[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED]

INVESTIGATION OF THE THERMIONIC PROPERTIES OF THE RARE-EARTH ELEMENTS

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Introduction

Several years ago a sample of so-called misch metal was tested in this Laboratory for its thermionic properties. The results of this test revealed the fact that misch metal is definitely more thermionically active than any of the commonly occurring metals. However, since misch metal is a mixture of several rare-earth metals, the first test left undetermined the question whether the observed activity is due to one or to several metals. An investigation was therefore undertaken to determine the thermionic properties of as many of the individual rare-earth metals as could be obtained in reasonably pure form.

Materials Tested

Chemically pure samples of the following metals were used in our tests: cerium, lanthanum, praseodymium, neodymium and samarium. Aluminum alloys of the following metals were used: yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

The five metals of the cerium group were obtained from chemically pure salts furnished to us by Professor C. James of the University of New Hampshire. The metals were prepared by the electrolysis of the fused anhydrous chlorides in quantities ranging from 50 g. for the samarium to several hundred in the cases of cerium and lanthanum. Analysis both analytical and spectroscopic showed the samples to be better than 99.8% pure.

Methods Used in Preparing Rare-Earth Metals

The method used in the preparation of metals of the cerium group was a modification of those used by Hildebrand and Norton[1] and by Muthmann.[2,3]

Both the anode and the electrolytic cell, which acted also as the cathode, were made of Acheson graphite. The cells used were in the form of blocks in which cylindrical holes were bored, varying in different experiments from 3.0 to 9.0 cm. in diameter. The anodes were in the form of rods varying

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[1] Hildebrand and Norton, *Pogg. Ann.*, **155**, 631 (1875); **156**, 466 (1875).

[2] Muthmann, Hofer and Weiss, *Ann.*, **320**, 231 (1902).

[3] The metals used in this investigation were all made prior to 1921. Recently Kremers and his co-workers have made use of similar methods in the preparation of some of the rare-earth metals [THIS JOURNAL, **45**, 614 (1923); *Trans. Am. Electrochem. Soc.*, **47**, 345 (1925)].

from 1.25 to 2.5 cm. in diameter. The voltage used varied from 6 to 15 v. and the current from 150 to 200 amperes.

In all of the electrolyses it was found that considerable quantities of metal were disseminated in small particles throughout the electrolyte and for this reason it was found necessary at the conclusion of each run to raise the temperature of the bath above the melting point of the metal produced. This permitted the disseminated particles to collect in a molten mass in the bottom of the cell. The temperature was increased usually by increasing the current through the cell for a short period of time.

No particular difficulty was met in producing the metals except in the case of samarium. Because of the high melting point of samarium, it was necessary to use an external heater in order to produce a temperature sufficiently high to collect the metal in a coherent mass. To the best of our knowledge this is the first time that any quantity of pure samarium has been produced in a coherent mass.

Two methods were used for removing inclusions from the metals produced in the electrolyses. In the first of these the metal was amalgamated with mercury, the inclusions being skimmed off the surface and the mercury removed by distillation in a vacuum. This left the metal in a finely divided and active state, so that at its first contact with air it took fire. Even when the vessel containing the powder was surrounded with liquid air the metal took fire as soon as air was admitted, sometimes with explosive violence. To prevent the particles taking fire it was found necessary to open the containing vessel in an inert gas and transfer under the inert gas to a magnesia crucible where the particles could be fused into a solid mass.

The writers wish to call attention to the fact that this experiment indicates that statements appearing in the literature purporting to give the kindling temperatures of metals of the rare-earth group have no value since no account was taken of the state of division of the material. From the experiment described above it appears obvious that the kindling point may be very considerably lowered by sufficient division of the particles.

The second method of freeing the metal from inclusions consisted of washing the metal with water to remove all adhering salt and carbide and remelting under a flux of pure sodium chloride.

The metals prepared by these methods were found on analysis to contain not more than 0.03% of carbon and 0.02% of iron.

