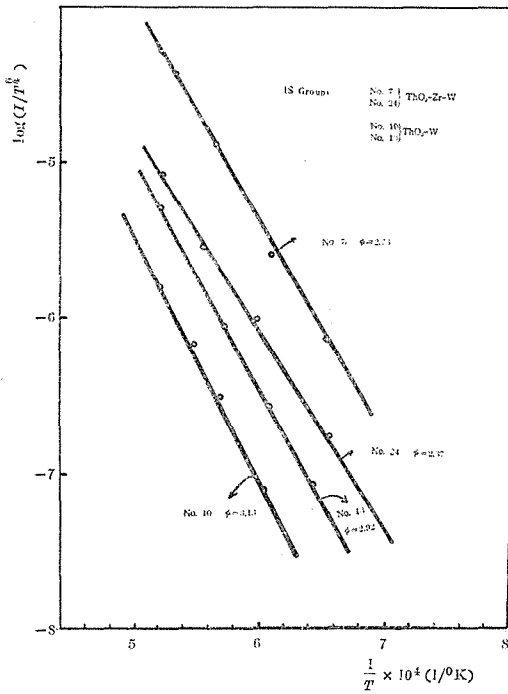
Fig. 6. Richardson lines (N-group).
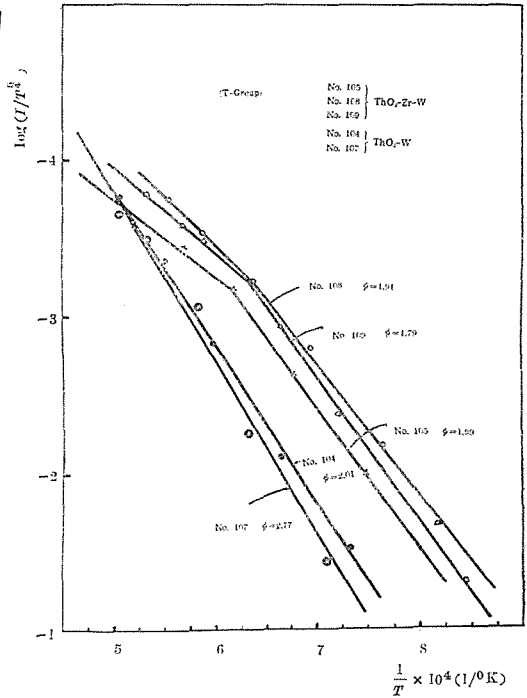
Fig. 7. Richardson lines (S-group).   Fig. 8. Richardson lines (T-group).

Table I shows the summary of measured values of work function from these results.

TABLE I. Measured values of work function of
"ThO₂—Zr—W" and "ThO₂—W".

Sample	"ThO₂-Zr-W"		"ThO₂-W"	Zr layer thickness	ThO₂ layer thickness
S group thorium oxalate —(heating)—thoria	2.65 2.42 2.37	2.73 e.V. 2.37	2.92 e.V. 2.91 3.13	0.012 mm 0.012	0.11 mm 0.14
N group thorium nitrate —thorium oxalate —thoria	1.96 1.78		2.91 1.99	} 0.012	0.15
T group chemically pure thoria for sale	1.79 1.99 1.91		2.01 2.70 2.77	} 0.03	0.05

From this table we see that the measured values distribute over the region from $(E + \chi)$ to $(E/2 + \chi)$, when we take $E = 2.7$ ev and $\chi = 0.43$ ev.

The values of E and χ thus estimated from the values of the work function, however, are not accurate unless quite many measurements are made. Meanwhile, the fact that the resistance of semi-conductor is represented as a function of E and χ allows us another way to measure E and χ from both the resistance and the equation of thermal electron emission. By this method, Arizumi and Ezaki (4) estimated the values of E and χ of " ThO_2—W " emitter as

$$E = 2.5 \text{ ev} , \qquad\qquad \chi = 0.7 \text{ ev} .$$

As the existence of zirconium has no direct effect on the emission at the surface as will be seen in the following, these values should coincide.

