

V_t in the formula should be interpreted as an "extrapolated" threshold voltage. With these restrictions as to the realm of validity of the formula, the essentially linear portions of the curves in Fig. 2 may be fitted by a function of the voltage of the form (1).

Finally, it may be added that other effects may contribute in determining the shape of the amplification curve at the true threshold voltage.

Thus, "end-effect," (that is, decrease of the field near the ends of the cylindrical cathode) would have the effect of suppressing a sharp rise of gas amplification but would not affect the magnitude of the threshold voltage. It is probable that the proposed explanation of the results constitutes the most important factor operative in determining the low voltage dependence of the amplification factor.

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Thermionic Properties of the Iron Group

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As a preliminary to the main problem, the temperature scales for Fe, Ni, and Co have been determined for vacuum heat treated specimens of the metals. The thermionic work functions found differ from those reported by other investigators and are as follows: β -Fe 4.48 ev, γ -Fe 4.23 ev, Ni 4.61 ev, and Co 4.40 ev. The probable cause for the difference between these results and those of others is discussed and the effect of minute quantities of certain impurities is described.

INTRODUCTION

THE thermionic and photoelectric properties of the members of the iron group have been investigated carefully by Glasoe,¹ Cardwell,^{2,3} Fox and Bowie,⁴ and others. However, recent ideas on heat treatment, as well as on the effect of small amounts of impurities, have changed the procedure sufficiently so as to justify a repetition of their work. Impurities become particularly important in studying metals with as low melting points as have the members of the iron group, since these impurities may, under prolonged heat treatment, diffuse to the boundary and thus give a highly impure surface. Obviously, since thermionic emission is to a major extent dependent on the surface conditions, the work function and the constant factor in Richardson's equation will be appreciably affected.

In order to obtain reliable results it is necessary to determine the temperature scales of the metals

under conditions of heat treatment as nearly identical as possible with those used in the thermionic studies. This determination has been carried out and the results have been published elsewhere.⁵

EXPERIMENTAL PROCEDURE

In making thermionic measurements it is in general more desirable to use a flat strip filament rather than a round one. The reason for this is that when a disappearing filament optical pyrometer is used in measuring the temperatures the deviation from Lambert's law is likely to give a non-uniform field if a round filament is used and a good match cannot be observed, thus increasing the error in the temperature measurement. In all the work described below flat strips of about 0.07 mm thickness and 2 to 3 mm width were used.

These filaments after being rolled to uniform thickness were cleaned carefully by dipping in chromic acid cleaning solution to remove greases

¹ G. N. Glasoe, Phys. Rev. **38**, 1490 (1931).

² A. B. Cardwell, Proc. Nat. Acad. Sci. **14**, 439 (1928).

³ A. B. Cardwell, Proc. Nat. Acad. Sci. **15**, 544 (1929).

⁴ G. W. Fox and R. M. Bowie, Phys. Rev. **44**, 345 (1933).

⁵ H. B. Wahlin and R. Wright, J. App. Phys. **13**, 40 (1942).

and other organic impurities from the surface. This procedure was followed by a careful washing and a slight etching of the surface with dilute hydrochloric acid. A final rinsing with hot distilled water followed. This method of cleaning gave results identical with those obtained when hot KOH was substituted for the chromic acid so that apparently the acid introduced no measurable impurities. After the cleaning, the filaments were not touched with bare hands.

The experimental tubes were the conventional single guard ring type with the filaments mounted in a U shape. The collector and guard ring were of molybdenum. These were given a prolonged intermittent induction heating in a Pyrex tube connected to one auxiliary vacuum system, after which they were assembled to form the main thermionic tube.

The assembled tubes, connected to a vacuum system, were baked for periods ranging from 100 hours to 500 hours at temperatures ranging from 450° to 300°C. The reason for this range in baking temperatures was so that a test could be made on the influence of high temperature baking on the work function. It has been suggested that if these high temperatures are maintained while the filament is being heated, the volatile constituents of the glass will react with the filament and will change the work function. An increase in the work function was observed when the filaments were heated during baking at 450°. This increase, however, was too small to ascribe it definitely to the procedure in heating.

