DECEMBER 15, 1933 PHYSICAL REVIEW VOLUME 44

The Effect of Alkali Ions on the Photoelectric Emissivity of Tungsten

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(Received August 24, 1933)

Known quantities of Na^+, K^+, Rb^+ and Cs^+ ions were deposited on tungsten and the changes in the photoelectric current measured. For wave-lengths below 2800A the current increases proportional to the fraction of the surface covered as long as f is small. The emissivity for longer wave-lengths is low at first, and then rises sharply beyond some critical value of f, which increases with the wave-length. The results indicate that the work function is not uniform over these composite surfaces; this makes it impossible to fix a definite threshold for the various values of f. The emissivity increases with temperature to about 500°C, where fatigue becomes appreciable. As the filament fatigues for photoelectric emission the positive ion emissivity increases, reaching a maximum when the threshold returns to that for clean tungsten. The results show that the alkali dissolves so rapidly in the tungsten that the dependence of the work function on f cannot be determined at temperatures above 500°C.

In a previous article the effect of small measured amounts of potassium on the photoelectric emissivity of iron was described.[1] In the present paper a similar study is made of the effect of small deposits of various alkali ions on the emissivity of tungsten.

Apparatus and Method

The technique employed in depositing a known amount of alkali on the tungsten was to pass a positive ion current for a definite period of time from a catalyst ion source[2] to the tungsten. The fraction of the tungsten surface covered by ions was obtained by dividing the surface area by the cross-sectional area of the ions multiplied by the number passed.[3]

The experimental setup was essentially the same as that used before except that the photocurrent was measured with an FP-54 Pliotron in place of an electrometer.

The tungsten emitting surface was a ribbon 6 cm long, 3 mm wide and 0.01 mm thick placed edgewise to the positive ion source. The sources were iron catalyst impregnated with the oxide of the alkali desired. The catalysts were thoroughly reduced in hydrogen at a temperature just below redness; the tungsten was glowed in hydrogen at approximately 1500°C and subsequently glowed in a vacuum at 1800°C until gassing ceased.

Since the positive ion emitters always gas slightly in operation, it was necessary to keep the pumps running continuously throughout each experiment. The pressure was maintained below the limit of a McLeod gauge, no other precaution being taken for extremely high vacuum.

In operation the tungsten was first glowed until a just detectable emission could be obtained with $\lambda 2483$. A known positive ion current was next passed from the catalyst to the tungsten for a given time. The photoelectric emissivity for the various mercury lines was then measured. The original threshold of the tungsten was restored by glowing a few minutes at bright redness, after which the process was repeated as desired. Substantially the same results were obtained when the alkali was deposited in successive amounts or at a single time.

The contamination of the surface by the deposition of atoms was measured by the difference in the photocurrents after an accelerating and a retarding potential for positive ions had been placed upon the tungsten for the same catalyst heating current and time. The emission from atoms exceeded that from ions for fresh catalysts but decreased rapidly with time. The results given were taken when the enhancement of the photocurrent due to the deposition of atoms was less than one percent of that due to ions.

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[1] A. Keith Brewer, Phys. Rev. **38**, 401 (1931).

[2] C. H. Kunsman, J. Frank. Inst. **204**, 635 (1927).

[3] The radii given by Pauling, J. A. C. S. **49**, 765 (1927), are: Na^+, 1.10A; K^+, 1.30A; Rb^+, 1.5A; Cs^+, 1.75A.