Recently obtained values of work function of " ThO_2—W " by several experimenters are as follows :

2.6 ev		by Wright (1)
2.67 ,	2.55	by Nanley (2)
3.08 .	2.96	by Yabumoto (3)
1.9 ,	3.2	by Arizumi (4)

Number of samples used in these measurements are from one to three.

The author has found that while in case of " ThO_2—W " emitter the work function before the necessary heat-treatment is generally very large and is lowered only after that process, in case of " ThO_2—Zr—W " emitter, a large emission can be obtained without that process, and thus the work function is originally small. This problem will be discussed in detail in the following.

Another fact to be noticed about these measured values is that, in some cases, a break appears on the Richardson line as shown in Fig. 8. This fact indicates that above certain temperature, the activation proceeds sufficiently and the sample shows the state of the so-called Nijiboer-type represented by equation (6), but below this temperature, it is in a state of poor activation or the so-called Willson-type represented in equation (5). The same phenomenon occurs in case of Wehnelt cathode of $(Ba\ Sr)\ O_2$. This break whose temperature is T_c, is given by putting $n \doteqdot N$ in the foregoing theoretical formula (3). Thus,

$$n = N = \left(\frac{n_0}{2}\right)^{\frac{1}{2}} \left(\frac{2\pi m k T_c}{h^2}\right)^{\frac{3}{2}} \exp\left(-\frac{eE}{2kT_c}\right),$$

$$I = A_3\, D_3\, T_c^{\frac{5}{4}} \left(\frac{n_0}{2}\right)^{\frac{1}{4}} \exp\left(-\frac{e(E/2 + \chi)}{kT_c}\right).$$

3. The evaporation of thorium atoms

(1) *Experimental apparatus*

Excess thorium atoms in " ThO$_2$—Zr—W " emitter or " ThO$_2$—W " emitter lie in interphases of the crystal lattice points. Therefore their evaporation is easier than that of thoria locating at the crystal lattice points. Accordingly the evaporation of thorium atoms occurs at a relatively lo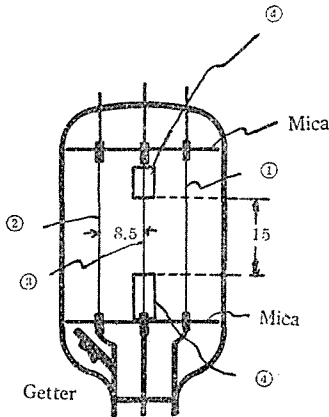w temperature as compared with that of thoria, whose evaporation is scarcely seen below 2000° K. A test tube to measure the evaporation of thorium is illustrated in Fig. 9. To make a comparison between the cases of "ThO$_2$—W " and "ThO$_2$—Zr—W " emitters, both emitters were assembled together in a single tube. ④ is intended to prevent thorium atom evaporation from ① and ② from spattering on the both ends of the filament ③ where temperature is not uniform.

Fig. 9. Tube diagram for measuring the evaporation of thorium.

① ThO$_2$–Zr–W emitter (0.22 ^{mm} dia)
② ThO$_2$–W emitter (0.22 ^{mm} dia)
③ Tungsten probe filament (0.24 ^{mm} dia)
④ Screen plate (same potential as ③)

When ① or ② is heated and kept at a certain temperature T, the evaporating thorium atoms spatter on ③ which was heated beforehand at 2500° K for ten minutes to clean up its surface completely and is now kept at 1500° K so that the spattered thorium atoms can diffuse on the surface by surface migration and form uniform monoatomic layer. Thus formed layer of thorium atoms causes a thermal emission from tungsten filament. The quantity of the emission depends upon the surface area covered by the monoatomic thorium atoms. We denote the ratio of covered area to the whole area with θ corresponding to the emission current I and θ_m corresponding to the maximum emission current I_m. The relation of θ/θ_m vs. I/I_m as shown in Fig. 10 has been already given by Brattain and Becker (8). Using this relation, the measured values shown in Figs. 12 and 13 can be rewritten in the relation of θ/θ_m vs. time t as shown in Fig. 14.