Owing to the small amount of material available it was not possible to prepare the yttrium group metals by electrolysis. Consequently, oxides of these metals were reduced by heating with powdered aluminum, yielding aluminum—rare-earth metal alloys. The lighter oxide particles were removed from the reduction product by elutriation with benzine, this treatment being followed by washing with concd. potassium hydroxide solution to remove the excess of aluminum metal. It was found that crystals of the alloy were left behind after this treatment, these crystals being practically unattacked by the potassium hydroxide during the short period of contact with the reagent. An attempt was also made to remove the excess of aluminum by heating to a high temperature in a vacuum with the intention of vaporizing the aluminum. It was found that, although some of the excess of aluminum could be driven off in this manner, eventually a point was reached where the two metals were vaporized together at a constant rate, thus preventing a complete separation.

The concentration of rare-earth metal in these alloys varied from about 10% for the rarer elements to about 60% in the cases of yttrium and gadolinium. The aluminum reductions with yttrium, gadolinium and erbium were made in this Laboratory using salts furnished by Professor James, who also provided the remaining metals in alloy form.

Methods Used in Taking Thermionic Measurements

The Boat Method.—In order to learn whether a material was appreciably thermionically active or not, a so-called boat method of testing was first used. This is a very direct way of taking thermionic measurements. The material to be tested was placed in a tungsten trough or boat-shaped container and heated electrically in a vacuum. A nickel plate was placed immediately above the container. The electron emission was measured as a function of the boat temperature. The apparatus is shown in Fig. 1.

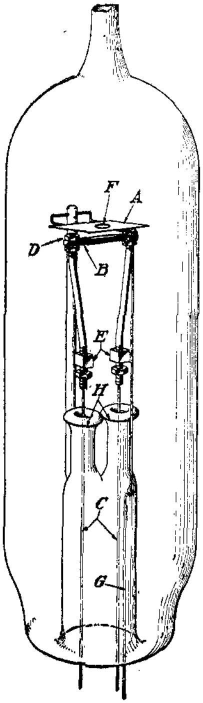

Fig. 1.

Two heavy copper leads C were sealed through a large glass bulb by means of the copper-glass seals H. Heavier nickel rods threaded and slit on the upper end were fastened to the copper leads by means of the specially designed nuts E. The boat B, made of a strip of tungsten or of molybdenum, was fastened to the nickel rods by the nickel nuts D. The nickel plate A, connected to the outside by the lead G, was placed about 0.6 cm. above the boat, and had a hole F in its center so that the materials to be tested could be dropped through to the boat.

In the experimental procedure, granulated or powdered material was dropped into the boat B through the hole F in the plate A, until the boat was practically half filled along its entire length. The containing bulb was sealed to the pump and highly evacuated. A potential of from 250 to 500 volts was applied between boat and plate, and a milliammeter was inserted in the circuit to measure the electron emission from the boat. The boat was heated by passing an alternating current of from 10 to 30 amperes through it, and its temperature was measured by means of an optical pyrometer. It was assumed that this temperature was the same as that of the test material; this, of course, was not strictly true, but since the data are all comparative the error can be neglected. The activity of the test material was determined by comparing the electron emission for various temperatures of the boat before and after inserting the material. To avoid errors in temperature readings due to condensation of metal vapors on the walls of the tube, a nickel shield controlled by a magnet was mounted in the tube, the shield being removed only while temperature readings were taken.