The technique finally adopted was to bake the tube for 24 hours at 450°C. The furnace was then removed and the collector and guard ring given an induction heating to such a temperature that they appeared a very dull red in a darkened room. The furnace was then replaced and the baking continued at 300°C. After twelve to twenty-four hours of this treatment, the filament heating was begun below red heat and the temperature gradually raised to about 1250°K. It was found that if the temperature was raised gradually so as to allow sufficient time for the small crystal units to grow into larger ones, prolonged heating at 1250°K could be carried out without undue evaporation. The low temperature induction heating apparently did not throw any non-volatile impurities onto the filament because

the same results were obtained when no induction heating was used as when it was used. However, the degassing time was materially reduced when induction treatment was combined with baking.

The experimental tubes were kept on the vacuum system continuously and the final vacuum reached with the filaments heated was 3×10^{-8} mm.

RESULTS

Iron

First sample: This was a specimen prepared electrolytically from a ferrous sulphate solution and an iron anode. The results were unreliable and a steady state could not be reached. A strip of this specimen annealed in hydrogen gave a distinct trace of hydrogen sulphide, showing an inclusion of sulphur in the electrolytic deposits. The liberation of the sulphur in the experimental tube contaminated it in such a way that subsequent backing failed to remove the contamination. The tube was therefore destroyed to prevent its future use. Probably a prolonged heating in hydrogen of iron prepared from a sulphate solution would remove the impurity.

Second sample: The second group of specimens was prepared electrolytically from a ferrous chloride solution and an armco iron anode. These specimens gave satisfactory results with prolonged vacuum heat treatment.

The procedure in preparing a specimen for the final data was to raise the temperature of the filament slowly to a final degassing value of 1250°K. Several days were generally taken to get it to this temperature. Care was then taken that the temperature did not at any time fall below the A_3 point (β - γ transition). After a stable condition had been reached and the thermionic data for γ -iron were taken, the temperature was lowered into the β -range and the heating continued. Care was now taken to keep the filament temperature below the transition point. When a steady state had again been reached and the data were obtained, the temperature was again raised (with two of the specimens) into the γ -region and further thermionic results recorded. These were found to be in agreement with the first ones.

The average of the results for 4 filaments,

which showed no appreciable temperature gradient, is:

Below β - γ transition,

$$\varphi = 4.48 \pm 0.06 \text{ ev, } A = 26 \text{ amp/cm}^2/T^2.$$

Above β - γ transition,

$$\varphi = 4.21 \pm 0.06 \text{ ev, } A = 1.5 \text{ amp/cm}^2/T^2.$$

Probably the most reliable value for the work function published is that which Glasoe¹ obtained photoelectrically. He reported a value of 4.77 ev. Glasoe heated his specimen to a relatively high temperature and then cooled it to room temperature before measurements were made. This procedure may account for the difference between his results and those reported here. For, when the iron passes from the γ to the β form, the equilibrium distribution of crystal planes on the surface of the specimen is disturbed and heating time in the β state must be allowed in order to reestablish this equilibrium—partly by thermal etching and partly by migration of atoms along the surface. The author attempted to check this hypothesis by making a set of determinations of the work function, immediately after the filament had been changed from the β to the γ and from the γ to the β . Because of a rapid initial change in the surface, reliable results could not be obtained. All that can be said is that the work function calculated was definitely higher than the equilibrium value. This would indicate that an appreciable part of the change in the work function with degassing reported by observers is not a degassing effect, but is due to the gradual establishment of the equilibrium distribution of crystal planes exposed to the surface.

Two qualitative observations on iron should be noted here. It was found that while the filaments showed no crystal structure visible with the naked eye initially, with continued heating, crystal growth took place, and single crystals extending the full width of the filament (about 2.5 mm) were sometimes observed. In general, the filaments had a "galvanized" appearance after heating. This effect was not noted with nickel and cobalt. It was also found that each time the filament passed through the A_3 point, it

warped and with repeated transitions twisted sufficiently to short circuit portions of the specimen.

Nickel

First sample: This was a specimen of cobalt free nickel prepared at the Research laboratory of the International Nickel Company by the electrolysis of a chloride solution and a platinum-iridium anode.