On the basis of these data, we can estimate the time rate of evaporation of thorium atoms.

In practice, ① or ② is heated at a certain temperature T, and at the same time, the emission from filament ③ (1500° K) is measured by the circuit shown in Fig. 11.
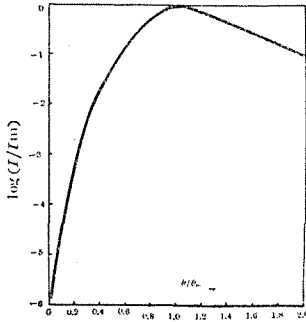

Fig. 10. Variation of electron emission from a thorium-covered tungsten filament as a function of θ, according to W. H. Brattain and J. A. Becker (8).

The emission grows larger in concert with the increase of the thorium atoms spattered on the filament ③ and reaches its maximum value I_m when filament ③ is coated almost entirely by thorium atoms. ($\theta_m \fallingdotseq 1$)   Then we heat the filament ③ for five to ten minutes at 2500° K to clean it up, and repeat the measurements in the same way at different temperatures of ① or ②. Thus we obtained the rate of evaporation at different temperatures, as shown in Figs. 12—14.

In Fig. 14, though the plotted points at a certain temperature should be on a
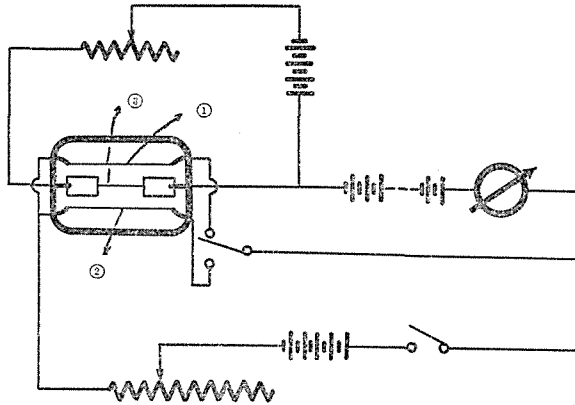

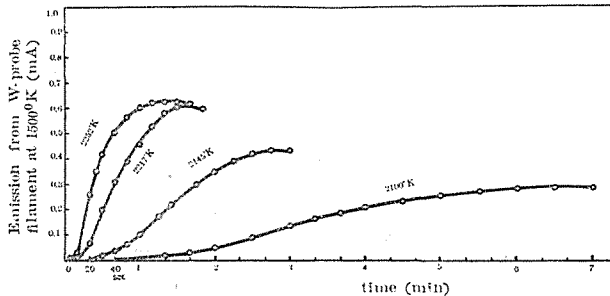Fig. 11.   Diagram of the measuring circuit for the evaporation rate.

Fig. 12.   Emission from the W-probe filament due to spattered thorium which evaporated from ThO_2-W emitter No. E44 at several temperatures.
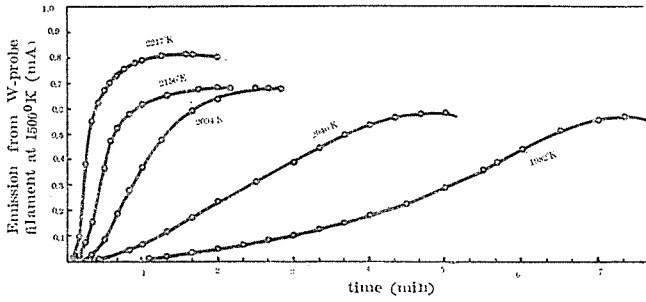
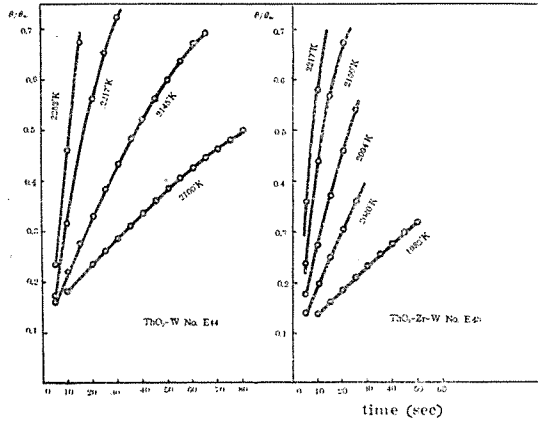Fig. 13. Emission from the W–probe filament for the ThO_2–Zr–W emitter No. E 43.