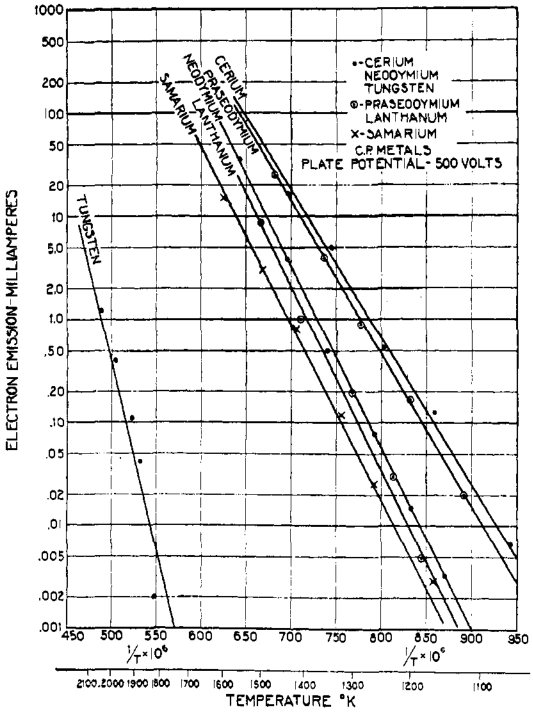

Fig. 2.—Thermionic activity measurements, boat method.

The "Shaking-On" Process.—The second method of testing was to shake a coating of the material on a metallic vacuum tube filament of known thermionic properties and then measure the filament activity. The procedure was to mount the bare filament in a tube assembly inside of a glass bulb. The material, with which the filament was to be coated, was powdered as finely as convenient, and a quantity of it was placed in the glass bulb. This bulb was then evacuated as highly as possible with a mercury-vapor pump. The tube was baked out and the bare filament was glowed at a high temperature for a few seconds to degasify the parts. The tube was then sealed off at a special contraction, made just above the regular one. The filament was then heated to an appropriate temperature which ranged from a dull red to a bright yellow while the powder was shaken on it. The quantity of powder that adhered depended mainly on the filament temperature. The filament current was then shut off, the tube was cut open between the two contractions and the excess of powder was poured out. The tube with the coated filament was then ready for pumping in the usual manner. A filament made in this way could be tested by simply measuring the space current at various power inputs.

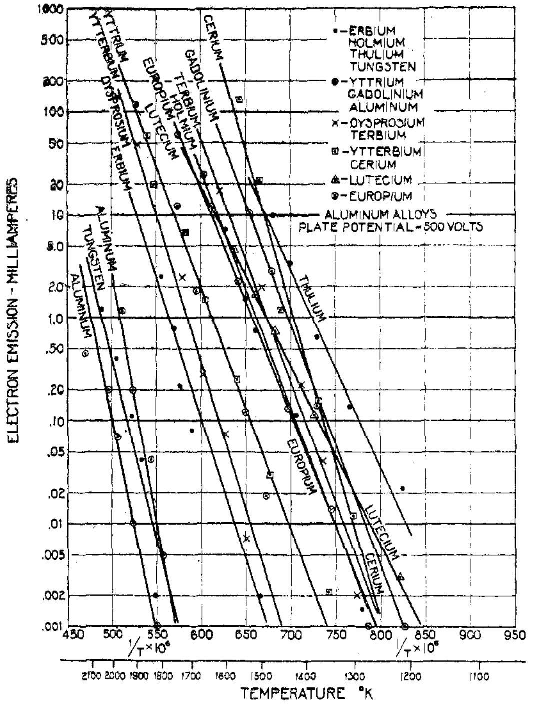

Fig. 3.—Thermionic activity measurements, boat method.

Results

The data taken by the boat test are plotted in Figs. 2 and 3. In Fig. 2 there are shown the thermionic activities of those metals which were obtained in pure form compared to that of the empty tungsten boat. It is at once apparent that the electron emission from these rare earths is about a million times as great as that from clean tungsten at the same temperature. Fig. 3 gives the data obtained for those of the rare-earth metals that were tested in the form of aluminum alloys. In this figure there is also shown a curve giving the activity of pure aluminum in the tungsten boat.

The data taken with filaments produced by the "shaking-on" process are shown in Fig. 4. In this case the data are plotted on power-emission charts of a type devised by Dr. C. J. Davisson of these Laboratories.[4] On these charts the coördinates have been so proportioned that, if the relation between thermionic emission and temperature follows Richardson's equation, the data when plotted give a straight line. It was not possible to test all the materials used in the boat test by this method since the materials did not in all cases stick sufficiently well to the filament to give a uniform coating.