Filaments of this material gave initial work functions of about 4.8 ev. Continued heating increased the φ to values ranging from 5.0 to 5.2 ev with A ranging from 800 to 3000 amp/cm²/T². Flashing to temperatures close to the melting point increased the work function if it produced any change at all. Eight filaments from this sample were used and various changes in heating were tried. The results for all were in the range listed above. These values are in the range reported by Glasoe¹ and Fox and Bowie.⁴

Second sample: This consisted of a sintered strip made from cobalt-free powder by the International Nickel Laboratory. The initial φ ranged from 4.8 to 5.0 ev with a high value for Richardson's A . Continued heating and flashing brought the value down until a final stable value was reached. The average for three specimens is

$$\varphi = 4.61 \pm 0.06 \text{ ev, } A = 30 \text{ amp/cm}^2/T^2.$$

Third sample: In order to test whether or not the difference between the two samples discussed above might be due to a platinum contamination from the anode, a sample was prepared in this laboratory. A nickel chloride solution containing 0.1 percent cobalt was used with low cobalt nickel shot as the anode material. The deposits were made on stainless steel from which they could be removed with ease. The first deposit was discarded in order that an equilibrium might be established between the composition of the electrolyte and that of the anode. This was felt to be essential so that the successive deposits would have the same composition.

Two filaments of this material gave identical results *viz.*,

$$\varphi = 4.61 \text{ ev, } A = 70 \text{ amp/cm}^2/T^2.$$

Thus, the φ agrees with the value obtained for the sintered sample, but the A has more than

twice the value. This may be due to the small amount of cobalt in the latter sample, and if so, may be of considerable interest and importance. However, before any conclusions are drawn further studies must be made with samples of varying cobalt content.

Fourth sample: A new deposit was made from the same electrolyte as was used in preparing sample 3. In this case platinum was used as the anode material.

This sample gave a work function which increased with continued heating and flashing to a final value in the same region as that obtained with sample 1. The behavior of this sample throughout the heating was similar to that of sample 1. The A in this case was abnormally high.

Fifth sample: This was a strip of high purity nickel which had been melted in a vacuum. The method of preparation is unknown. This failed to give good voltage saturation and as the results would be meaningless, no data were taken.

It would seem from a comparison of the results of the first four samples that platinum when used as an anode material has a marked effect on the thermionic properties. The amount of platinum contamination may not be enough to influence the volume properties markedly, but as pointed out earlier, a prolonged heat treatment may cause it to diffuse to the surface and thus create a highly impure surface condition. The thermal etching of the surface may also uncover more platinum and increase the surface concentration. The fact that with samples 1 and 4 continued heating increased the work function might be taken as evidence of either or both of these processes. In the case of samples 2 and 3, where possible platinum contamination was absent, continued heat treatment decreased ϕ .

Cobalt

The results on cobalt are not as satisfactory as those on iron and nickel, in that the spread between runs was greater. All the thermionic data were taken above 1120°K, in the region where the metal has a face-centered cubic structure.

First sample: This specimen was made electrolytically from a reagent quality cobaltous chloride solution with cobalt cubes as anode material. The metal was again deposited on stainless steel.

The results of studies with eight filaments gave

$$\phi = 4.41 \pm 0.10 \text{ ev}, \quad A = 41.$$

Second sample: The electrolyte used in this case was from the same supply as above, but an anode of spectroscopic graphite was used. The behavior of these filaments was so nearly the same as that of specimen 1, that one can conclude that no serious contamination is introduced when graphite is used.

The work function given above is higher than the value (4.12 ev) listed by Cardwell³ for the face-centered cubic form of cobalt. The author is at a loss to explain the difference.

From the observations listed above, one must conclude that the problems encountered in the preparation and treatment of metals increase as the temperature to which the metal can be heated is lowered. Whereas in the case of a high melting point, low vapor pressure metal such as tungsten or molybdenum, a large part of metallic impurities may be removed by high temperature heating, this is not always possible in the case of low and intermediate melting point ones. Great care must therefore be taken so as to eliminate, during the preparation of the metal, non-volatile impurities even though they are present in minute quantities. This is borne out by the results on nickel described above.

It is the author's belief that as a result of the evidence presented above, the work functions of the members of the iron group can be fixed as

β -Fe	$4.48 \pm 0.06 \text{ ev},$	$A = 26$
γ -Fe	$4.21 \pm 0.05 \text{ ev},$	$A = 1.5$
Ni	$4.61 \pm 0.05 \text{ ev},$	$A = 30$
Co	$4.41 \pm 0.10 \text{ ev},$	$A = 41.$

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