Fig. 14. Time variation of θ, indicated by θ/θ_m *vs.* t from Figs. 12 & 13.

straight line passing through the origin, the obtained values show some deviation. This is due to the insufficient purification of the surface of ③, and partly due to the fact that the thoria evaporating from the surface of ① or ② spatters on the surface of ③ and decreases its effective area for emission. The measurement was made at temperatures 1900° —2200° K at which the evaporation speed is relatively high, for if made at lower temperatuses the evaporation will be slow and the experiment will take so long time that chances of other errors may occur.

(2) *Experimental results*

The quantity of evaporation of thorium-atoms from the filament ① at the temperature $T°$ K, per unit area of the surface and per unit time, is given by

$$Q = Q_0 \exp\left(- \frac{eE_{ev}}{kT}\right),\qquad(8)$$

where Q_0 is a constant, and eE_{ev} is the activation energy for evaporation.

When the surface area is covered by the spattered thorium atoms at the ratio θ, the increase $d\theta$ in time dt is related with Q by

$$Qdt = \alpha \frac{d\theta}{1 - \theta}, \quad (\theta < 1)$$

where α is a constant determined by the geometrical relation between the filament ③ and the filament ①. Then we have

$$Q = \frac{\alpha}{1 - \theta}\frac{d\theta}{dt} = -\alpha\frac{d}{dt}\log(1 - \theta). \tag{9}$$

From (9) and (8), we get

$$\log\left[-\frac{d\log(1 - \theta)}{dt}\right] = \text{const} - \frac{eE_{\text{ev}}}{kT},$$

and differentiating this with respect to $1/T$, we have

$$E_{\text{ev}} = -1.97\frac{\Delta\log_{10}\left[-\dfrac{d\{\log(1 - \theta)\}}{dt}\right]}{\Delta\left(\dfrac{10^4}{T}\right)}, \quad (\text{ev}) \tag{10}$$

or

$$E_{\text{ev}} = -4.575 \times 10^4\frac{\Delta\log_{10}\left\{-\dfrac{d\log(1 - \theta)}{dt}\right\}}{\Delta\left(\dfrac{1}{T} \times 10^4\right)}. \quad (\text{cal/g-atom}) \tag{11}$$

If we calculate the quantity shown in equation (10) from the measured values in Fig. 14, we obtain Fig. 15, and the values of E_{ev} summarized in the following Table II.

The discrepancy among the values in Table II can be understood to have come from the fact that the activation energy for evaporation may be large or small in accordance with the attraction between thorium atoms at the surface and this attraction depends on the density of thorium atoms.

A similar case is seen in the measurement of the evaporation of thorium atoms from the thoriated tungsten filament performed by Andrew (9) and Langmuir (10), in which the former obtained the value
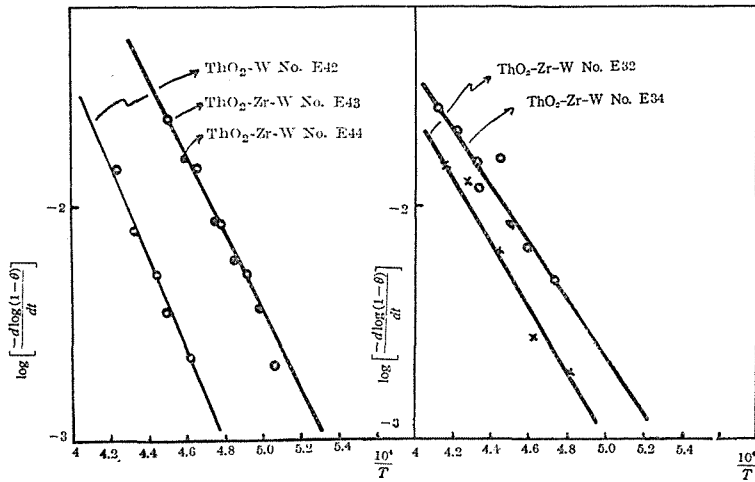
Fig. 15. Evaporation lines calculated from experimental data.