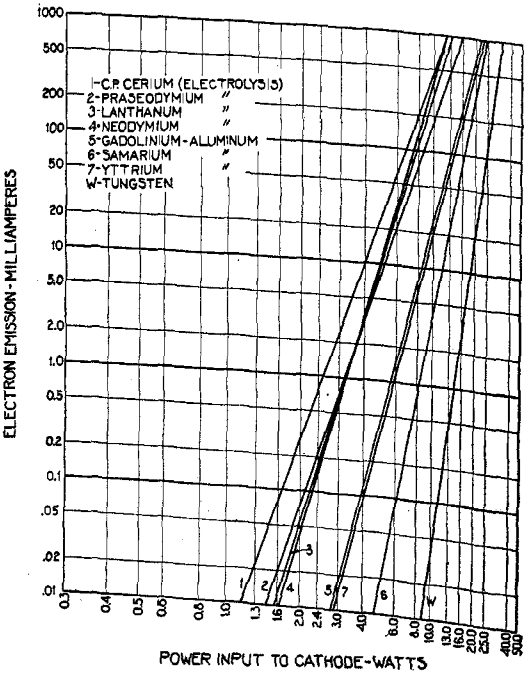

Fig. 4.—Thermionic activity measurements, shaking-on method.

Discussion

Due to inherent difficulties in the methods that had to be used in making the measurements, no great accuracy can be claimed for the data here presented. It is believed, however, that the curves presented in these figures indicate approximately the relative activities of the metals investigated. The activities found for the aluminum alloys of the yttrium group

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[4] Van der Bijl, "The Thermionic Vacuum Tube and its Applications," McGraw-Hill Book Co., New York, 1920, p. 82. King, *J. Optical Soc. Am.*, **8**, 79 (1924).

metals have undoubtedly been affected adversely by the presence of the aluminum. That this is so is indicated by the fact that a greater activity was found for pure cerium, as shown in Fig. 2, than for a 50–50 aluminum-cerium alloy, the curve for which is shown in Fig. 3. It is obvious from the curve shown in Fig. 3 for aluminum-tungsten that the increased emission due to these alloys cannot be ascribed to the presence of the aluminum.

The authors take pleasure in expressing their thanks to Mr. Lawrence Ferguson of this Laboratory for his assistance in taking these measurements.

Summary

1. Data are presented in this paper which indicate that rare-earth metals of the cerium and yttrium groups are without exception much more active thermionically than the commonly occurring metals. The electron emission from some of these rare earth metals was found to be about a million times as great as that from clean tungsten at the same temperature.

2. Two methods for the determination of the thermionic activities of materials obtainable in powdered form have been described.

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[Contribution from the Chemistry Department of Columbia University, No. 522]

THE SEPARATION OF RADIUM AND OF MESOTHORIUM I FROM BARIUM BY THE IONIC MIGRATION METHOD

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The separation and concentration of radioactive substances is an important problem which appears amenable to treatment by the ionic-migration method, and we have therefore performed experiments to ascertain to what extent the method is applicable to the separation of radium and its isotope mesothorium I from the barium by which they are always accompanied. The standard commercial procedure involves a long series of fractionations of the barium residues, and it has already been shown in the case of typical rare-earth mixtures that a much more rapid and convenient separation may be effected by taking advantage of differences in ionic mobility rather than differences in solubility.

As the details of technique have been fully described in previous reports,[1] it will suffice here to state that the method depends on the fact that if radium and barium ions possess appreciably different mobilities, the migration, in the process of electrolysis, of a section containing these ions will be accompanied by a gradual concentration of the faster ion in front and of the slower behind. The boundaries of the moving section may be maintained sharp by causing it to be preceded by a still faster ion and

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[1] Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 9, 75 (1923). Kendall and Clark, *ibid.*, **11**, 393 (1925).