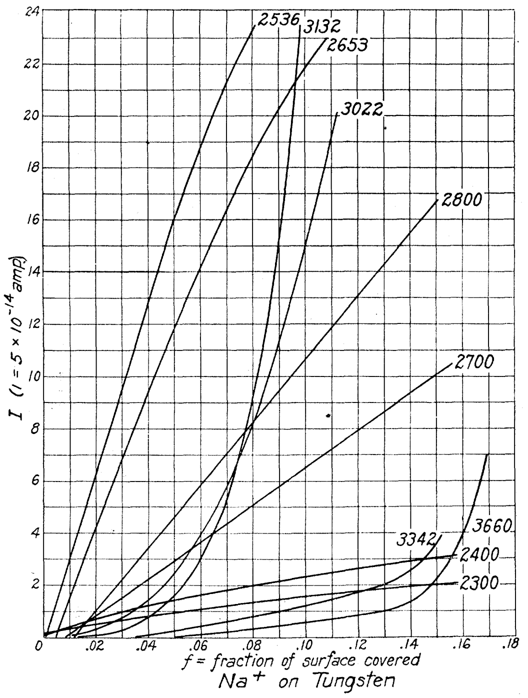

FIG. 1. Effect of fraction of surface covered by sodium ions on the photo-emission of tungsten under excitation by various mercury lines.

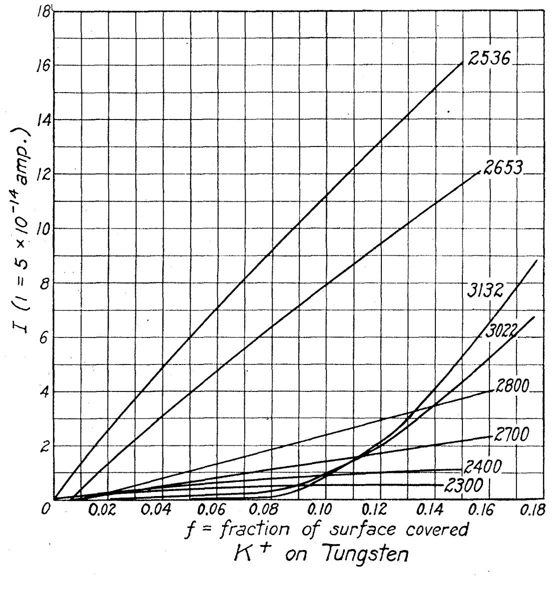

FIG. 2. Effect of fraction of surface covered by potassium ions on the photo-emission of tungsten under excitation by various mercury lines.

RESULTS

The effect of the fraction of the surface covered (*f*) by the different alkali ions on the emissivity for the various mercury lines is shown in Figs. 1, 2 and 3.

Readings were taken for difference in f of 0.0025 up to $f=0.02$, and for differences of 0.01 thereafter. The points all fell closely on the curve, the curves in general being drawn through the points. The results obtained with rubidium lie intermediate between those of potassium and caesium. The temperature of the tungsten filament when these results were taken was about 250°C, chosen because it was below where "fatigue" became appreciable and yet was sufficiently high for the emissivity of the surface to become constant within a few minutes after the alkali was deposited.

It will be noted that results are given only for small values of f; above a specific fraction covered

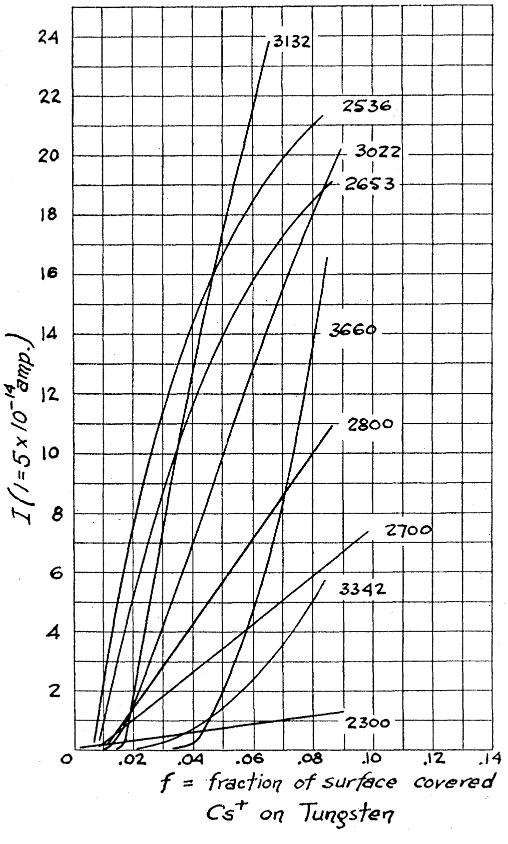

FIG. 3. Effect of fraction of surface covered by caesium ions on the photo-emission of tungsten under excitation by various mercury lines.