TABLE II.

Activation energy for evaporation of thorium from thoria emitter.

Emitter Sample number	" Th O_2—W " type	" Th O_2—Zr—W " type
E 43		3.34 ev (72,500) cal/g-atom
E 3.4		2.43 (56,400)
E 3.2		2.78 (64,400)
E 4.4	5.48 ev (127,000) cal/g-atom	3.4 (78,800)
E 4.2	4.02 (93,300)	
		(mean value)
		3.0 (69.500)

177000 cal/g-atom while the latter 204000 cal/g-atom. This difference is explained by them as attributable to the fact that in case when the value of θ is large, the attraction between thorium atoms weakens the adsorption of thorium atoms into the tungsten base metal.

In case of the thoria emitter, however, excess thorium atoms lie in interphases of the lattice points. Therefore the activation energy for evaporation may be lower. According to Fan's measurement [11], a smaller value of 466000 cal/g-atom was obtained for evaporation of thorium atom in case of sintered cathode made by mingling tungsten and thoria at the rate of 30 : 70 and then sintering them.

In case of barium atom in (Ba Sr) O_2, the values distribute from 3.1 ev to 2.75 ev and the mean value is 2.9 ev. These facts show that the value 3.0 ev we obtained is reasonable.

4. On the activation of thoria emitter by zirconium

(1) *Activation mechanism of thoria emitter*

In the process of electron emission from " ThO_2—Zr—W " emitter, the most remarkable feature is that any additional process for activation is unnecessary. We can imagine that this is because oxygen's affinity to zirconium is strong and oxygen easily makes absorbed diffusion into zirconium lattices and therefore the balance between oxygen in thoria and oxygen-free zirconium at the contact surface of thoria and zirconium is broken, and as a result a part of thoria supplies oxygen atoms into zirconium by absorption. Thus thorium atoms remain within thoria in a state of excess metal and the oxygen atoms diffuse into zirconium.

While in case of (Ba Sr) O_2 emitter oxygen atoms of Ba O fly into vacuum if vacuum is in a high degree and excess Ba atoms are produced on the surface, in case of thoria-emitter, however, such phenomenon does not occur because the dissociation of thoria is not easy. Accordingly, the reduction of thoria occurs only on the base metal. Thus produced thorium atoms diffuse towards the surface according to its concentration distribution. Meanwhile, the evaporation incessantly continues, and a steady state appears when the supply of thorium atoms by the diffusion and their consumption by evaporation balance. The quantity of emission is large or small depending on the number of thorium atoms in the steady state.

The speed of the thermal diffusion of oxygen into zirconium is very high (12). (Zirconium makes solid solution with oxygen atoms uniformly until the quantity of oxygen reaches 40 atomic percent.) Therefore, thoria which contacts with zirconium, is reduced and a very large number of thorium atoms is produced even at lower temperatures. Accordingly, in the case of " ThO_2—Zr—W " emitter it may be assumed that it is the thermal diffusion of thorium atoms in the thoria layer, that limits the supply of thorium for the evaporation. In case of " ThO_2—W " emitter, the situation is the same at high temperatures, but at low temperatures, it is not, as the reduction of thoria at the contact surface with tungsten becomes very difficult against the case of the contact with zirconium. (It has been said that below $2400°$ K reduction is quite difficult.) In the latter case we understand that the dissociation is the factor that limits the supply of thorium to the surface.

To ascertain our view, we proceed as follows. In the case of " ThO_2—Zr—W " emitter or high temperature " ThO_2—W " emitter, a steady state is brought about when the diffusion of thorium in thoria

and the evaporation of thoria at the surface balance. As the evaporation is proportional to the number n_0 of thorium atoms on the surface, we have

$$A \exp\left(-\frac{eE_{\mathrm{diff}}}{kT}\right) = B n_0 \exp\left(-\frac{eE_{\mathrm{ev}}}{kT}\right),$$

where A and B are constants, and eE_{diff} is the apparent activation energy for diffusion and eE_{ev} the activation energy for evaporation of thorium respectively. Thus, we get

$$n_0 = c \exp\left\{-\frac{e\left(E_{\mathrm{diff}} - E_{\mathrm{ev}}\right)}{kT}\right\}. \tag{12}$$

n_0 can be measured by the instantaneous measurement at low temperature $(1400°\mathrm{K})$, since the emission is proportional to n_0.

So we obtain

$$\log I = \mathrm{const} - \frac{e\left(E_{\mathrm{diff}} - E_{\mathrm{ev}}\right)}{kT}. \tag{13}$$

In the other case, the steady state is limited by the production of thorium atoms by the reduction of thoria. Denoting the activation energy for reduction of thoria on the tungsten surface with eE_r, in the same way as in equation (13), we obtain

$$\log I = \mathrm{const} - \frac{e}{kT}\left(E_r - E_{\mathrm{ev}}\right), \tag{14}$$

or

$$\log_{10} I = \mathrm{const} - 5040\left(E_r - E_{\mathrm{ev}}\right). \tag{15}$$

(2) *Experimental results and discussion*

Emitter of the emission test tube is kept at $T°\mathrm{K}$, and when a steady state among the dissociation of thoria, diffusion and evaporation of thorium is almost reached, the temperature is suddenly lowered to $1400°\mathrm{K}$ and emission is measured instantaneously. We repeat such measurement at intervals of three to five minutes and see that the emission settles at a certain value which shows that a steady state is reached. An example of the results of experiment is shown in Fig. 16 and in the form of $\log I$ *vs.* $1/T$ in Fig. 17.

The measurement is made at temperatures between $1400°\mathrm{K}$ and $2200°\mathrm{K}$. Above $2300°\mathrm{K}$, both "$\mathrm{ThO_2}$—Zr—W" and "$\mathrm{ThO_2}$—W" make solid solution, and become inadequate as emitter.

It is obviously seen in Fig. 17 that in case of "$\mathrm{ThO_2}$—W" emitter,

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the emission curve consists of two straight lines which show that below 1700° K emission is scarce and over 1700° K emission increases rapidly and becomes useful as an emitter. This behavior is explained as follows. At 1700° K, reduction of thoria at the contact surface with tungsten begins and thorium atoms produced diffuse toward the surface and
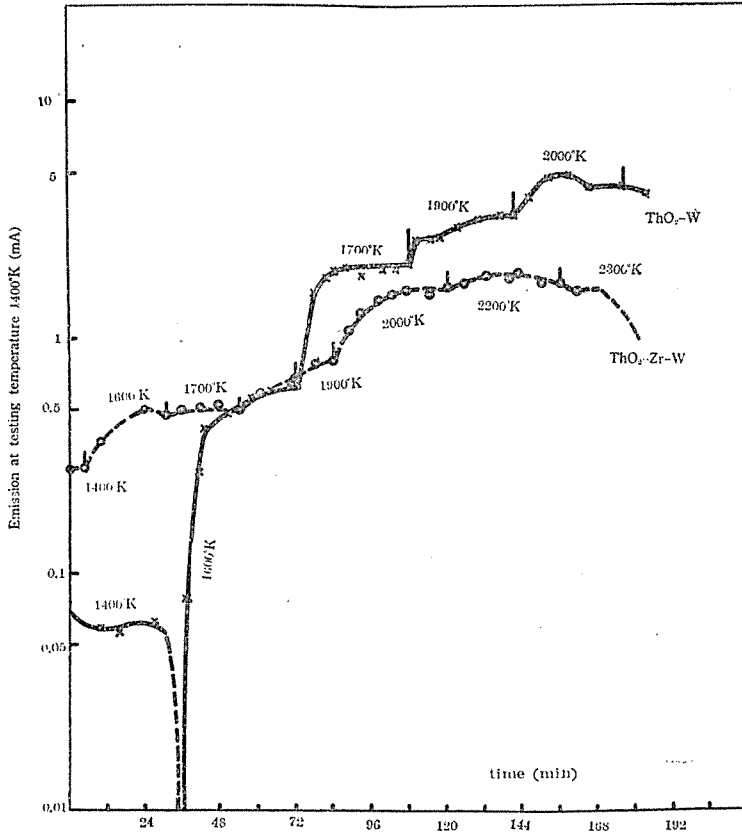