for each ion the emissivity no longer increased with the deposition of more ions. This specific value is about $f=0.16$ for Na, $f=0.13$ for K and $f=0.05$ for Rb and Cs. It is possible that the inability to build up larger layers by this method is due both to evaporation and to an increased solution of the alkali in the tungsten at the higher concentrations.

The results show that for λ2700 and λ2800 the photocurrent increases linearly with f. For shorter wave-lengths the curves are only slightly concave downward; for longer wave-lengths they rise sharply above a certain critical value of f.

The effect of the chemical nature of the adsorbed ions on the intensity of the photoelectric current is comparatively small. The relative efficiency is in the order of caesium, rubidium, sodium and potassium. The fact that sodium showed a slightly greater effect than potassium is surprising but several check experiments invariably gave the same results.

The effect of temperature on the photocurrent is similar for the different surfaces. From room temperature to 300°C the current increased by about 50 percent. Above 300°C the current rose more rapidly to about three times the original value at 500°C; at the higher temperatures the filaments fatigued badly. Caesium on tungsten ($f=0.01$) showed only a few percent fatigue in an hour at temperatures below 300°C; at 500°C the photocurrent dropped to a small value in the course of several hours, while at 700°C it dropped to that of pure tungsten in a few minutes. The other filaments behaved similarly.

Since the photocurrents respond only to alkali that is on the surface, the fatigue effect just described must result either from an evaporation of alkali off the surface or from a solution in the tungsten. A test of these two possibilities was made by studying the positive ion emission of the tungsten, before and after the alkali was deposited. In these experiments the tungsten filament was glowed until no positive ion emission could be detected below 950°C to 1000°C. A quantity of alkali was then deposited on the tungsten and the temperature determined where a positive ion current could be detected, after which the photoelectric emissivity for the various frequencies was measured. From time to time the change in the positive ion current as well as the photoelectric current was measured, the filament temperature being kept practically constant.

In Table I are the results obtained from rubidium on tungsten at 560°C. The interval of time between successive readings of the positive ion current varies between twenty and thirty minutes.

TABLE I. *Positive ion and photocurrents from rubidium on tungsten.*

I^+	I_{2536}	I_{2700}
4.0×10^{-12} amp.	18.5×10^{-13} amp.	2.0×10^{-13} amp.
11.0	9.0	.9
12.5	8.2	.8
17.5	6.7	.65
27.0	6.2	.5
34.0	5.2	.3
41.0	2.3	0.0

These results, typical of all the alkali deposits, show clearly that while the photocurrent fatigues with time the positive ion current increases to its greatest value at the point where the photoelectric threshold reaches that for pure tungsten, i.e., where the surface is free of adsorbed alkali. This, in light of the fact that an equivalent positive ion current would not be obtained from the tungsten previous to the deposition of the alkali at a temperature 500°C above that used in these experiments, is a direct indication that the photoelectric fatigue observed at temperatures above 300°C must be due to a solution of the alkali within the tungsten. This conclusion is not surprising since such a solution should be expected from the chemistry involved. The evaporation probably does not contribute materially to the loss of alkali from the surface until much higher temperatures are reached. It seems apparent, therefore, that the effect of adions on the work function cannot be obtained by any method necessitating the heating of the tungsten appreciably above 300°C.

An attempt was made to determine the fraction of the deposited alkali that could be evaporated from the tungsten in the form of positive ions. After the tungsten surface became free of alkali the positive ion current remained nearly constant for an appreciable time, then gradually fatigued to a negligible value. This fatiguing effect made an accurate estimation impossible although it is evident that the quantity of positive ions deposited and emitted is of the same order of magnitude.

The thermionic emission of electrons yielded no direct information regarding the dependence of the work function on the fraction of the surface covered under the conditions of these experiments. In the case of rubidium for $f=0.01$ a thermoelectron emission was detectable at 700°C but it did not increase with temperature in the usual manner below 875°C. These temperatures are well above those at which the photoelectric measurements show that rubidium dissolves rapidly in the tungsten. The difference between these results and those reported by Ives[4] is doubtless due to the thickness in the layer of adsorbed alkali.

A determination of the variation in the photoelectric threshold with f involves considerable uncertainty since the data presented in Figs. 1, 2 and 3 show that the composite surfaces exhibit a varying degree of photosensitivity over a wide range of frequencies. Thus in Fig. 1 the detection of a photocurrent for $\lambda 3660$, for instance, is more dependent on the sensitivity of the apparatus than on some specific value of f.

In Fig. 4 the emissivity per unit light intensity is plotted against the wave-length. The continuous lines are for caesium and the dotted lines for sodium. The numbers refer to the values of f expressed in hundredths. The intensity of the various lines was measured with a Hilger thermopile.

The curves for $f=0$ and $f=0.01$ show sharp feet and are characteristic of those obtained from clean surfaces. The curves for larger values of f exhibit a marked enhancement in the photoelectric yield for the longer wave-lengths, the point of greatest emissivity shifting towards the red as f increases. This shift is more pronounced for caesium than for sodium.

Discussion of Results

Results of the type presented in this paper are in general accord with the ion grid theory proposed by Becker.[5] This theory presumes that the work function of a composite emitter is lowest at some point near the ion and increases to that for the clean metal at a distance of order of ten diameters removed.

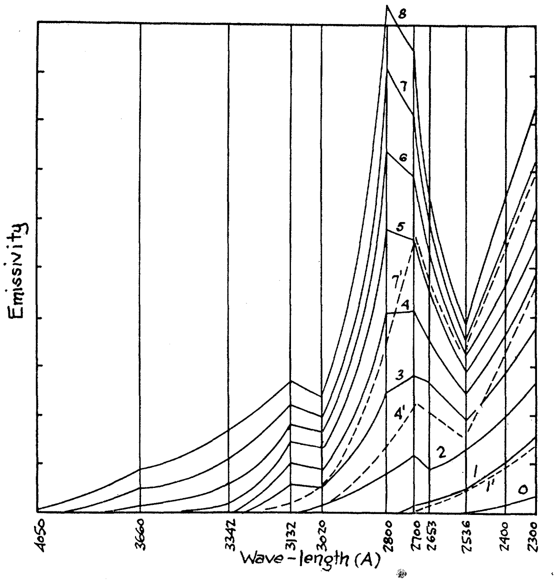

FIG. 4. Emissivity of tungsten to unit light intensity as a function of wave-length.

It is not surprising therefore that emission characteristics for wave-lengths above and below the threshold for the clean metal are distinctly different. For wave-lengths near or below the threshold of tungsten the photocurrent increases in a perfectly definite manner with the concentration of the adions, a change of $f=0.01$ resulting in a change in current equivalent to a shift in threshold of approximately 65A for sodium and potassium and 85A for caesium. This is due to the fact that the entire surface is photoelectrically active for these frequencies.

The emissivity for wave-lengths considerably above the threshold of tungsten is very low for small values of f, indicating, possibly, that only a small region about the ion is photosensitive. As f increases a point is reached, specific for each frequency, where the emissivity undergoes a rapid increase; this suggests that the entire surface has now become photosensitive. The observation that the point of inflection in these curves occurs at higher values of f for the longer wave-lengths is to be expected.

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[4] H. E. Ives, Astrophys. J. **64**, 128 (1926).

[5] J. A. Becker, Trans. Am. Electrochem. Soc. **55**, 21 (1929).