Fig. 16. Thermoionic activity during activation process.

constantly make up for the atoms consumed by evaporation and then the emission becomes stable. Above that temperature, alike in case of " ThO_2—Zr—W " emitter, the steady state is limited by the diffusion of thorium atoms in the thoria. This corresponds to the fact that the emission line in this region is parallel to that of " ThO_2—Zr—W " emitter.

Meanwhile, in case of " ThO_2—Zr—W " emitter the lines correspond to the fact that the steady states are limited by the diffusion throughout.

The results of the measurement thus well verifies our view. Table III has been summarized from Fig. 17, equation (13) and equation (15).
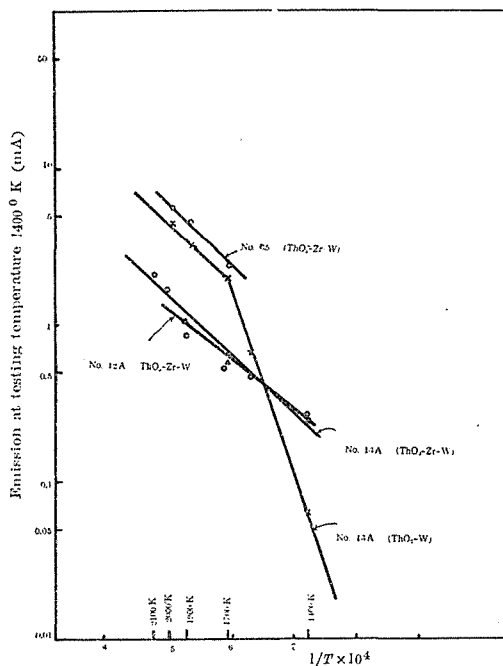

Fig. 17. Thermoionic emissivity of two types of
emitter at various temperatures.
(T=temp. of emitter)

TABLE III. Activation energy for diffusion of Th in ThO_2
and that for reduction of ThO_2 on W.

Emitter's sample number	" $Th\,O_2$–Zr–W " emitter		" $Th\,O_2$—W " emitter			
	E_{diff}—E_{ev}	E_{diff}	E_{diff}—E_{ev}	E_r—E_{ev}	E_{diff}	E_r
N 1.3 A	0.788	3.788	0.785	2.345	3.785	5.345
1.2 A	0.636	3.638				
3.5	0.887	3.887				

$E_{ev} = 3.0$ (ev)

It can be considered that these values are generally smaller than those in case of diffusion in an ordinary crystal, because thoria has a semi-conductor structure with lattice defects. For instance, the values for diffusion of thorium atoms in tungsten obtained by Langmuir (13), Fonda (14) and others in case of body diffusion, surface diffusion and

intercrystalline surface diffusion are 120000, 66400 and 90000 cal/g-atom respectively. To obtain the activation energy for reduction of thoria on zirconium, instead of tungsten, the author is now carrying experiment by means of secondary electron emission.

5. Conclusion

In short, zirconium in "ThO_2—Zr—W" emitter has a great influence on the production of excess thorium atoms. By placing it under the thoria to supply impurity thorium atoms constantly, the operation of the emitter is stabilized at low temperature, without any special high temperature process which is indispensable for "ThO_2—W" emitter to make emission.

The most important application of ThO_2—Zr—W" emitter will be found in magnetron or klystron which generates high peak power and requires the emitter of low resistance blocking layer and of high stability.

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